THE CHARACTERIZATION OF PRIORITY HAZARDOUS SUBSTANCES DISTRIBUTION AT THE LEVEL OF ABIOTIC COMPARTMENTS (WATER/SEDIMENT) OF THE OLT RIVER BASIN, IN THE INDUSTRIAL PLATFORM AREA RAMNICU VALCEA

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This paper aims to evaluate pollution priority hazardous substances in the Olt river ecosystems induced by the industrial platform Ramnicu Valcea.
There is generally insignificant soil pollution caused organochlorine substances (1,2 Dichloroethane, Trichloroethylene, 1,2,4 trichlorobenzene ether β,β'diclordiizopropilic, perchlorethylene) and heavy metals (nickel, cadmium, copper, zinc, lead). There was a significant pollution with copper in the point S7, point was situated at approx. 50 m east of Monomer plant, vicinity pool DA 602 (wastewater treatment).
In general the water samples from the Olt river and the accumulation lakes on the Olt river not found pollution of a heavy metals, nickel, copper, cadmium, zinc and lead. The exception is the point P7 (Cremernari) in which nickel was within grade quality. For organochlorine substances analyzed in the sections is

observed that 1,2-dichloroethane, trichlorethylene and perchlorethylene took values that are within the limits imposed by the Order no. 161/2006, and 1,2,4 trichlorobenzene and ether β, β 'diclordiizopropilic falls below the detection limit of the method.
In sediment samples collected from the Olt River and the accumulation lakes on the Olt river is found higher concentrations of nickel in the sections S1, S2, S3, S6, all sections situated upstream of the platform, copper in sections S3 and S6, , cadmium in section S7 (Cremenari), lead in sections S1, S3, S6, S9, zinc in the sections S1 , S3, S6, S7, sections S1, S3, S6, situated upstream of the platform.
Also observe that in all sections, 1,2 dichloroethane, trichlorethylene, perchlorethylene, 1,2,4 trichlorobenzene and ether β, β 'diclordiizopropilic, taking values below the detection limit of the method.
From the results it is observed accumulation of metals (nickel, copper, zinc and lead) greater in the upstream industrial platform Ramnicu Valcea, downstream sections from which one can deduce that pollution sources could be Ramnicu industrial activities located in Valcea upper Olt.

Keywords: priority hazardous substances, pollution, water surface, sediment, soil

1. Introduction

The Water Framework Directive 2000/60/EC is probably the most significant European legislation in force in the field of water in the last years [1]. This policy requires further specific measures for pollution control and sets environmental quality standards for 33 priority substances and certain other priority pollutants, which are established in the more recent Directive 2008/105/EC. These priority pollutants are characterized by high toxicity, high environmental persistence or/and high hydrophobicity. Some of them cause endocrine disruption effects on marine organisms and consequently, they could represent a risk to environment and human health [2].

Water pollution caused by toxic metals and organic compounds remains a serious environmental and public problem. Moreover, faced with more and more stringent regulations, water pollution has also become a major source of concern and a priority for most industrial sectors. Heavy metal ions, aromatic compounds (including phenolic derivatives and polycyclic aromatic compounds) and dyes are often found in the environment as a result of their wide industrial uses. They are common contaminants in wastewater and many of them are known to be toxic or carcinogenic. For example, chromium (VI) is found to be toxic to bacteria, plants, animals and people. Mercury and cadmium are known as two of the most toxic metals that are very damaging to the environment [3].

The presence of metals in industrial and urban wastewater is one of the main causes of water and soil pollution. Accumulation of these elements in wastewater depends on a number of local factors, including the industry type, peoples' way of life, and their awareness of the impacts to the environment by careless disposal of wastes. Metals in urban wastewater originate mainly from domestic activities, industrial activities, and storm water runoff. Metal discharges to the environment not only cause acute toxicity to aquatic

organisms, microorganisms, and plants, but also strongly reduce microbial activity, which adversely affects biological wastewater treatment plants (WTPs) [4].

The purpose of the present study was to evaluate the status of priority hazardous substances in soil, water and sediments. The sampling points have been selected for this study at the zone situated around the industrial platform Ramnicu Valcea area.

2. Experimental part

2.1. Description of studied area

The studied area was a section of approx. 100 km long in the lower basin of the Olt River. The Olt River is one of the most important rivers in Romania being the largest and the longest (615 km) Romanian tributary of the Danube River. It flows through the counties of Harghita, Covasna, Brasov, Sibiu, Ramnicu Valcea, Olt and Teleorman. The Olt River flows into the Danube near Turnu Magurele, at Islaz.

The wastewater effluents of the industrial platform are discharged into the Olt River. The lower course of the Olt River includes 15 lakes in order to produce electricity and for irrigation water. The average flow of the Olt River is 140 m^3 / s.

The surface water and sediments samples were collected in the thirteen sections, situated upstream and dowstream of the industrial platform (Table 1).

Nickel, copper, cadmium, zinc, lead, 1,2 dichloroethane, 1,1,2-trichlorethylene, 1,2,4-trichlorobenzene and perchlorethylene were studied because these priority hazardous substances are found in the chemical processes developed at Râmnicu Vâlcea industrial platform.

Table 1
SAMPLING POINTS OF THE WATER / THE SEDIMENT

Nr. Crt	Denumire proba	Sampling points of the water / the sediment
1	P_1	Water/sediment samples collected from the Olt river - Călimăneşti Caciulata approx. 25 km from the Ramnicu Valcea Municipality
2	P_2	Water/sediment samples collected from the Olt river, Ramnicu Valcea upstream - Fedelesoiu approx. 10 km from the Ramnicu Valcea Municipality
3	P_3	Water/sediment samples collected from the Olt river, Ramnicu Valcea downstream and upstream of the Pârâul Sărat and Priza Olt, aprox.7 km from the Ramnicu Valcea platform
4	P_4	Water/sediment samples collected from the Pârâul Sărat - Stolniceni
5	P_5	Water/sediment samples collected from the Pârâul Sărat – Căzănești
6	P_6	Water/sediment samples collected from the Olt river, upstream the Ramnicu platform Valcea - Section Priza Olt, approx. 5 km from the platform
7	P_7	Water/sediment samples collected from the Olt river, approx. 8-10 km downstream the Ramnicu Valcea platform - Section Cremenari
8	P_8	Water/sediment samples collected from the Olt river, downstream the Ramnicu Valcea platform, approx. 12 km the Section Cremenari,– Section Băbeni - Marcea

9	P_9	Water/sediment samples collected from the Olt river, Zavideni (lake), approx. 15 km from the Section Babeni Marcea
10	P_{10}	Water/sediment samples collected from the Olt river, upstream from the Dragasani, approx. 16 km from the Section Zavideni
11	P_{11}	Water/sediment samples collected from the Olt river, dowstream from the Dragasani (lake Strejesti), approx. 25 km from the Dragasani
12	P_{12}	Water/sediment samples collected from the Govora river, upstream from the WWTP SC OLTCHIM SA
13	P_{13}	Water/sediment samples collected from the Govora river, dowstream from the WWTP SC OLTCHIM SA

2.2. Metals determination in water samples

The concentrations of Cu, Ni, Pb and Cd were determined with atomic absorption spectrometer, equipped with an air-acetylene flame. Concentrations of heavy metals in the water, sediment and soil were assessed according to the standards by the environmental legislation, respectively.

All the samples were filtered through a 0.45–μm filter and were then acidified at the time of collection with HNO_3 (5mL/L). Then, a 100 mL aliquot of the sample well mixed has been transferred in a beaker. The sample was covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate at 90 to 95°C until the volume was reduced to 15-20 mL. After cooling the final volume was adjusted to 100 mL with ultra-pure water.

2.3 Metals determination in sediment samples

The sample was mixed thoroughly to achieve homogeneity and was sieved if necessary. For each digestion procedure 1-2 g sample (wet weight) and 1.0 g sample (dry weight) have been transferred in a digestion vessel. For ICP-MS analyses 10 mL of 1:1 HNO_3 were added, mixed and covered with a watch glass or a vapor recovery device. The sample was heated to 95 ° C and refluxed for 10 to 15 minutes with boiling. The sample was allowed to cool, added 5 mL of concentrated HNO_3, and reflux for 30 minutes. If brown smoke was generated, indicating oxidation of the sample by HNO_3, this step is repeated (addition of 5 mL concentrated HNO_3) until smoke emanated is not being brown. After cooling, 2 mL of water and 3 mL of H_2O_2 30% were added until effervescence was minimal or until the general sample appearance was unchanged. Then the sample was heated until the volume was reduced to about 5 ml. After cooling, it was diluted to 100 mL with water.

2.3. Organochlorine compounds determination in water samples

The contents of organochloride compounds were determined by chromatography coupled with mass spectrometry (GS-MS).

A sample was taken and discarded glass bottle filled with enough water so that there was no residual sample volume of 200 mL. Add to the sample the extraction solvent (pentane), close and vigorously mix using a magnetic shaker or a mechanical shaker for 5 minutes to ensure that the extractant has been finely dispersed in the sample in order to obtain a reproducible recovery.

After mixing, allow the sample container to stand up to separate layers. Pour off the top layer directly using a pipette solvent. Immediately proceed with gas chromatographic analysis.

2.3.1. Determination of 1,2,4 -trichlorobenzene

Samples of water were taken in a brown glass bottle with a nominal capacity of 1 liter to 5 liters. The pH was verified and, if necessary, adjusts the pH immediately after collection to be within the range of 5 to 7.5. In order to prevent decomposition of the sample, the samples were carefully taken as soon as possible (preferably within 24 hours).

The sample volume was one liter. Add 30 mL of extraction solvent (heptane) and stirred for at least 10 minutes. The contents transferred to a separating funnel with adequate capacity and standing to allow phase separation. It was put back to the bottle bottom and the aqueous phase sample extraction was repeated twice with 20 mL and 30 mL extraction solvent. Sodium sulfate was added to the vial. It was stirred for 1 min, left to stand for 5 minutes and clarified extract is passed to the evaporator. Sodium sulfate was washed with an additional 10 mL to 20 mL of the solvent, and the solvent is introduced into the evaporator.

2.3.2. Organochlorine compounds determination in sediment samples

For samples that contain volatile components no pre-treatment was necessary. Amount of 30 grams of wet soil was weighted in a glass iodometrical beaker. Add 50 mL of methanol and stirred 30 min., add 50 mL with pentane and stirred for another 30 min. The liquid phase was filtered through a filter paper with medium porosity and into a 500 mL separatory funnel there are 250 mL of distilled water, washed the soil with 10 mL pentane. The funnel was stirred 5 min. allowing separation and discard the organic phase. The organic layer was passed through a filter with anhydrous Na_2SO_4 into a hermetic closed glass. The funnel and the layer with Na_2SO_4 was rinsed with 5 mL of pentane and added to the organic layer.

3. Results and discussion

3.1. Content of priority hazardous substances in soil

In order to investigate soil pollution with priority hazardous substances samples from industrial area Ramnicu Valcea were collected from an area of 2 km^2. The collecting points are located approx. 50 m of facilities with risk of accidental pollution.

Figure 1 show the evolution of the concentrations of heavy metal in soil during the period March - April 2013. The results were compared with the limits imposed by the national legislation [5].

From the results observed, generally, nickel, cooper, zinc and cadmium concentrations was falling values in normal limits and thresholds the alert / less sensitive types of use, except the point S7 were the copper concentration

exceeds the threshold for intervention/types use less sensitive. The concentrations of metals higher in the second levels (II, III) than in the first level (I), can be attributed to historical pollution. Historical pollution is caused by faulty operation of facilities, improper storage and by the lack of environmental legislation in the past.

In the soil samples analyzed from the industrial platform Ramnicu Valcea was found an insignificant pollution with nickel, zinc and cadmium but a significantly pollution with copper.

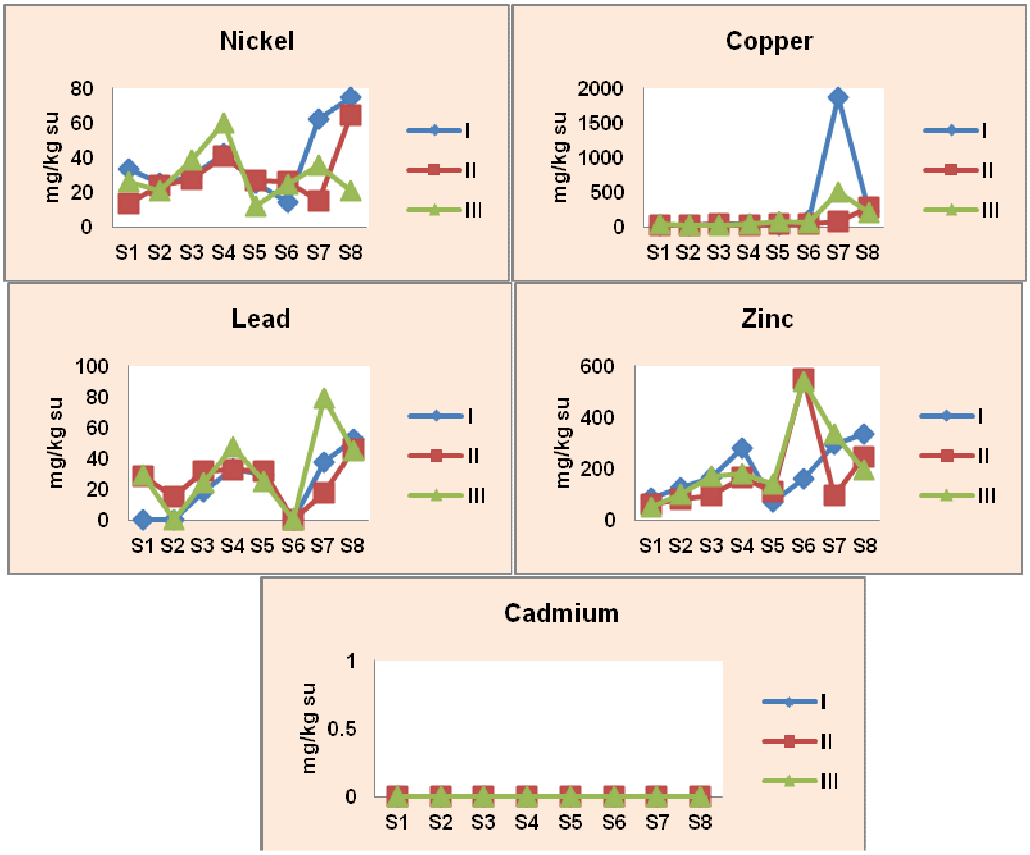

Fig.1. Evolution of the concentration of heavy metals in soil

3.2. Content of priority hazardous substances in surface water

Table 2 shows the evolution of the concentrations of priority hazardous substances in the thirteen sections, during the period March - April 2013. The results were compared with the limits imposed by the national legislation [6].

From the characterization of water samples collected from sections located in the Olt River upstream industrial platform Ramnicu Valcea were noted:

Heavy metals, showed lower concentrations than the limits Ord.161/2006 in all sections analyzed, taking values below the detection limit of the method. Regarding substances analyzed oraganoclorurate 1,2-dichloroethane, trichlorethylene, perchlorethylene, 1,2,4 Trichlorobenzene and ether β,β'

diclordiizopropilic, taking values below the method detection limit and below the limits specified in the legislation (Ord 161/2006).

In sections downstream from the discharge of the industrial wastewater from platform Ramnicu Valcea revealed:

Heavy metals (nickel, copper, cadmium, lead, zinc) had concentrations below the limits Nr.161/2006 Order, taking values below the method detection limit, except for the point P7 (Cremenari) where nickel was assigned to the class the V^{th} of quality (0.13 mg / L).

The results observed for organochlorine substances in surface water were as follows: 1,2-dichloroethane with values between 1.02 – 1.95 μg / L as compared to limit of 10.0 μg/ L from the national legislation, 1,1,2-trichlorethylene with values between 0.06 – 0,35 μg / L, perchlorethylene with values between 0.34 – 4.7 μg / L and 1,2,4-trichlorobenzene and ether β,β' diclordiizopropilic having values below the detection limit.

Regarding the water samples from the Sărat stream, heavy metals, copper, cadmium and zinc concentrations were below the limits Order Nr.161/2006, taking values below the detection limit of the method, while nickel was within the class 3^{rd} of quality (0.048 mg / L) and lead to stay within the class 5^{th} of quality (0.055 mg / L). Organochlorine substances analyzed have had values that are within the limits imposed by the Order Nr.161/2006.

Have been collected water samples from the Govora river, upstream and downstream from the biological treatment plant OLTCHIM. In samples taken upstream of the treatment plant, heavy metals had values below the method detection limit while in the samples downstream of the station cadmium and nickel were classified in the class 3^{rd} of quality and lead in the class 5^{th} of quality. Regarding analyzed organochlorine substances they had values below the detection limit of the method, both upstream and downstream of the treatment plant.

3.3. Content of priority hazardous substances in sediments

From data indicated in Figure 2 can be observed that the concentrations of heavy metals from sediments in the upstream points are higher compared with the downstream points

Nickel had values between 11.96 and 63.3 mg / kg D.M. upstream of the platform and values between 11.7 and 33.8 mg / kg D.M. downstream from the platform, compared to limit of 35.0 mg / kg D.M.. Higher concentrations of nickel were found in sections S1, S2, S3, S6, all the sections situated upstream from the platform.

Copper had values between 5.1 to 1021.2 mg / kg D.M. upstream of the platform and values between 4.78 and 64.0 mg / kg DM downstream from the platform, compared to limit of 40.0 mg / kg D.M.. Higher concentrations of copper were found in sections S3 and S6, the sections situated upstream from the platform.

Table 2.

CONTENT OF PRIORITY HAZARDOUS SUBSTANCES IN SURFACE WATER

Nr.crt.	Sampling site/ Period		pH	Cadmium	Nickel	Copper	Zinc	Lead	1,2- DCE	1,1,2- TCE	PCE	1,2,4- TCB	Eter β,β '
			Unit.pH	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	mg/L
1	P1	March	7.03	<0.005*	<0.01*	<0.01*	0.038	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	6.64	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
2	P2	March	7.05	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	6.78	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
3	P3	March	7.06	<0.005*	<0.01*	<0.01*	0.0005	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	6.89	<0.005*	<0.01*	<0.01*	0.0005	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
4	P4	March	7.26	<0.005*	<0.01*	<0.01*	0.0005	0.055	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.13	<0.005*	<0.01*	<0.01*	0.0005	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
5	P5	March	7.42	<0.005*	0.048	<0.01*	0.0005	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.36	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
6	P6	March	7.13	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	0.06	4.7	<0.002*	<0.05*
		April	7.08	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	1.5	<0.002*	<0.05*
7	P7	March	6.96	<0.005*	0.13	<0.01*	0.011	<0.05*	1.95	0.74	2.4	<0.002*	<0.05*
		April	7.14	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	0.98	<0.002*	<0.05*
8	P8	March	7.04	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	1.02	0.35	0.78	<0.002*	<0.05*
		April	6.89	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	0.34	<0.002*	<0.05*
9	P9	March	6.59	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	6.92	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
10	P10	March	7.07	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.15	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
11	P11	March	6.95	<0.005*	<0.01*	<0.01*	0.011	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.08	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
12	P12	March	7.30	<0.005*	<0.01*	<0.01*	0.0005	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.18	<0.005*	<0.01*	<0.01*	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
13	P13	March	6.54	0.0018	0.048	<0.01*	0.0005	0.055	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*
		April	7.03	<0.005*	<0.01*	0.02	<0.005*	<0.05*	<0.05*	<0.05*	<0.05*	<0.002*	<0.05*

Cadmium was below the method detection limit (<1.0 mg / kg DM), both upstream and downstream of the platform. In section S7 (Cremenari) was found a concentration of 4.67 mg / kg DM compared to limit of 0.8 mg / kg D.M.

Lead indicator has values between 13.99 to 195.1 mg / kg D.M. upstream of the platform and values between 14.5 to 121.7 mg / kg D.M. downstream from the platform, compared to limit of 85 mg / kg D.M.. Higher concentrations of lead were found in sections S1, S3, S6, S9, sections S1, S3, S6.

Zinc indicator has values between 43 to 191.68 mg / kg D.M. upstream of the platform and values between 6.1 to 59.19 mg / kg D.M. downstream from the platform, compared to limit of 150.0 mg / kg D.M.. Higher concentrations of zinc were found in sections S1, S3, S6, S7, sections S1, S3, S6.

This means that an important amount of heavy metal pollutants is coming from upstream of industrial platform. The sources of pollution can be the city of Ramnicu Valcea and industrial activities located in upper part of the Olt River. Another explanation for lower concentration of heavy metals in points C and M is the presence of Govora Dam that retains important amounts of sediments.

Also observe that in all control sections, 1,2 dichloroethane, trichlorethylene, perchlorethylene, 1,2,4 trichlorobenzene and ether β,β' diclordiizopropilic taking values below the detection limit of the method.

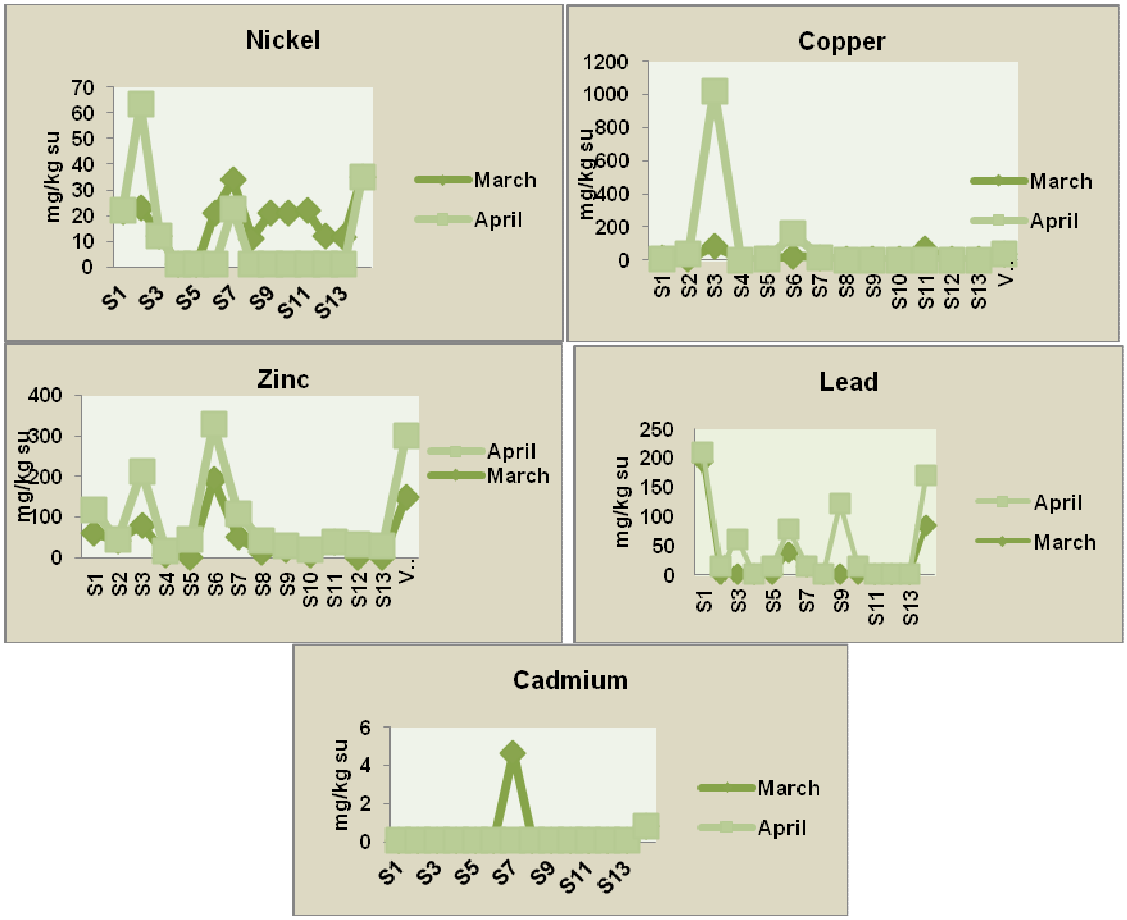

Fig.2. Evolution of the concentration of heavy metals in sediments

Conclusions

The pollution risk with priority hazardous substances of water and sediments in the Olt River around the industrial platform Ramnicu Valcea area has been evaluated within the period March – April 2013.

The presence of heavy metals was observed in the samples of soil collected inside of industrial platform. Excepting one situation, point S7, the concentrations of cooper was under threshold of intervention.

Regarding the Olt River water, generally, was not detected a significant pollution by the priority hazardous substances analyzed.

However, in the Olt River sediments from industrial platform Ramnicu Valcea area higher concentrations of heavy metals were observed upstream the platform. The organochlorine substances analyzed had values that fall within the limits imposed by the current legislation.

One can conclude tha according to the data obtained, there was no major environmental impact on the accumulation priority hazardous substances in the ecosystems of the Olt River, in the industrial platform Ramnicu Valcea area.

References

1. *** Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. OJ L 348, 24.12.2008, p. 84
2. BOUZAS, A., SECO, A., AGUADO, D., MARTI, N., SEGOVIA-MARTÍNEZ, L., Mar. Pollut. Bull., **62**, 2011, p. 615–625
3. FAZ, A., ACOSTA, J. A. AND MARTINEZ-MARTINEZ, S., Environ. Monit. Assess., **169** (1-4)**,** 2010, p. 519-30
4. USTUN G. E., J. Hazard. Mater., **172**, 2009, p. 833-838
5. *** Order 756/1997 Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 756/1997 for the approval of the Regulatory concerning environmental pollution assessment
6. *** Order 161/2006, for the approval of the Norms regarding the classification of surface water quality in order to establish the ecological status of the water body