- ORAL PRESENTATIONS -

ASSESSMENT OF THE POTENTIAL ECOLOGICAL RISK WITH HEAVY METALS IN SURFACE SEDIMENTS FROM ACCUMULATION LAKES ON THE SECTOR INFERIOR OF THE OLT RIVER

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Abstract. The aim of this paper is to assess the heavy metal pollution and potential ecological risk in surface sediments from accumulation lakes on the sector inferior of the Olt River: *Govora, Babeni-Marcea, Zavideni, Dragasani and Strejesti*. 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. 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 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 surface sediments from accumulation lakes on the sector inferior of the Olt River; calculating the *pollution load index (PLI)*, *the Nemerow pollution index (PI*) and *potential ecological risk (RI)* in order to evaluate the potential ecological risk.

Keywords: heavy metals, surface sediment, accumulation lakes, potential ecological risk

AIMS AND BACKGROUND

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[1].

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 mechanisms physical and chemical complexes of the adsorption, depending on the nature of the matrix of the sediment and the adsorption properties of the compounds[2, 3].

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[4].

Environmental pollution by heavy metals has become a global phenomenon with a special significance. The introduction of heavy metals in aquatic systems causes the deterioration of a number of biochemical processes that lead to dam-age of the flora and fauna of the aquatic system[5].

Sediment has widely been studied for anthropogenic impacts on the aquatic environment[6]. Various studies have reported sediment quality assessments, distribution and contamination of heavy metals and quantification of pollution load in sediments of different rivers such has the Haihe River, China[7], the Jialu River, China[8], the Lancang River, China[9], the Turag River, Banglades[10], the Hindon River, India[11], the Chao Phraya River, Thailanda[12], the Kurang River, Pakistan[6], the Euphrates River, Turcia[13], the Euphrates River, Iraq[14], the Olt River, Romania[15, 16], the Danube River, Romania[17, 18], water reservoirs Bakomi, Rozgrund and Vindsachta, Slovakia[19], the Shkodra lake, Albania[5].

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 surface sediments from accumulation lakes on the sector inferior of the Olt River; calculating the pollution load index (PLI), the Nemerow pollution index (PI) and potential ecological risk (RI) in order to evaluate the potential ecological risk.

EXPERIMENTAL

To assess the heavy metal pollution and potential ecological risk in surface sediments from accumulation lakes on the sector inferior of the Olt River, samples were collected from the upper layer of sediment, in five accumulation lakes: Govora, Babeni-Marcea, Zavideni, Dragasani and Strejesti. Sediment samples were collected in February 2015 from 9 sites distributed along the study area (Fig.1).

Determination of metals

Sediments samples into plastic bags were collected, and preserved by adding a small amount of concentrated nitric acid. Samples were air-dried. Mix the sample thoroughly to achieve homogeneity and sieve (< 0.2 mm), if appropriate and necessary. For each digestion procedure, weigh to the nearest 0.01 g and transfer 2.0 g sample (dry weight) to a digestion vessel. The digestion test samples by AAS, was made by adding a mixture of 5 ml HNO_3 (65%) and 15 ml of HCl (38%). The sample is kept for 16 hours at room temperature to permit slow oxidation of the organic matter in the sediment. Reaction mixture temperature is increased slightly until it reaches boiling point and is maintained for 2 hours, then let cool. The mixture is passed through filter paper and collected in a 100 mL flask. The filter paper was washed with HNO_3 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.

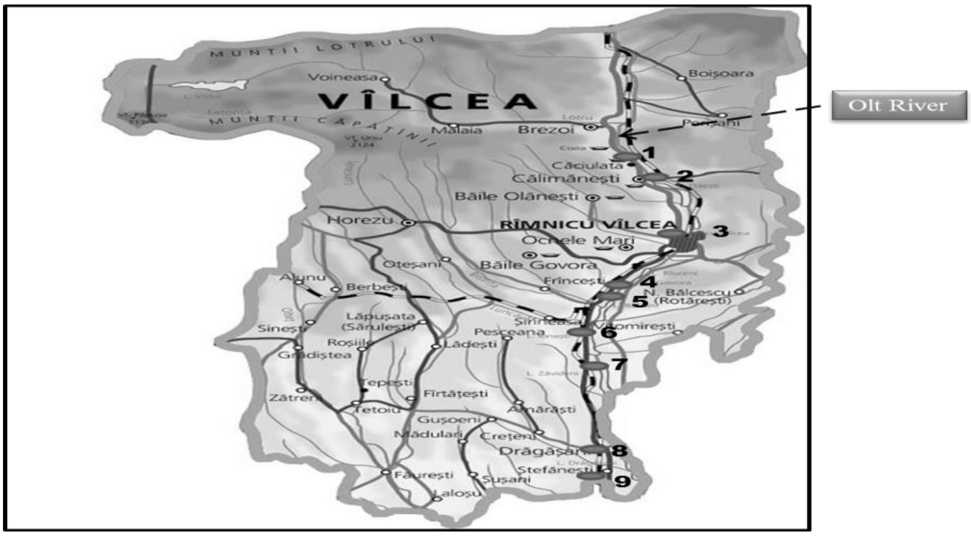

Figure 1. Localization points

Quantification of sediment pollution

For assessment of the pollution degree with heavy metals in sediment four parameters have been used: Contamination factor (CF), 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).

Depending on its value, the sediment pollution degree is classified as shown in Table 1.

$$CF = \frac{C_{metal}}{Bn} \quad (1)$$

Table 1. Contamination levels of sediments according to values of contamination factor

Contamination factor (CF)	Contamination level
CF<1	Low
1≤CF<3	Moderate
3≤CF<6	Considerable
CF>6	Very high

Pollution load index (PLI)

Pollution load index (PLI) is calculated as the following (Eq. 2):

$$PLI = (CF1 \times CF2 \times CF3 \times ....CFn)^{1/n} \quad (2)$$

where, *„n"* is the number of metals, *CF* is contamination factor.

The PLI provides simple bat 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[20], (PI; Eq. 3) was used to determine whether or not sampling sites were polluted in comparison with the criteria given in Table 2.

$$PI = \sqrt{\frac{(\overline{CF})^2 + (CF\max)^2}{2}} \quad (3)$$

Table 2. Nemerow pollution index sediment quality indicators

PI value Qualification of sediment	PI value Qualification of sediment
PI < 0.7	Non-polluted sediment
0.7 < PI < 1	Nearly polluted sediment
1 < PI < 2	Lightly polluted sediment
2 < PI < 3	Moderately polluted sediment
3 < PI	Seriously polluted sediment

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[7, 10, 21, 22] (Tables 4).

The index is calculated as the following equations (4), (5), (6), (7), (8):

$$CF = \frac{C_{metal}}{Bn} \quad (4)$$

$$CH = \sum_{i=1}^{n} CF \quad (5)$$

$$mCH = \frac{\sum_{i=1}^{n} CF}{n} \quad (6)$$

$$Ef = Tf \times CF \quad (7)$$

$$RI = \sum_{i=1}^{n} Ef \qquad (8)$$

where CF is the contamination factor; C_H is the polluted coefficient of many metals; mC_H 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[12]: Cd=30, Cr=2, Cu=Ni=Pb=5, Zn=1, Hg=40.

Table 3. Grade standard of Ef and RI[4]

Pollution coefficient (Ef)	Pollution index (RI)	Pollution level
<40	<150	Light ecological risk
40-79	150-299	Middle ecological risk
80-159	300-600	Strong ecological risk
160-320	>600	Very strong ecological risk
>320	-	Extremely strong ecological risk

RESULTS AND DISCUSSION

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 nine points. Table 4 shows the concentrations of heavy metals in sediments from accumulation lakes on the sector inferior of the Olt River. The analyzes were compared with the national legislation regulations[23]. The concentration range of metals in sediments is: 16.8 and 107.3 mg/kg d.w. for ***Ni***, 9.19 and 473 mg/kg d.w. for ***Cu***, 8.86 and 42.6 mg/kg d.w. for ***Cr***, 6.2 and 74.9 mg/kg d.w. for ***Zn*,** 0.74 and 3.36 mg/kg d.w. for ***Hg***. The metals ***Pb*** and ***Cd*** had values below the detection limit of the method. Higher concentrations of ***Ni*** were found in sediments of the points S2 and S4 (upstream of the industrial platform), ***Cu*** was found of the points S2, S3 and S4 (upstream of the industrial platform), ***Zn*** was found in sediments of the points S2, S4 (upstream of industrial platform) and S5 (dowstream of the industrial platform – accumulation lake Babeni) while higher concentrations of ***Cr*** was found in sediments of the point S2 (upstream of the industrial platform). Higher concentrations of ***Hg*** were found in sediments of the points S2, S3, S4 (upstream of the industrial platform) and S5 (downstream of the industrial platform – accumulation lake Babeni).

From the results are observed accumulation of metals (Ni, Cu, Zn, Cr and Hg) greater in the upstream of the industrial platform Ramnicu Valcea to the downstream sections, which can be deduced that such pollution sources could be Ramnicu Valcea city and industrial activities placed upstream from the Olt River. Another explanation for the lower concentration of heavy metals in points situated downstream of the industrial platform is the presence the Govora dam, which retains significant amounts of sediment[15].

Table 4. The content of metals in sediments of the Olt River (mg/kg d.w.)

Sample designation	The period	pH	Cr	Ni	Cu	Zn	Cd	Hg	Pb
S1	February 2015	7.85	<1.0	<1.0*	9.19	12.08	<0.1*	**0.99**	<1.0*
S2	February 2015	7.71	42.6	**57.9**	**44.2**	74.9	<0.1*	**1.78**	<1.0*
S3	February 2015	8.28	7.85	<1.0*	**473.0**	13.3	<0.1*	**3.36**	<1.0*
S4	February 2015	7.98	<1.0*	**107.3**	**52.7**	65.9	<0.1*	**0.98**	<1.0*
S5	February 2015	8.05	9.28	29.4	21.9	46.4	<0.1*	**1.04**	<1.0*
S6	February 2015	8.16	<1.0*	16.8	<1.0*	<1.0*	<0.1*	**0.74**	<1.0*
S7	Februarie 2015	8.11	8.96	<1.0*	11.54	21.0	<0.1*	**0.85**	<1.0*
S8	February 2015	8.09	8.86	<1.0*	11.40	6.20	<0.1*	**0.8**	<1.0*
S9	February 2015	8.15	<1.0*	<1.0*	11.64	27.2	<0.1*	**0.84**	<1.0*
Order No.161/2006	**Quality standard**	**-**	**100**	**35**	**40**	**150**	**0.8**	**0.3**	**85**

* The limit of detection of the method

Assessment of sediment contamination

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

Contamination factor (CF)

From the determination of contamination factor (CF) in sediments from the Olt River was found a *moderate contamination* with ***Ni*** in point S3 **(**upstream of the chemical platform - lake accumulation Govora) and downstream of the chemical platform in points: S7 (Zavideni accumulation lake), S8 (Dragasani accumulation lake) and S9 (Strejesti accumulation lake), with ***Zn*** in point S3 (upstream of the chemical platform - Govora accumulation lake) and downstream of the chemical platform in point S7 (Zavideni accumulation lake). There was found a *moderate contamination* with ***Hg*** in point S2 (upstream of Ramnicu Valcea - approx. 10 km) and in point S5 (downstream of the chemical platform - lake accumulation Babeni) with ***Cr*** in point S4 (upstream of the chemical platform - lake accumulation Govora) and downstream of the chemical platform in points: S6 (Babeni accumulation lake) and S9 (Strejesti accumulation lake). There was a *considerable contamination* with Hg upstream of the chemical platform in point S3 (Govora accumulation lake), with ***Cu*** in point S4 (upstream of the chemical platform - Govora accumulation lake) and with ***Zn*** in point S4 (upstream of the chemical platform - lake accumulation Govora) and in point S5 (downstream of the chemical platform - Babeni accumulation lake). There was found a *high contamination* with ***Ni*** in point S2 (upstream of the Ramnicu Valcea), in point S4 (upstream of chemical platform - Govora accumulation lake), in points S5 and S6 (downstream of the chemical platform - Babeni accumulation lake (S5 and S6), with ***Cu*** in point S3 **(**upstream of the chemical platform - Govora accumulation lake), with ***Zn*** in point S2 (upstream of the Ramnicu Valcea - approx. 10 km) (Tables 5a and 5b).

Table 5a. Contamination factor (CF) for heavy metals in sediments of the Olt River

Sample designation	Cr		Ni		Cu		Zn	
	CF	Level	CF	Level	CF	Level	CF	Level
S1	1	1<CF<3	1	1<CF<3	1	1<CF<3	1	1<CF<3
S2	42.6	**CF>6**	57.9	**CF>6**	4.8	**3<CF<6**	6.2	**CF>6**
S3	7.85	**CF>6**	1	1<CF<3	51.47	**CF>6**	1.1	1<CF<3
S4	1	1<CF<3	107.3	**CF>6**	5.73	**3<CF<6**	5.45	**3<CF<6**
S5	9.28	**CF>6**	29.4	**CF>6**	2.38	1<CF<3	3.84	**3<CF<6**
S6	1	1<CF<3	16.8	**CF>6**	0.11	<1	0.08	<1
S7	8.96	**CF>6**	1	1<CF<3	1.25	1<CF<3	1.74	1<CF<3
S8	8.86	**CF>6**	1	1<CF<3	1.24	1<CF<3	0.51	<1
S9	1	1<CF<3	1	1<CF<3	1.27	1<CF<3	2.25	1<CF<3

Table 5b. Contamination factor (CF) for heavy metals in sediments of the Olt River

Sample designation	Cd		Hg		Pb	
	CF	Level	CF	Level	CF	Level
S1	1	1<CF<3	1	1<CF<3	1	1<CF<3
S2	1	1<CF<3	1.8	1<CF<3	1	1<CF<3
S3	1	1<CF<3	3.39	**3<CF<6**	1	1<CF<3
S4	1	1<CF<3	0.99	<1	1	1<CF<3
S5	1	1<CF<3	1.05	1<CF<3	1	1<CF<3
S6	1	1<CF<3	0.74	<1	1	1<CF<3
S7	1	1<CF<3	0.85	<1	1	1<CF<3
S8	1	1<CF<3	0.80	<1	1	1<CF<3
S9	1	1<CF<3	0.85	<1	1	1<CF<3

Pollution load index (PLI)

Regarding of pollution load index (PLI), values are above 1 (PLI> 1) in most of the points, from where is apparent "*that there is a deterioration in the quality of sediments*", hence there was a heavy metal pollution, except the point S6 (downstream of the chemical platform - Babeni accumulation lake), value are less than 1 (PLI< 1), indicating no pollution (Table 6).

Table 6. Pollution load index (PLI) and Nemerow index (PI) for heavy metals from sediments of the Olt River

Sample designation	PLI	Pollution level	PI	Pollution level
S1	0	Unpolluted	0	Unpolluted
S2	**5.2**	**Polluted**	**42.55**	**Seriously polluted**
S3	**2.78**	**Polluted**	**37.01**	**Seriously polluted**
S4	**3.11**	**Polluted**	**76.87**	**Seriously polluted**
S5	**3.01**	**Polluted**	**21.34**	**Seriously polluted**
S6	0.73	Lightly polluted	**12.06**	**Seriously polluted**
S7	**1.46**	**Polluted**	6.53	**Seriously polluted**
S8	**1.24**	**Polluted**	6.43	**Seriously polluted**
S9	**1.13**	**Polluted**	1.8	Lightly polluted

Nemerow pollution index (PI)

From the calculation of Nemerow Index (PI), in sediments from Olt River, was found a level of pollution *"heavily polluted"* in the majority points, except the point S9 (Strejesti accumulation lake) where was found a level of pollution "lightly contaminated" (Table 6).

Table 7. Ecological risk index for heavy metals from sediments of the Olt River

Sample designation	Cr	Ni	Cu	Zn	Cd	Hg	Pb	RI	Grade Hakanson Pollution level
	E_f	E_f	E_f	E_f	E_f	E_f	E_f		
S1	2	6	5	1	30	40	5	**89**	Light ecological risk
S2	85.2	**347.4**	24.0	6.2	30	**71.91**	5	**569.7**	**Strong ecological risk**
S3	15.7	6.0	**257.3**	1.1	30	**135.75**	5	**450.9**	**Strong ecological risk**
S4	2	**643.8**	28.67	5.45	30	39.6	5	**754.5**	**Very strong ecological risk**
S5	18.6	**176.4**	11.9	3.84	30	42.02	5	**287.7**	**Middle ecological risk**
S6	2	**100.8**	0.5	0.08	30	29.9	5	**168.3**	**Middle ecological risk**
S7	17.9	6	6.2	1.74	30	34.34	5	**101.2**	Light ecological risk
S8	17.7	6	6.2	0.51	30	32.32	5	**97.7**	Light ecological risk
S9	2	6	6.3	2.25	30	33.93	5	**85.5**	Light ecological risk

Potential ecological risk (RI)

In sediments from Olt River it was found a low ecological risk of heavy metal downstream of the chemical platform Ramnicu Valcea: Zavideni accumulation lake (S7), Dragasani accumulation lake (S8) and Strejesti accumulation lake (S9). In sediments from Babeni Accumulation Lake (S5 and S6) situated downstream of the chemical platform Ramnicu Valcea was found a *moderate ecological risk* with heavy metal. The points located upstream and downstream from the city Ramnicu Valcea (S2 and S3) was found a *strong ecological risk*, given risk factor potential ecological risk (Ef) of Ni and Hg to a point upstream of Ramnicu Valcea (S2) from which it is apparent that there is a greater degree of pollution with metals Ni and Hg while to point downstream of Ramnicu Valcea (S3) the risk is given by Cu and Hg, which proves that there a degree of pollution higher by metals Cu and Hg. In sediments from Govora accumulation lake (S4) situated upstream of the platform Ramnicu Valcea was found a *very strong ecological risk* of heavy metal, given the risk of potential ecological risk factor (Ef) of Ni and Cu from which it is apparent that there a degree of pollution higher by Ni and Cu metals (Table 7).

CONCLUSIONS

In sediments from accumulation lakes on the sector inferior of the Olt River, the pollution load index (PLI) indicated a heavy metal pollution in most points, except the point S6 (downstream of the chemical platform - Babeni accumulation lake), value are less than 1 (PLI< 1), indicating no pollution. The Nemerow index (PI) indicated a level of pollution *"heavily polluted"* in the majority points, except the point S9 (Strejesti accumulation lake) where was found a level of pollution "lightly contaminated". In sediments from Olt River it was found *a low ecological risk* of heavy metal, downstream of the chemical platform Ramnicu Valcea: Zavideni accumulation lake (S7), Dragasani accumulation lake (S8) and Strejesti accumulation lake (S9). In sediments from Babeni Accumulation Lake (S5 and S6) situated downstream of the chemical platform Ramnicu Valcea was found a *moderate ecological risk* with heavy metal. The points located upstream and downstream from the city Ramnicu Valcea (S2 and S3) was found a *strong ecological risk*. In sediments from Govora accumulation lake (S4) situated upstream of the platform Ramnicu Valcea was found a *very strong ecological risk* of heavy metal. From the results are observed accumulation of metals (Ni, Cu, Zn, Cr and Hg) greater in the upstream of the industrial platform Ramnicu Valcea to the downstream sections, which can be deduced that such pollution sources could be Ramnicu Valcea city and industrial activities placed upstream from the Olt River.

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