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# INFLUENCE OF HEAVY METALS ON THE ENVIRONMENTAL FROM TARNITA MINING AREA

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**Abstract:** This paper presents aspects related to water pollution with heavy metals from the Tarnita mining area before and after the cessation of the mining activity. The impact of heavy metals on waters is important because these metals have a negative impact on both human health and aquatic ecosystems. All research data showed that, even the mining activities from this area were suspended, the sterile still pollutes the soil and water.

**Key words:** heavy metals, mining activity, Tarnita mining area, water pollution, tailing pond.

## Introduction

The environment is the result of the interference between a number of human activities-dependent elements and natural ones consisting of renewable (water, air, soil, flora, fauna), unrenewable (minerals, fossil fuels) and permanent (solar, wind, geothermal energy) resources. Intensive

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developments of human and economic activities determine significant changes of these interferences resulting in biodiversity loss and disturbance in the regulation mechanisms of climatic systems.[1, 2]

Industrial activities are the main source of environmental pollution, such as water pollution with heavy metals, organic and inorganic waste, soil pollution with residues from mining and non/ferrous metallurgy and air pollution produced by release of large amounts of toxic gases into the atmosphere.[3]

Mining activities represent one of the most pollutant sources for human communities or natural ecosystems. The risk of pollution from mining sites lasts even after the cessation of mining activities. In all sites where the mining activities exist, the environmental problems are present. These problems manifest theirselves as natural land degradation, air and water pollution, negative impact on terrestrial and aquatic ecosystems, human health and socio-economic.[4, 5]

In this paper, the environmental pollution problems from Tarnita mining area are being discussed. Here, the water pollution with heavy metals originating from the mining exploitation Tarnita is taken into consideration. It is important to analyze the impact of heavy metals on water because these metals have a negative impact both on human health and aquatic ecosystems (Table 1).

**Table 1.** Impact of heavy metals on human health and waters.

| Heavy metal | Impact | | References |
|---|---|---|---|
| | **To humans** | **To waters** | |
| Pb | Affects the central and peripheral nervous system; circulatory and digestive systems; kidneys | Acute toxicity to plants, animals and microorganims | 6 |
| Hg | Causes brain damage leading to blindness; mental abnormalities; acute intoxications affecting digestive system and kidneys, death | Chronic effects | 7 |
| Cd | Induces respiratory and kidney disorders; cancer | Poisonous to flora and fauna; decalcification bodies | 7 |
| Cu | Affects the liver, kidneys and eyes; neurological disturbances | Toxic to plants | 8 |
| Fe | Affects heart and liver; causes the disease called siderosis | | 8 |
| Cr | Is irritant to skin and mucous; induces circulatory disorders; allergic reactions; affects the nervous system; cancer | Poisonous to marin plankton and fish | 9 |
| Ni | Induces allergic reactions; affects lung and kidney tissue; cancer | High toxicity to plants, is approx. 8 times more toxic than Zn | 8 |
| As | Vomiting; cardiac dysfunction; skin cancer | Affects the plant growth | 9 |
| Zn | Epigastric pains; affects the central nervous system, muscles and cardiovascular system | Changes in physical and physico-chemical properties; reduces the biological activity | 8 |
| Mn | Motor and mental disorders; Parkinson | | 9 |

**General aspects about the Tarnita mining area**

Tarnita mining area is geographically located in the north-east of Romania, in Suceava County (Figure 1). This mining area falls into the category of mining whose activity have been stopped due to exhaustion geological reserves, very difficult geo-mining conditions and very high of operating costs. Hence, the mining activity in Tarnita area has been stopped in 2006 due to economic inefficiency.

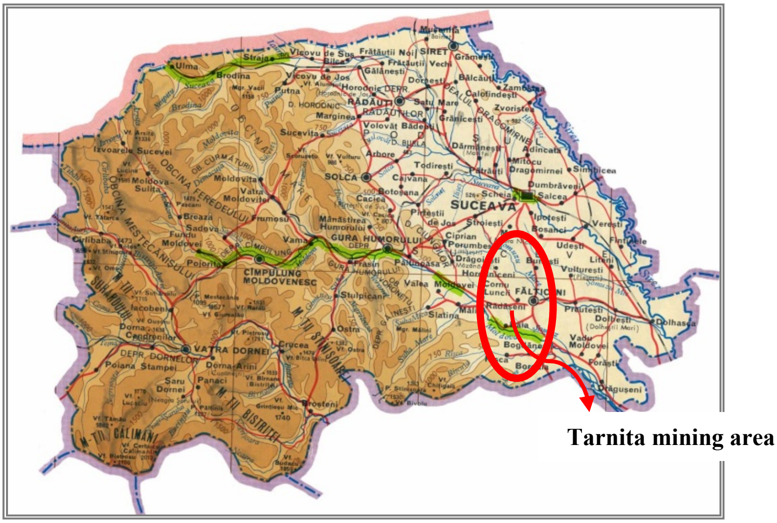
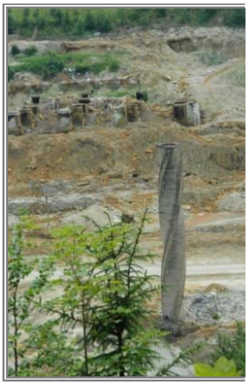



**Figure 1.** Geographically positioning of Tarnita mining area.[10]

The industrial preparation unit Tarnita (Figure 2) is located on the territory of Ostra, on the banks of Brateasa and Tarnicioara, right tributary of the Moldova River. This industrial unit belongs to S.C. MINBUCOVINA S.A. Vatra Dornei that was processing non-ferrous minerals from Lesu Ursului and baritine from Ostra and Alunis quarries.[10 – 12]

Before the cessation of mining activities[13]



After the cessation of mining activities (images from its own arhive)

**Figure 2.** The Industrial Preparation Unit Tarnita.

Lesu Ursului deposits are composed of multilayered pyrite ore accumulations and polymetallic sulphides. The rocks from this area can be classified in:

- porphyrogene rocks compact, gray, siliceous;
- marcastic and sericito-chlorite schists;
- chlorite schists with sulphydes – pyrite, chalcopyrite, blend and galena;
- graphite schists.

The useful minerals present in Lesu Ursului deposits are divided into four levels:

- first area – impregnation of copper-ferrous ores;
- second area – compact polymetallic and impregnation of copper-ferrous ores at 180 m from first area;
- second/third area – compact polymetallic and impregnation of copper-ferrous ores at 400 m from second area;
- third area – compact polymetallic and impregnation of copper-ferrous ores at 800 m from second area.

Baritine deposits from Ostra and Alunis quarries are present in high quantity in gneisses of Rarau as lenses, nests and impregnations. The thickness of the ore from the surface of terrestrial crust ranges between 10 and 45 m.

After the cessation of the mining of copper and baritine deposits from Ostra-Tarnita area, huge amounts of sterile has left, which are stored in four tailing ponds: Poarta Veche, Ostra, Tarnicioara (deposited the largest amount of sterile) and Valea Strajii (Figure 3). This sterile pollutes the environment (water, soils, air) with sever negative effects.

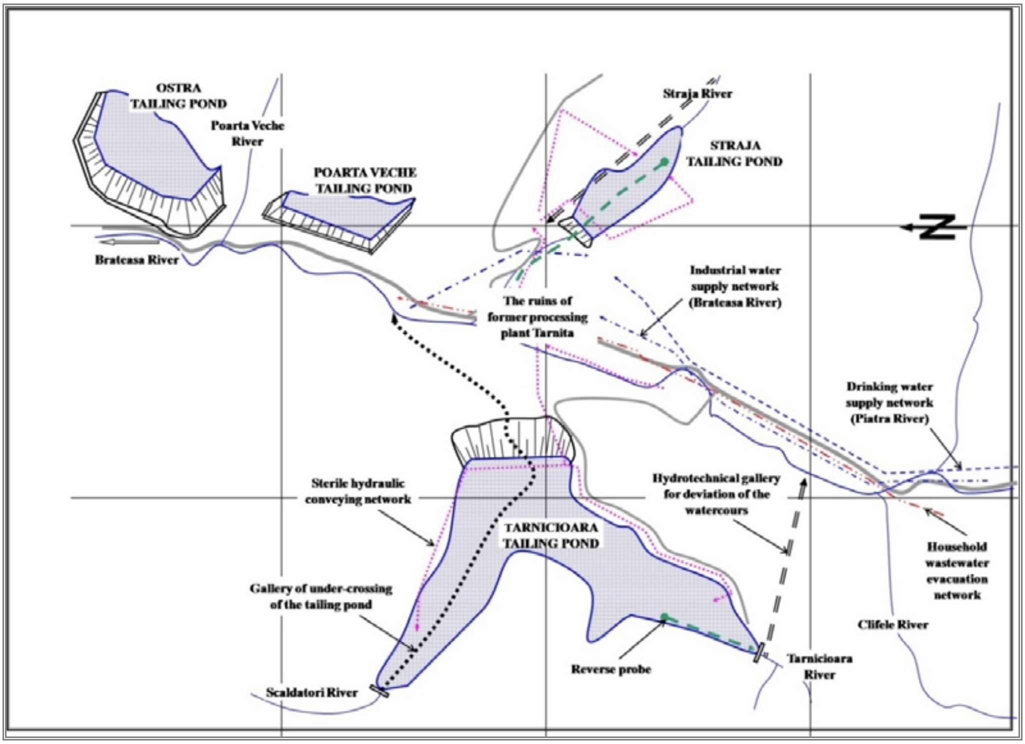



**Figure 3.** The location of sterile tailing ponds from Ostra-Tarnita area.

There is a risk that the tailing ponds will crack and infiltrate into the soil and groundwater, and this catastrophe would affect the population and infrastructure from downstream area. In Tarnita mining area, the main risk factor on the environmental and the population is the Tarnicioara tailing pond, which is 80 m high, occupies an area of 28.5 hectares and contains approximate 15.5 mil. tones of sterile. The stability of this tailing pond is very fragile. For example, in June 2006, extremely strong rains have silted grates from the entrance gallery under-crossing the pond. For desilting, huge human and financial efforts were needed, in order to prevent an ecological disaster. Currently, the ecological rehabilitation works to Tarnicioara tailings pond are carried in extent of approximate 90 %.[8]

Due to large size of tailing ponds, it is practically impossible to regenerate the area they occupy, artificial deserts being all that is left. Mineral residues and toxic wastes that results from tailing ponds have a very low biodegradation degree so that water degradation occurs immediately and irreversibly. Even the mining activity in this area was stopped in 2006, the sterile deposited in all four tailing ponds polluted the environment both the short and long term, affecting irremediably the waters and soil, flora and fauna. On the other hand, Tarnicioara tailing pond falling within a class of ponds that would causes immense damages in social, ecological and economic point of view, because Tarnicioara tailing pond depositing the largest amount of sterile from Ostra-Tarnita area.[14, 15]

Tarnicioara tailing pond (Figure 4) suffered a series of stability disturbances related to the direct effect of groundwater and discharge system of clarified water. These disturbances have been reported both during operation and after the cessation of mining activity in 2006.

Before the cessation of mining activity, these disturbances have been reported as suffusion phenomenon, crash funnels, clogging and breaking of reverse probes. In 2002, due to the torrential rains an exfiltration on slope pond has occurred that have a high concentration in heavy metals. The analysis from Environmental Protection Agency Suceava achieved in 2002 November highlighted a concentration in heavy metals that exceeded the maximum permissible concentration values. Thus, iron had a concentration of 204.17 mg/L (maximum permissible limit is 0.3 mg/L); zinc was 22.97 m/L (maximum permissible limit is 0.1 mg/L); cooper was 0.039 mg/L (maximum permissible limit is 0.03 mg/L); manganese was 14.27 mg/L (maximum permissible limit is 0.05 mg/L).


**Figure 4**. Tarnicioara tailing (images on the massive sterile and at its base) (images from its own arhive).

Is should also be noted that after the torrential rains from 2002 several ravines have been appeared on main slope of tailing pond. On the other hand, the level of waters in piezometric probes has significant increased with excess of sliding level.[16]

All these disturbances have led to affecting of water quality from main emissary – Brateasa River, even if every time has operatively intervened to eliminate the damages and to ensure the stability of tailing pond.

The cessation of mining activity and finishing the Tarnicioara tailing pond operation do not determine the disappearance of risks due to the way that sterile resulting from mining activity is being stored. The major risks of continual deterioration of environmental from Ostra-Tarnita area remain because it is impossible to anticipate the behavior of these sterile tailings under special conditions such as abundant rains.

After the cessation of mining activity, in June 2006, due to the torrential rains from Tarnita area the danger of flooding the sterile beach appeared together with major risks to breaking of balance tailing and sliding of sterile mass deposited in Tarnicioara tailing pond. The effects on the environment would be catastrophic if it affects the water quality, flora and fauna, and human settlements. These catastrophic effects are assigned to huge volume of sterile deposited here.[16, 17]

In present there have been identified water exfiltrations ravines on main slope of tailing pond and the inverse and piezometric probes that are clogged. To reduce the risks and the natural disasters due to entraining the huge mass of sterile deposited in Tarnicioara tailing pond, stabilization and rehabilitation works were carried out. But these stabilization and rehabilitation works of Tarnicioara tailing pond did not prevent the water pollution from this area, especially Brateasa River. Thus, has been found that:

- Brateasa River pollution occurs as a result of the minerals solubilization inside the mass of sterile;
- minerals solubilization occurs as a result of oxidative action of the sulfate and iron ions, process that is favored by the presence of some bacteria as *Thiobacillus ferooxidans*;
- reddish color of the water from Brateasa River (Fig. 5) is due to the precipitating of iron hydroxide;

- the mineral solubilization occurs continuously, including in the cold season, because the oxidation reactions are exothermic.

**Figure 5.** Reddish waters and sediments of Brateasa River (images from its own arhive).

After analyzing the exfiltrations in the Tarnicioara tailing pond, it was found that:

- these have a content in heavy metals over the maximum permissible limit, due to the phenomenon of acid drainage and biosolubilization of sulfides from mass sterile;
- the loading in heavy metals is smaller in the summer time as a result of dilution due to the rainfalls richest and, as consequence, to the higher water debits that infiltrates into the mass of sterile;
- the heavy metals loading at the base of the tailing pond is less than that of the superior area, due to the presence into the sterile mass of the carbonated minerals with neutralizing acidity potential. These

carbonated minerals can contribute to partial neutralizing of groundwater.[17, 18]

Tarnicioara tailing pond is in a critical state, considerably accentuated by the abundant rains from the last years. This critical state is due to the huge volume of sterile deposited (over 15 mil. tones) and the surface occupied by tailing pond (approx. 30 ha with 80 m height). Fitting works carried out to the Tarnicioara tailing pond have proved insufficient. Due to these coordinates, the Tarnicioara tailing pond falls into the Class II risk, whose damage would cause bigg social, ecological and economic destructions.

In Tarnicioara tailing pond case, the risk of pollution is complex, having an anthropic (structure damage) and natural risk component (floods caused by the obstructions of stream beds rivers from surrounding area).

Sterile deposited in Tarnicioara tailing pond has negative effects on the environment such as:

- negative effects on the soil – the area occupied by the tailing pond is compromised; it becomes artificial desert. Restoration of soil and fauna from this area requires a very long time, from 60 to 100 years.
- negative effects on the waters –are felt especially in stream beds Brateasa River (most affected), Straja and Tarnicioara. These negative effects are due to the rainwater entrainment and the sterile from the slope.
- negative effects on the flora – due to the contaminated groundwater with sediment particles from slope and fluids load with heavy metals over the permissible limit.
- negative effects due to the greenhouse gas emissions from the metal sulfides oxidation.

Negative effects on the surrounding waters can be described based on the type of specific pollutants and sterile tailing ponds remaining after mining activity cessation. Besides the sterile deposited in tailing ponds and rainwater contaminated, from mining activity, the other residual substances resulted can contributes to considerable deterioration of waters, flora and fauna quality. In this regard one can be noted:

- solid residues under suspensions form – determines the increasing the amount of fine grained and colloidal of solid suspensions, as well as the increasing of content in heavy metals salts. This modifies the pH value and the taste of the water. All this leads to the decantation of suspensions on the bottom river beds, covering with mineral powders of bordering lands and fauna suppression during abundant rainfalls and flood rivers. Suspensions with high load in heavy metals (Cu, Zn, Fe, Pb, Ba) have negative effects on the water biocenosis by changing the pH. These waters become inadequate for irrigation and household use.
- liquid residues under wastewater – that mixed with water emissaries and leaching into the groundwater cause a significant change in quality indicators with negative influences on the aquatic ecosystems and potability. Practically the water becomes unfit for human and animal consumption.
- gaseous residues formed by suspension particles and gas emissions ($H_2S$, $SO_x$ etc.) – arrived into the surface waters through rainfalls and affects the quality indicators.[18 – 21]

This paper presents the comparative results obtained by analyzing the water samples from Ostra-Tarnita area, samples collected before and after the cessation of the mining activity. Some of the results for water samples collected before and after the cessation of mining activity were obtained with the contribution of the National Environmental Protection Agency Suceava.

## Results and discussion

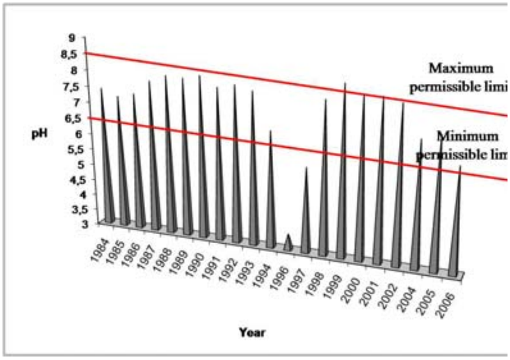
According to the *Norms Concerning the Classification of Surface Water Quality* maximum permissible concentrations of heavy metals in water were established (Table 2).[23, 24]

**Table 2**: Maximum permisible limits for heavy metals in water.

| Quality indicator | M.U. | I | II | III | IV | V |
|---|---|---|---|---|---|---|
| Cr | µg/L | 25 | 50 | 100 | 250 | > 250 |
| Cu | µg/L | 20 | 30 | 50 | 100 | > 100 |
| Zn | µg/L | 100 | 200 | 500 | 1000 | > 1000 |
| As | µg/L | 10 | 20 | 50 | 100 | > 100 |
| Ba | mg/L | 0,05 | 0,1 | 0,5 | 1 | > 1 |
| Se | µg/L | 1 | 2 | 5 | 10 | > 10 |
| Co | µg/L | 10 | 20 | 50 | 100 | > 100 |
| Pb | µg/L | 5 | 10 | 25 | 50 | > 50 |
| Cd | µg/L | 0,5 | 1 | 2 | 5 | > 5 |
| Fe | mg/L | 0,3 | 0,5 | 1,0 | 2 | > 2 |
| Hg | µg/L | 0,1 | 0,3 | 0,5 | 1 | > 1 |
| Mn | mg/L | 0,05 | 0,1 | 0,3 | 1 | > 1 |
| Ni | µg/L | 10 | 25 | 50 | 100 | > 100 |

The folowing parameters were analyzed: pH and Fe, Cu and Zn concentrations. Results obtained after water sampling were analysed are shows in Figures 6 – 9.

It can be seen that before the cessation of mining activity, the pH values tend to reach the maximum permissible limit, with exceeding it in 1998 – 2001 period. Also, in 1996 the pH value registered was 3.5. This acid pH value can be due to the deterioration of water discharge system, on the main slope. This led to the formation of a funnel collapse, which was filled with water as an artesian fountain. It is possible that the funnel may be activated the dissolving process of minerals with sulfur.

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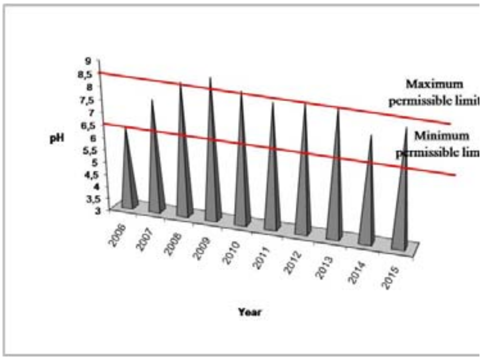
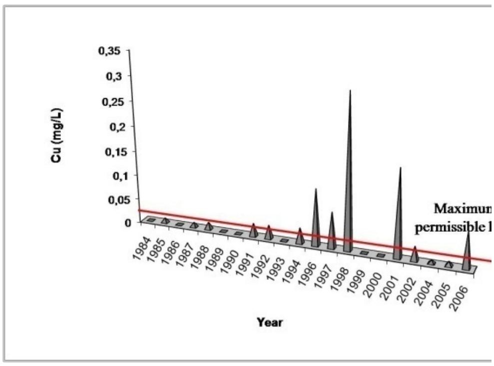



After the cessation of mining activities

**Figure 6**. pH variation of water samples collected from Brateasa and Valea Strajii Rivers.

After the cessation of mining activity, the pH values become very close to the maximum permissible limit, with exceeding this. In can be seen that in 2006, year when the mining activity was stopped, the pH water value decrease to 6. In this year, due to the torrential rainfall and higher water debits that infiltrated into the mass of sterile, there have been the risks of flooding and breaking the Tarnicioara tailing pond with slippage of the huge sterile mass deposited in it.

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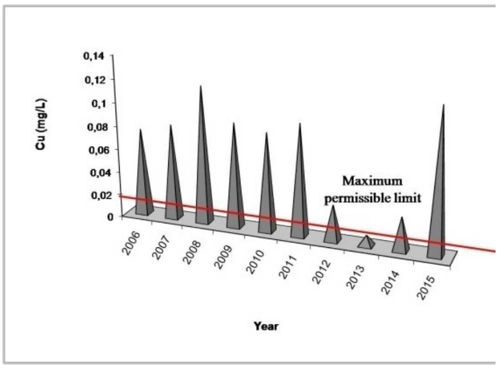
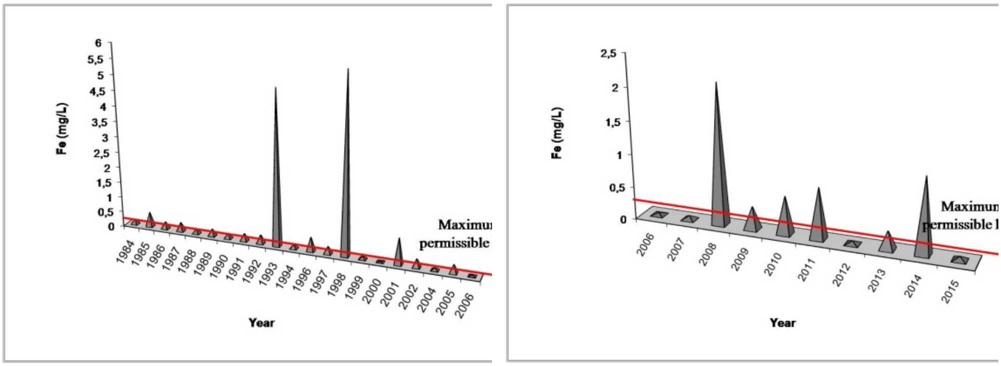


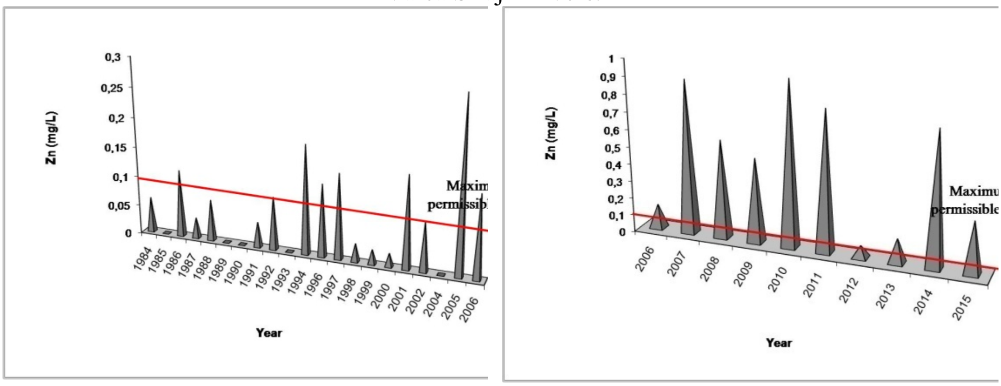

After the cessation of mining activities

**Figure 7**. Variation of Cu concentration of water samples collected from Brateasa and Valea Strajii Rivers.




Before the cessation of mining activities After the cessation of mining activities

**Figure 8**. Variation of Fe concentration of water samples collected from Brateasa and Valea Strajii Rivers.




Before the cessation of mining activities After the cessation of mining activities

**Figure 9**. Variation of Zn concentration of water samples collected from Brateasa and Valea Strajii Rivers.

The data obtained on the Cu, Fe and Zn concentrations (Figures 7 – 9) in water samples collected suggest that the maximal permissible limit was exceeded both before and after the cessation of mining activity. Moreover, these exceeding correspond to more negative events that have taken place over time such as damaging probes that ensures optimal functioning of tailing pond, clogging sieves and torrential rainfall. The last cause, torrential rainfall, determined significant exceeding of concentration values for heavy metals analyzed. The dissolving process of metal salts that occurs inside of tailing pond explained such results.

Data from Figures 7 – 9 shows that the cessation of mining activity did not lead to a decrease of heavy metals concentration in rivers water as it was to be expected. With increase rainfall, the values of heavy metals concentration increased too. Moreover, due to the rainfall the ravines were formed that increased the risk of slippage of sterile mass deposited in Tarnicioara tailing pond. This means that the cessation of mining activity did not determine the risks disappearance due to the residual mass of sterile after ore mining. This way of depositing the sterile resulted from mining leads to continuing deterioration of the environment from Ostra-Tarnita area. Nobody can predict the behavior of these sterile tailing ponds under special conditions such as torrential rainfall.

**Experimental**

Water samples were collected during the four seasons, especially downstream of Preparation Unit Tarnita. Experimental results registered in 1984 – 2014 were obtained with contribution of National Environmental Protection Agency Suceava. Experimental results registered in 2015 were obtained by analyzing of water samples at Water Quality Laboratory from Bacau, Romania.

For the results to be relevant, collecting samples was necessary to be done within several ways:

- instantaneous samples – collected manually to preset time;
- hourly average composition samples – collected continuously (automatically). This way of collecting have a higher degree of representativeness and allow detection of accidental pollution;
- samples consisting of several samples – collected automatically to preset time using submersible samplers placed at different depths;
- flow proportional samples – used to control effluent quality.

Water samples were collected from Brateasa Rivers in containers of brown glass tightly closed. It is necessary to use brown glass to prevent the contamination of the water samples with material from container. This would cause erroneous results. For analysis, volumes of samples between

0,5 – 1 L were collected at different levels so that analyzes to provide accurate results.[22]

## Conclusions

- The water pollution can be caused by the natural factors such as volcanic eruption. However, most of the substances with higher pollution risk are coming from human activity such as the mining, as we analyzed here.
- Storing the waste in tailings pond raises serious problems of stability and degradation of environmental quality. The major risk is the infiltration in soil and groundwater of tailings, which results in their pollution with heavy metals and other chemical substances used in extraction and minerals preparation.
- Pollution and risk for human communities or natural ecosystems around the mining sites not disappears with suspending the mining activity.
- After the pond conservation, the pollution risk can last for decades as a function of mineral composition of tailings, nature of reagents used in mineral preparation, rainfall, as well as surface and groundwater dynamics.
- Despite the fact that the mining activities from Tarnita area were suspended, the sterile continues to pollute soil and water long term.

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