Aquatic ecosystems have been affected by various types of contaminations around the globe in the recent few years. Traces metals are one of the most common pollutants which have severely deteriorated aquatic ecosystems [1-2].

Heavy metals in aquatic environment are distributed among aqueous phase, suspended particles and sediments. Suspended particles play an important role controlling the reactivity, transport and biological impacts of metals and other substances in aquatic environment and provide a crucial link for chemical constituents between water column, sediments and food chain [3].

Heavy metals are among the most persistent of pollutants in the ecosystem such as water, sediments and biota because of their resistance to decomposition in natural condition. Metal have low solubility in water, get adsorbed and accumulated on bottom sediments [4].

The increase the heavy metal content in the reservoirs is shown notably by increasing their concentration in bottom sediments. Accumulation of heavy metals in the environment results primarily from human activity. In addition, an important role in the “enrichment” heavy metal reservoirs they have natural processes, such as the disintegration of rocks and volcanic activities. Sediment is the ultimate destination for heavy metals discharged into the environment. The accumulation of heavy metals in sediment through physical and chemical mechanisms complexes of the adsorption, depending on the nature of the matrix of the sediment and the adsorption properties of the compounds [5-6].

The lake sediments are basic components of our environments as they provide nutrients for living organism. Lake bottom sediments are sensitive indicators for monitoring contaminants as they can act as a sink and a carrier for pollutants in the aquatic environment. Thus, the lake sediment analysis plays an important role in evaluating pollution status in aquatic environment [7].

Sediment has widely been studied for anthropogenic impacts on the aquatic environment [8]. Various studies have reported sediment quality assessments, distribution and contamination of heavy metals and quantification of pollution load in sediments of different rivers such as the Haihe River, China [9], the Jialiu River, China [10], the Lancang River, China [11], the Turag River, Bangladesh [12], the Hindon River, India [13], the Chao Phraya River, Thailand [14], the Kurang River, Pakistan [8], the Euphrates River, Turcia [15], the Euphrates River, Iraq [16], the Olt River, Romania [17], the Danube River [18-19], water reservoirs Bakomi, Rozgrund, and Vindsacha, Slovakia [20].

The main aspects of the present work are to: determine to content and spatial distribution of heavy metals (Cd, Cu, Ni, Zn, Pb, Cr, Hg) in the Jiu River surface sediments; calculating the contamination factor (CF), the geoaccumulation index (Igeo), the pollution load index (PLI), the Nemerow pollution index (PI) and potential ecological risk index (RI) in order to asses toxicity of the sediments.

Experimental part
Areas studied

Jiu River is formed by the union of the two streams, West Jiu and East Jiu, in the Petrosani Depression. West Jiu has a length of 51km and a hydrographic basin area of 534 km², rises in the Retezat Mts at an altitude of 1760m, the glacial bucket to Scorota. West Jiu is bordered on the right the Volcan massif and left of Retezat. Due to the fact that during its limestone rocks are present, the river and its tributaries have dug impressive gorges and waterfalls. The most important tributaries on the right are Oslea, Girbovul and Valea of Pești stooping over, and on the left Buta, Crevedia and Aninoasa.
East Jiu has a length of 28 km and basin covers an area of 479 km². The river is born in the eastern part of the Petrosani Depression between Șureanul and Paring. Tributaries on the right are Răscoala, Voievodul, Bilele and Taia.

Jiu River flow regime is characterized by high waters in spring and early summer, when there are frequent floods, fed from the snowmelt and high rainfall, sometimes torrential. Jiu waters are used in the Petrosani Depression washing coal coke needed in the preparation and the Rogojelu, Turceni, Isalnita for power plants and chemical plant. Quarrying of lignite deposits in Rovinari imposed Ceauru Dam construction, the lake formed with the purpose to retain water and to prevent floods.

Sediment samples were collected in Mai 2014 from 12 sites distributed along the study area (fig.1) and (table 1).

Methods of analysis

Determination of metals

Sediments samples were collected into plastic bags, and preserved by adding a small amount of concentrated nitric acid. Samples were air-dried. The samples were mixed thoroughly to achieve homogeneity and were sieved (< 0.2 mm), as the case. For each digestion procedure, about 2 g of sample (dry weight) was transferred in to a digestion vessel, followed by addition of mixture consist in 5 mL HNO₃ (65%) and 15 mL HCl (38%). The sample is kept for 16 h at room temperature to permit slow oxidation of the organic matter from the sediment. Reaction mixture temperature is increased slightly until it reaches boiling point and is maintained for 2 h, then let cool. The resulted mixture is passed through filter paper and collected in a 100 mL flask. The filter paper was washed with HNO₃ 0.5 M acid aqueous solutions. 100 mL flask is filled up to the mark with distilled water. Determination of the heavy metals in sediments was performed according to ISO 11466/1999 and ISO 11047/1999.

Quantification of sediment pollution

For assessment of the pollution degree with heavy metals in sediment four parameters have been used: Contamination factor (CF), Geo-accumulation index (Igeo), Pollution load index (PLI), Nemerow pollution index (PI) and the Ecological risk index (RI).

Contamination factor (CF)

The contamination factor (CF) was used to determine the contamination status of sediments and it is calculated as the ratio obtained by dividing the concentration of each heavy metal in the sediment \(C_{metal}\) by the concentration in background \(Bn\) (eq.1). The concentrations in background for Cd, Ni, Cu, Pb, Zn, Cr and Hg are 0.1, 1.0, 1.0, 1.0, 23.6, 13.6, and 1.21 mg/kg, average of the samples S1, S2 and S10. Depending on its value, the sediment pollution degree is classified as shown in table 2.

\[
CF = \frac{C_{metal}}{Bn}
\]
Geo-accumulation index (Igeo)

Geo-accumulation index to determine metals contamination in sediments and can be calculated using the following formula (2):

$$I_{\text{geo}} = \log_2 \left[ \frac{C_n}{B_n} \right]$$  \hspace{1cm} (2)

where:

- $C_n$ is the concentration of element $n$;
- $B_n$ is the background value in sediment.

Pollution load index (PLI)

Pollution load index (PLI) is calculated as the following equation (3):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$  \hspace{1cm} (3)

where, $n$ is the number of metals, $CF$ is contamination factor.

The PLI provides simple but comparative means for assessing a site quality, where a value of PLI < 1 denotes perfection; PLI = 1 presents that only baseline levels of pollutants are presented and PLI > 1 would indicate deterioration of site quality.

Nemerow pollution index (PI)

The Nemerow pollution index [21], (PI; eq. 4) was used to determine whether or not sampling sites were polluted in comparison with the criteria given in table 4.

$$PI = \left[ \frac{(CF)^2 + (CF \text{ max})^2}{2} \right]$$  \hspace{1cm} (4)

Potential ecological risk (RI)

In 1980, Lars Hakanson reported an ecological risk index for aquatic pollution control; therefore, Hakanson' method has been often used in ecological risk assessment as a diagnostic tool to penetrate one of many possible avenues towards a potential ecological risk index, i.e., to sort out which drainage area, reservoir, and substances should be given special attention (tables 5-6) [1, 9, 12, 22].

The index is calculated as the following equations (5) - (9):

$$CF = \frac{C_{\text{metal}}}{B_n}$$  \hspace{1cm} (5)

$$CH = \sum_{i=1}^{n} CF$$  \hspace{1cm} (6)

$$mCH = \sum_{i=1}^{n} CF$$  \hspace{1cm} (7)

$$E_f = T_f \times CF$$  \hspace{1cm} (8)

$$RI = \sum_{i=1}^{n} E_f$$  \hspace{1cm} (9)

where:

- $CF$ is the contamination factor;
- $C_n$ is the polluted coefficient of many metals;
- $mCF$ is the modified degree of contamination factors;
- $E_f$ is the potential ecological risk factor of single metal;
- $T_f$ is the biological toxicity factor of individual metals, which are defined as Cd=30, Cr=2, Cu=NI=Pb=5, Zn=1, Hg=40 [14, 21].

Results and discussions

Heavy metal concentration in sediments

To assess the contamination degree of sediments in the studied area, samples were collected from the upper layer of sediment, in twelve points.

Table 6 shows the concentrations of heavy metals in sediments of the Jiu River, West Jiu River and East Jiu River. The results were compared with the national legislation regulations (table 7) [23].

The concentration range of metals in sediments is: 17.53 to 89.43 mg/kg d.w. for Ni, 2.35 to 34.34 mg/kg d.w. for Cu, 8.73 to 49.06 mg/kg d.w. for Cr, 16.93 to 145.05 mg/kg d.w., 0.42 to 10.64 mg/kg d.w. for Hg and 1.59 to 1.84 mg/kg d.w. for Cd. Higher concentrations of Ni were found in sediments of the points S5 (downstream of locality Uricani), S6 (upstream of locality Uricani) and S9 (upstream of locality Petrila) while higher concentrations of Cd was found in sediments of the points S4 (downstream of Mining Lupeni), S5 (downstream of locality Uricani) and S6 (upstream of locality Uricani). Hg was found in higher concentrations than the limit imposed by legislation, in all points analyzed.

Assessment of sediment contamination

For assess the heavy metal pollution of sediments were used parameters: the contamination factor (CF), the
geoaccumulation Index (Igeo), the ecological risk index (RI), the pollution load index (PLI) and Nemerow pollution index (PI).

**Geo-accumulation index (Igeo)**

From the calculation of Geo-accumulation index (Igeo), in the sediments of Jiu River, Cr ranged from Class 0-2 with a level of pollution from unpolluted to moderately polluted, Ni with pollution levels unpolluted (Class 0) in the upstream and downstream Bumbești Jiu, downstream of Vulcan Mining, upstream and downstream of Rovinari Energy Complex (S12), with Cd in upstream and downstream of Bumbești Jiu (S1 and S2), downstream of Vulcan Mining (S3), with Hg upstream of Bumbești Jiu (S1) and downstream of Livezeni (S7), with Cr upstream of Bumbești Jiu (S1), upstream and downstream of Livezeni (S7 and S8) and downstream of Rovinari Energy Complex, with Pb upstream and downstream of Bumbești Jiu (S1 and S2), downstream of Vulcan Mining (S3), upstream and downstream of Uricani (S9), upstream of Petrila (S3 and S4), upstream of Uricani (S6), with Pb downstream of Lupeni (S4), downstream of Livezeni (S7) and upstream of Petrilă (S9) (table 8).

**Contamination factor (CF)**

In sediments from the Jiu River, there was a moderate contamination with Ni, upstream and downstream of Bumbești Jiu (S1 and S2), with Zn upstream and downstream of Bumbești Jiu (S1 and S2), downstream of Vulcan Mining (S3), upstream of Uricani (S6), downstream of Livezeni (S7) and downstream of Turceni Energy Complex (S12), with Cd upstream and downstream of Bumbești Jiu (S1 and S2), downstream of Vulcan Mining (S3), with Hg upstream of Bumbești Jiu (S1) and downstream of Livezeni (S7), with Cr upstream of Bumbești Jiu (S1), upstream and downstream of Livezeni (S7 and S8) and downstream of Rovinari Energy Complex, with Pb upstream and downstream of Bumbești Jiu (S1 and S2), downstream of Vulcan Mining (S3), upstream and downstream of Uricani (S6 and S5), downstream of Petrilă (S8), upstream and downstream of Energy Complex Rovină (S10 and S11) and downstream of energy complex Turceni (S12). A considerable contamination with Hg was found downstream of Mining Vulcan and Lupeni (S3 and S4), with Cr and Zn upstream of Petrilă (S9). A very high contamination with Ni was found upstream and downstream of Lupeni (S4 and S5), upstream of Uricani (S6), upstream and downstream of Petrilă (S8 and S9) and downstream of Livezeni (S7), with Cr downstream of Vulcan and Lupeni Mining (S3 and S4), downstream of Livezeni and Petrilă (S7 and S8), with Zn downstream of Petrilă (S8), with Cd upstream and downstream of Lupeni (S4 and S5), upstream of Uricani (S6), upstream of Petrilă, upstream and downstream of Rosină Energy Complex (S10 and S11) and downstream of Turceni Energy Complex (S12), with Hg upstream of Uricani (S6), with Pb downstream of Lupeni (S4), downstream of Livezeni (S7) and upstream of Petrilă (S9) (table 8).

**Geo-accumulation index (Igeo)**

From the calculation of Geo-accumulation index (Igeo), in the sediments of Jiu River, Cr ranged from Class 0-2 with a level of pollution from unpolluted to moderately polluted, Ni with pollution levels unpolluted (Class 0) in the upstream and downstream Bumbești Jiu, downstream of Vulcan Mining, upstream and downstream of Rovinari Energy Complex, a strong polluted levels (Class 4) downstream of Livezeni and downstream of Petrilă, a strong to very strong polluted (Class 5) downstream of Lupeni Mining and upstream of Petrilă, a very strong polluted (Class 6) upstream and downstream of Uricani. Cu with a level of pollution polluted (Class 0) upstream and downstream of Bumbești Jiu, upstream and downstream of Uricani, upstream of Petrila, upstream of Rovinari Energy Complex, a strong polluted levels (Class 4) downstream of Lupeni and Vulcan Mining, downstream of Livezeni, downstream of Petrilă and downstream of Energy Complex Rovină and a strong to very strong polluted (Class 5) downstream of Turceni Energy Complex. Zn with pollution levels in unpoluted (Class 0) at moderate to strongly polluted (Class 3) downstream of Petrilă, Cd pollution levels in unpolluted (Class 0) to a strongly polluted levels (Class 4) downstream of Lupeni Mining, upstream and downstream of Uricani, Hg with a moderate polluted (Class 2), downstream of Vulcan and Lupeni Mining and a moderate to strongly polluted (Class 3) upstream of Uricani and downstream of Energy Complex Rovina and while Pb a strong to very strongly polluted (Class 5) downstream of Lupeni.
Mining and downstream of Livezeni and a very strong polluted (Class 6) upstream of Petrila (table 9).

Pollution load index (PLI)
Regarding of pollution load index (PLI), PLI > 1, in the most of the points, indicating polluted sediments, except in the downstream of Bumbești Jiu, values are less than 1 (PLI< 1), indicating no pollution (table 10).

Nemerow pollution index (PI)
From the calculation the Nemerow index (PI) was found a level of pollution "unpolluted" downstream of Bumbești Jiu, pollution levels "lightly contaminated" upstream of Bumbești Jiu and pollution levels "seriously polluted" downstream of Lupeni and Vulcan Mining, upstream and downstream of Uricani, downstream of Livezeni, upstream and downstream of Rovinari Energy Complex and downstream of Turceni Energy Complex (table 10).

Potential ecological risk (RI)
In sediments from the Jiu River it was found a small ecological risk upstream and downstream of Bumbești Jiu, a moderate ecological risk downstream of Petrila, a strong ecological risk downstream of Vulcan Mining, downstream of Uricani, downstream of Livezeni, upstream and downstream of Rovinari Energy Complex and downstream of Turceni Energy Complex and a strong ecological risk downstream of Lupeni Mining, upstream of Uricani and upstream of Petrila (table 11).

Correlation of metals
Pearson's correlation coefficients for the investigated metals are depicted in table 12. In sediment samples the best correlations were found for the following pairs of metals: Zn-Cr (r=0.79352), Cd-Ni (r=0.80393), Hg-Ni (r=0.63829), Hg-Cd (r=0.669069), Pb-Cr (r=0.73107). These correlations among metal-metal pair may be an indication of common sources of these metals as well as similar geochemical characteristics. It is observed a positive correlation Cd - Ni, Cd - Hg and negative correlation Cd - Cr, Cd - Cu, Cd - Zn and Cd - Pb, and a positive correlation Hg - Ni, Hg - Cd and negative correlation Hg - Cr, Hg - Cu, Hg - Zn and Hg - Pb.
Conclusions

In sediments of the Jiu River from the calculation of pollution load index (PLI) was found a heavy metal pollution in most points, except point downstream of Bumbesti Jiu where the PLI < 1 where no was found pollution with heavy metals analyzed. From the calculation the Nemerow index (PI) was found a level of pollution “unpolluted” downstream of Bumbesti Jiu, pollution levels “lightly contaminated” upstream of Bumbesti Jiu and pollution levels “seriously polluted” downstream of Lupeni and Vulcan Mining, upstream and downstream of Uricani, downstream of Livezeni, upstream and downstream of Petrișa, upstream and downstream of Rovinari Energy Complex and downstream of Turceni Energy Complex. In sediments of the Jiu River there is low environmental risk upstream and downstream of Bumbesti Jiu, a moderate ecological risk downstream of Petrișa, a strong environmental risk downstream of Vulcan Mining, downstream of Uricani, downstream of Livezeni, upstream and downstream of Rovinari Energy Complex and downstream of Turceni Energy Complex, and a strong ecological risk downstream of Lupeni Mining, upstream of Uricani and upstream of Petrișa.

Acknowledgements: The authors acknowledge the financial support from the Ministry of Education- State Authority for Research Scientific, technological development and innovation through the Proiect PN 09-13 02 17, “The environmental risk assessment with the pollution indices” and the sectoral Operational Programme Human Resources Development (SOP HRD), financed from European Social Fund and the Romanian Government under the contract number POSDRU/159/1.5/S/137390.

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Manuscript received: 12.11.2014