The Groundwater Quality of the Area Tailings Mining Ponds in the North of Romania

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Mining activities are recognized as generating adverse effects on the environmental quality. The waste resulted from ore processing activities settled on the ponds was established as a significant pollution source of the soil and groundwater in the site areas. The paper presents the spatio-temporal variation of the characteristics of groundwater in the area of a waterproofed pond, located near two other tailings ponds, unenriched, of an age of over 30 years. Groundwater quality is highlighted in an area situated in the north of the country in terms of metals content determined in several seasonal campaigns.

Keywords: groundwater, metals, tailing ponds

Groundwater is one of the most important natural resources located in the aquifer below the earth's surface [1]. It is well known that groundwater is a valuable natural resource which must be protected from deterioration and chemical pollution [2].

Groundwater from aquifers comes from precipitation falling onto the soil surface through seepage. This process may involve a number of substances that lead to contamination of groundwater and surface water which drains it [3].

Water pollution is generally defined as a direct or indirect change of its normal composition, as a result of human activities.

The presence of pollutants in the atmosphere and at ground level is due to a rapid industrialization which has developed globally. As a consequence, there is a high concern for assessing the impact produced both on the environment and on human health [4].

Environmental impact assessment is considered to be an effective means of promoting the integration of environmental issues and natural resources into the program development [5,6].

Regarding the assessment of the environmental impact of industrial activities, there were constant concerns to define the specific conceptual framework, which then served as a basis for developing experimental models. Afterwards, conceptual and experimental models have evolved for investigating and evaluating of soil, groundwater and surface water quality which allowed quantifying the impact on the environment [7- 10].

Conceptual models included all available information describing the analyzed areas considered relevant for the study. Experimental models have included establishing the limits of study areas, locating points of sampling, choosing the analyzed quality indicators.

In case of exploitation and processing mining activities it is a known fact that these represent major sources of environmental pollution with metals, so that evaluating and reducing their impact is of particular importance.

Some examples of areas contaminated with heavy metals in Romania are: Baia Mare, Rosia Montana, Certej, Oas, as a result of carrying out mining activities from ancient times [11-15].

By far, the activities carried out in the mining sector produce large amounts of waste that induce negative effects on the environment. For this reason, a higher priority must be given to the mining sector than any other industrial branch or human activity that generate waste [16].

The storage of waste from mining processing, in certain scenarios, can lead to negative effects on the environmental components such as water (underground, surface) and soil, posing severe and sometimes irreversible threats [17]. Constituents from these deposits may change in time and space and act synergistically or antagonistic to each other, the severity of the effects being dependent on their evolution.

As a result of atmospheric dust containing metals from deposited tailings and of hydrogeological flows in these sites, the contamination of ecological systems are subjects to disseminate at a long distance from the source of pollution. It is widely recognized that, once a mining deposit was created, it remains a threat that requires constant surveillance for a period which extends to thousands of years [18].

For these reasons, continuously monitoring of the environmental quality (soil, groundwater, surface water) is necessary for the identification of the hazard, of its nature, duration and extent, even after the cessation of specific activities.

In this context, the results of environmental research presented in this work, performed in a Romanian mining area with a long activity are of particular relevance.

Experimental part

Materials and methods

Study area

The study area is located in the northern part of Romania, in a region where intense and very old mining activities represented in particular a source of mineral resources exploitation, but also a source of livelihoods for the inhabitants.

These activities generated a large amount of waste composed of mining tailings, tailings derived from preparation plants, ore traces of different granulation, various compositions, often dangerous.

The deposits which stored these wastes over the years represent a continuous source of environmental pollution

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Fig. 1. Location of the three ponds

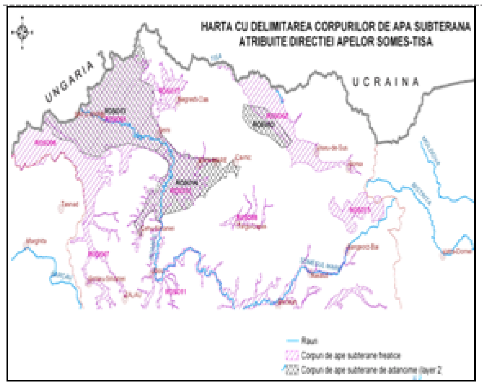

Fig. 2. Delimitation of ROSO14 groundwater body

Fig. 3. Wells location of around Aurul tailings pond

in the studied region, as well as a potential source of risk for the environment and the human community.

Through leaching, these deposits (dumps and tailings ponds) have significantly polluted the soil, groundwater and surface water in the site area with heavy metals.

The aim of this study was to investigate the spatio-temporal variation of the groundwater characteristics in the area of a waterproofed pond (Aurul Pond), located near two other tailing ponds from Baia Mare (Sasar Pond and Flotatia Centrala Bozanta Pond).

The location sites of the three neighboring ponds is presented in figure 1.

For both tailing ponds, Sasar and Flotatia Centrala Bozanda, specific activities were carried out without special measures for sealing the pond, the only sealing being provided by less permeable natural layers in the area. For ensuring environmental protection, Aurul Pond was built on compacted land with a high density polyethylene membrane.

The groundwater in the considered area is part of the water body corresponding to ROSO14 Baia Mare area, belonging to Administration of Somes-Tisa Water Basin (fig. 2).

The ROSO14 is a deep pressure water body with up to 12 aquifers in the depth range of 45m to 326 m. This groundwater body's type is porous and permeable, being developed in the Panonian deposits of Baia Mare Depression, within an area of 733 square kilometers.

Sampling points

Three seasonal campaigns were carried out on the perimeter of Aurul tailing pond, their locations being shown in figure 3.

According to the methodology for field investigation, both the GPS coordinates for control wells and the groundwater level were determined in three seasonal campaigns (spring, summer, autumn). The measurement results are presented in table 1.

In order to achieve the study's objective, an experimental model for the investigation and assessment of groundwater quality was set in the analyzed area.

The investigation methodology was applied as follows:

a)Field investigation involved the determination of the GPS coordinates using a Garmin GPS Map CSx60 receiver, the measurements of the groundwater level in control wells using a special measuring tape provided with a sensor that emits sound upon water contact and water sampling in accordance with applicable standards.

Groundwater sampling was carried out after removing three times the volume of water present in each well [19]. All samples were collected in polyethylene bottles (1 L). Each bottle has been previously rinsed with water collected from the wells to eliminate the traces of impurities from glass manufacture and then the sample was collected. In order to avoid oxidation processes that can occur in water-

Table 1
DATA REGARDING GROUNDWATER SAMPLING POINTS FROM AURUL POND

Sample	Location	GPS coordinate	Groundwater level (m)
P1	Control well Aurul tailing pond, SV direction	N 47°38'33" E 023°27'45"	0.5-2.2
P2	Control well Aurul tailing pond, V direction	N 47°38'47" E 023°28'00"	0.7-3
P3	Control well Aurul tailing pond, V direction	N 47°38'55" E 023°28'11"	0.85-3
P4	Control well Aurul tailing pond, N-NE direction	N 47°39'03" E 023°28'40"	0.75-2.5
P5	Control well Aurul tailing pond, E direction	N 47°38'43" E 023°28'41"	0.75-3
P6	Control well Aurul tailing pond, SE direction	N 47°38'32" E 023°28'14"	0.45-1.5
P7	Control well Aurul tailing pond, SE direction	N 47°38'25" E 023°27'58"	0.45-2
P8	Control well Aurul tailing pond, N-NV direction	N 47°39'02" E 023°28'17"	0.75-2
P9	Control well Aurul tailing pond, S-SE direction	N 47°38'26" E 023°27'57"	0.55-2
P10	Control well Aurul tailing pond, E direction	N 47°38'43" E 023°28'41"	0.75-2

atmosphere interface, the bottles were completely filled and then airtight closed. The samples were kept and transported in freezers (4^{0}C) and then processed for further analysis in the laboratory [19,20].

b)Laboratory investigations involved pH measurement and analytical determinations of the heavy metals (Cu, Zn, Pb, Cd, Ni, Fe, Mn). These indicators are limited according to Order no. 621/2014 on the approval of threshold values for groundwater in Romania - ROSO14 water body [21].

The *p*H measurements were performed using the pH meter WTW Multi 9430.

For the determination of heavy metal content in the collected samples, these were acidified to reach a *p*H=2 with a mixture of hydrochloric acid and nitric acid (aqua regia), in accordance with the US EPA 3015:1994 - Microwave assisted acid digestion of aqueous samples and extracts [22, 23]. The samples resulted from digestion were cooled, quantitatively transferred in a 100 mL volemetric flask with ultrapure water. The ultrapure water was obtained using the Millipore Milli-Q System. The heavy metal elements concentrations were determined by spectrophotometry using PinAAcle 900T Atomic Absorption Spectrometer – a Perkin Elmer spectrometer and an Inductively Coupled Plasma Mass Spectrometer Aurora M90 Brucker equipment [20, 24, 25]. The operating parameters for AAS and ICP-MS are shown in table 2, respectively table 3.

For the determination of the above-mentioned indicators, water quality standards in force were used.

Results and discussions

The investigation performed in the laboratory regarding the quality of groundwater in all three campaigns proved the presence of heavy metal elements in concentrations that exceed, in majority of cases, the limit values for groundwater according to Romanian Order no. 621/2014 on the approval of threshold values for groundwater in Romania - The ROSO14 water body (table 4).

The obtained results are represented in graphic form (figs. 4 to 8).

Figure 9 shows the variation of the *p*H and figures 10 and 11 show the iron and manganese concentrations in the investigated wells in three seasonal campaigns.

Regarding *copper* concentrations, in each of the three campaigns about 80% of samples were higher than the threshold value. The values were significant in NV wells (P3 – more than 100 times) and on E-SE wells (P5, P7: concentrations higher than 40 times).

Zinc content was situated over the admitted value especially in autumn season, as the highest value recorded

Table 2
THE OPERATING PARAMETERS FOR AA SPECTROMETER

Element	Wavelengths (nm)	Acetylene / Air flow rate (L/min)	Calibration curve range (mg/L)	LOQ (µg/L)	Precision (%)
Mn	279.5	2.5/10	1-5	3.6	2.81
Zn	213.9	2.5/10	1-5	2.3	2.55
Fe	248.3	2.5/10	1-5	4.4	3.22

Table 3
THE OPERATING PARAMETERS FOR ICP-MS

Plasma flow rate		18 L/min	*Nebulizer flow*	1.0 L/min
Auxiliary flow rate		1.65 L/min	*Sampling depth*	6.0 mm
Sheath gas		0.2 L/min	*Power RF*	1.45 kW
Isotopic abundance		*Calibration curve range (µg/L)*	*LOQ (µg/L)*	*Precision (%)*
Cd	112	10-50	0.77	0.46
Cu	63	10-50	0.60	1.23
Pb	207	10-50	0.64	1.95
Ni	60	10-50	0.66	1.74

Table 4
THE THRESHOLD VALUES FOR GROUNDWATER ACCORDING TO ORDER NO. 621/2014

Indicator	MU	Limit value	Indicator	MU	Limit value
Copper	mg/L	0.1	Nickel	mg/L	0.02
Zinc	mg/L	5	Iron	mg/L	-
Lead	mg/L	0.01	Manganese	mg/L	-
Cadmium	mg/L	0.005			

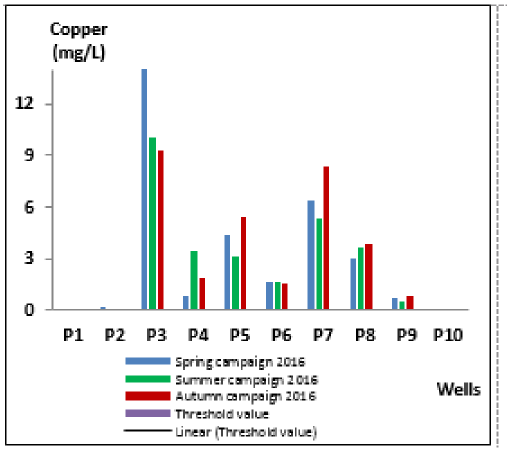

Fig. 4. The variation of copper in groundwater from Aurul tailings Pond area

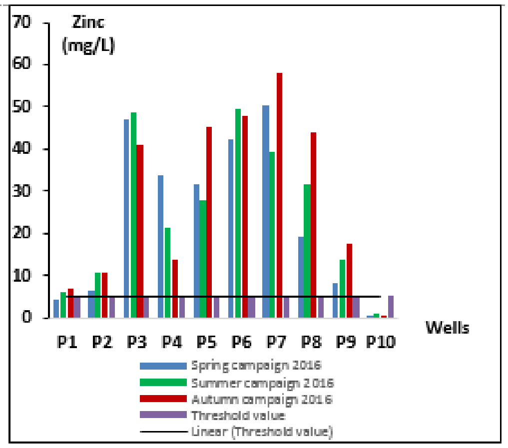

Fig. 5. The variation of zinc in groundwater from Aurul tailings Pond area

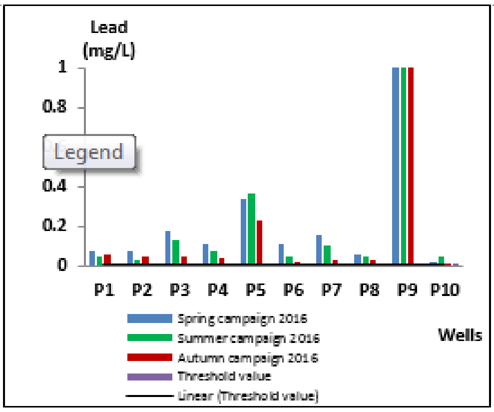

Fig. 6. The variation of lead in groundwater from Aurul tailings Pond area

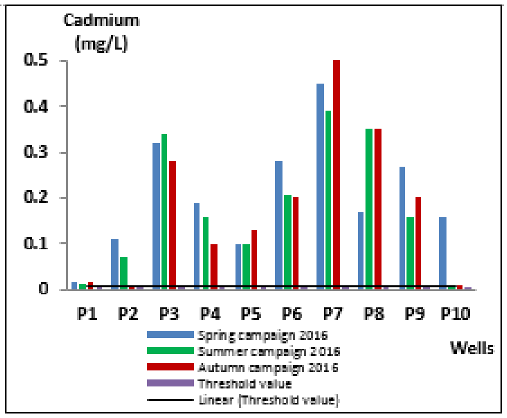

Fig. 7. The variation of cadmium in groundwater from Aurul tailings Pond area

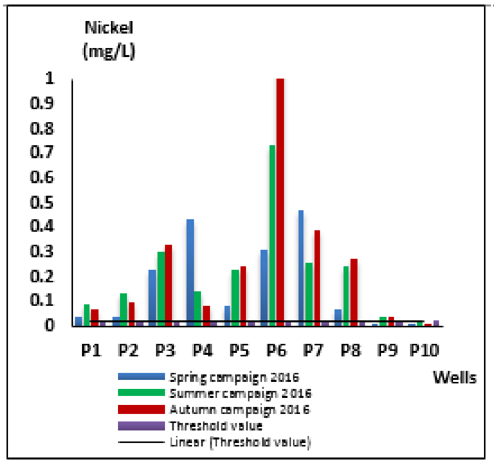

Fig. 8. The variation of nickel in groundwater from Aurul tailings Pond area

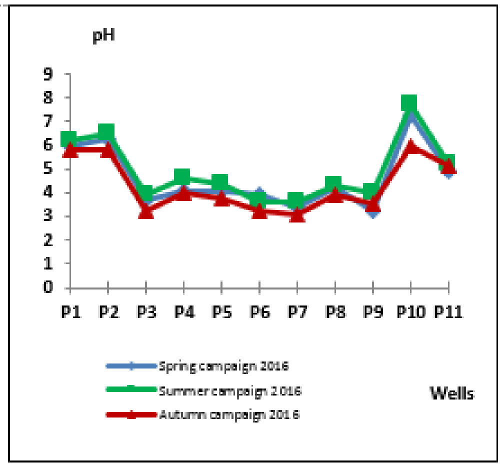

Fig. 9. The variation of *p*H in groundwater from Aurul tailings Pond area

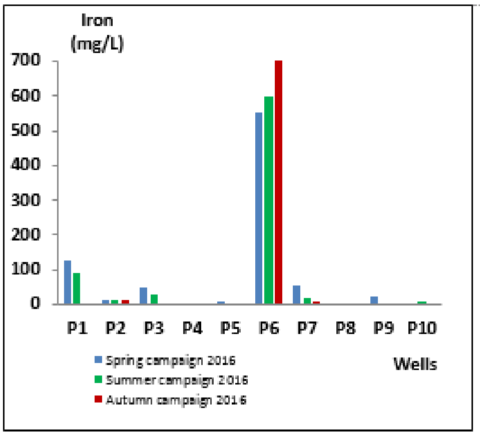

Fig. 10. The variation of iron in groundwater from Aurul tailings Pond area

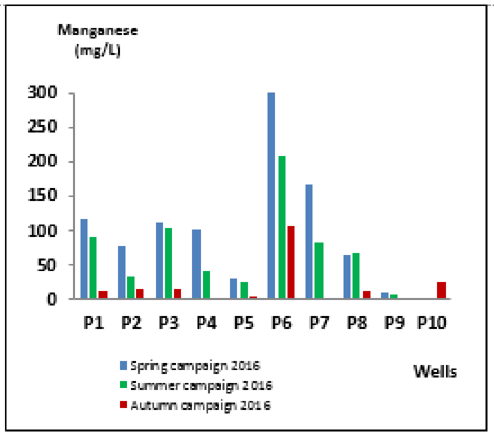

Fig. 11. The variation of manganese in groundwater from Aurul tailings Pond area

was around 60 mg/L in P7 sampling point. Only the values reported in P10 were situated under the threshold.

Regarding *lead* concentrations, exceeding of the threshold value were recorded in each of the three campaigns. The most polluted well was P9, located on the SE side, where the threshold value was exceeded up to 135 times.

Regarding *cadmium* content, with two exceptions, all investigation campaigns recorded exceeding of the threshold value; the most significant were the wells of the SE side (P7 - up to 108 times, P6 and P9 up to 58 times) and the wells of the NV side (P3, P8 - up to 70 times).

Nickel content were registered to exceed of the thresholds (in all three campaigns). Only the values reported in P10 were situated under the threshold.

The *pH* values determined in each of the wells did not show significant differences between campaigns, hovering in the same domain (acid/ easy acid/ neutral).

In all three campaigns, there were wells which had an acidic pH - easy acid (3.1 to 4.6), located in the NV of the pond (P3 and P8) and the SV of the pond (P6, P7, P9).

Iron contents in the wells varied between approx.1 mg/L up to hundreds mg/L; the highest values (hundreds mg/L) being recorded in P6 located in the SV of the pond.

In the majority of wells, the *manganese* concentrations showed decreasing values from the spring campaign to summer campaign, respectively autumn campaign; a possible explanation would be a better solubilization of Mn during the rainier season.

The highest values of Mn (hundreds mg/L) were determined in P6 well, situated near the Sasar pond.

Conclusions

The results of the investigations conducted in all three seasonal campaigns for the hydro-observation wells of the Aurul tailings pond have indicated that the groundwater is polluted with heavy metal elements (Fe, Mn, Ni, Zn, Cd, Pb).

Regarding the temporal variations of the groundwater quality, it was noted that the highest values determined for some metals (Fe, Cd, Mn, Pb) occurred in the spring campaign (for all wells). This situation could be explained by an increasing solubilisation of those metals due to rich precipitation during the investigated period.

Higher concentrations of heavy metals in the wells were determined where the *p*H was acidic. This fact reveals a better solubility at an acidic *p*H (P3 on the NV side of the pond or P6, P7, P9 on the SE side of the pond).

Regarding the spatial variation of the heavy metals contamination level of the groundwater, a high concentration of the pollution was observed in particular on the SE side of the pond . This could be due to the close proximity of the Sasar pond site in which was built lacking safe conditions for the environment except for the natural impermeable layer of clay, affecting groundwater quality in the area.

Increased groundwater acidity and heavy metals accumulation in the soil in the studied area undoubtedly led to the deterioration of the groundwater quality in the area. This was due to the natural phenomena of bacterial leaching that took place gradually within the tailings mass and to the wind-driving of tailings fractions during dry periods.

Also, the groundwater pollution with some metals and its acidic character, identified within the NV side of the pond (P3), can be explained by the presence of metals within the lithological structure of the area, and by the presence of clay that promotes the accumulation and maintaining of significant concentrations in groundwater.

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