

**ASSESS THE DEGREE OF ACCUMULATION OF SUBSTANCES
PRIORITY/HAZARDOUS POLLUTANTS IN SOIL AND SEDIMENT SOURCES
AROUND THE OLT RIVER, UPSTREAM AND DOWNSTREAM OF
WASTEWATER DISCHARGES FROM INDUSTRIAL PLATFORM RAMNICU
VALCEA**

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Abstract

This study was realized in order to determine the degree of substances priority/hazardous pollution in the industrial chemical platform of Ramnicu Valcea. Samples were collected in two campaigns, in February and June 2010 and nickel, copper, cadmium, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene from water, soil and sediments was analyzed.

The results show that heavy metals in sediments collected from the Olt river, (Priza Olt and Cremenari), had higher concentrations than in National Legislation. Also notice that in all three points, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene taking values below the detection method.

Concentrations of heavy metals in water were lower than the limits imposed by National Legislation. For organochlorine substances analyzed in three points, an increase of concentration for 1,2 dichloroethane, trichlorethylene and perchlorethylene in sections downstream of the chemical platform of Ramnicu Valcea (Cremenari and Babeni Marcea) to the Priza Olt upstream section of the platform.

The concentrations of nickel, copper, cadmium, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene in soil samples respect the limits by the Environmental Legislation.

In Priza Olt and Cremenari points, were found a degree of accumulation of heavy metals higher compared Babeni Marcea point, located in downstream of wastewater discharges of chemical platform. There was an accumulation of organochlorine in sediments in the three points.

1. Introduction

The studied area was a portion of 20 km long in the lower basin of Olt River. This area is located at 12 km south of the city of Ramnicu Valcea and in a closer vicinity of an industrial (main chemical) platform. Olt River is one of the

most important rivers in Romania and is the largest and the longest Romanian tributary of the Danube river. It flows through the counties of Harghita, Covasna, Brasov, Sibiu, Ramnicu Valcea, Olt and Teleorman. Olt River flows into the Danube near Turnu Magurele, Islaz. It has a length of 615 km.

The purpose of the present study was to evaluate the status of hazardous pollutants contamination in soil, water, sediments, to compare it to a historical record in one of the Olt River reservoirs located close to the industrial area, where are mainly chemical plants, and to assess the impact of this contamination on fish and vicinity human population. The sampling points were selected for this study because it is situated near the industrial area.

The local economy is mainly influenced by the great undertakings of the chemical industry, which makes 46.49% of the county's industrial production. The wastewater effluents of the industrial (chemical) platform are discharged into the Olt River. The lower course of Olt river includes 15 lakes in order to produce electricity and for irrigation water. The average flow of Olt River is $140 \text{ m}^3\text{s}^{-1}$, with variations from month to month, $25\text{-}300 \text{ m}^3\text{s}^{-1}$. [1]

2. Materials and methods

There was selected two type of sampling points. Water and sediment samples that was collected in two campaigns, in February and June 2010. Nickel, copper, cadmium, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene was analyzed from water, soil and sediment. The surface water samples and sediments samples were collected in 3 sections, distributed upstream and downstream of chemical industrial area. This points was: Priza Olt (PO), $45^\circ 2'20''\text{N}$, $24^\circ 18'41''\text{E}$; Cremenari (C), $44^\circ 58'50''\text{N}$, $24^\circ 16'56''\text{E}$; and Babeni-Marcea (M), $44^\circ 55'3''\text{N}$, $24^\circ 14'52''\text{E}$.

Second type of samples was soil samples. The soil samples were collected in eight sites, on two levels deep, level I (10 cm) and level II (30 cm) respectively, from the industrial area (platform) of Ramnicu Valcea, $45^\circ 2'22''\text{N}$, $24^\circ 15'0''\text{E}$. The soil samples were collected on two levels (10 cm and 30 cm), into shading polyethylene plastic bags, and taken to the laboratory. [1]

3. Results and discussion [1]

3.1. The content of hazardous pollutants in surface water

They water samples was collected from the Olt River, one point upstream and two points downstream of the industrial area (platform). The distribution of those points was conditioned by hydro-geographical characteristic of Olt River basin in above mentioned area: flow, effluents, dams, etc.

The concentrations of hazardous pollutants, including Ni, Cu and Cd in effluents of chemical platform are presented in Table 1. Nickel concentration was lower than 0.36 mg/L, cooper concentration was lower than 0.06 mg/L, and cadmium concentration was lower than 0.083 mg/L, respectively. The average concentrations of heavy metals in two industrial effluents, indicated in Table No.1, were close to or lower than standard values (limits).

Table No. 2 shows the concentrations of hazardous pollutants in the three collecting point named: Priza Olt (PO), Cremenari (C), Babeni- Marcea

(M). Concentrations of nickel and cadmium of water upstream from the industrial area, PO, showed below the limits indicates in Romanian Environmental Legislation for Surface Water and standards, values that are similar with European legislation (Order No. 161-2006) and copper to stay within the class III of quality (0.06 mg/L). In C point, section downstream from the discharge of chemical wastewater, cadmium concentration was below the limits of Environmental Legislation for Surface Water, copper concentration to stay within class III of quality and nickel concentration to stay within class IV of quality. In M point, section downstream from the discharge of chemical wastewater, heavy metals (nickel, cadmium) showed concentrations below the limits of National Legislation for Surface Water and copper to stay within class III of quality. The result showed that the concentrations of heavy metals were correlated with each other, demonstrating a common trend of concentration variation in water. For many situations concentrations were close to method detection limit. For organochlorine substances analyzed in three points, an increase of concentration for 1,2 dichloroethane, trichlorethylene and perchlorethylene in sections downstream of the chemical platform of Ramnicu Valcea (C and M) to the (PO) upstream section of the platform.

3.2. The content of hazardous pollutants in sediments

To assess the degree of contamination of sediments in the studied area were sampled from the upper layer of sediment, in the some three points: PO, C, M. Table No. 3 shows the concentrations of hazardous pollutants in sediment of Olt River. Nickel concentration was between 10.5 and 116.36 mg/kg D.W. compared to the standard value (35 mg/kg D.W.), copper concentration was between 18.12 and 98.68 mg/kg D.W. compare to the standard value (40.0 mg/kg D.W.), cadmium concentration was between 2.1 and 2.93 mg/kg D.W. compare to the standard value (0.8 mg/kg D.W).

In sample S-PO/I the nickel concentration was 3.0 times higher than standard value, for cooper and cadmium of 2.5 and 2.6 times, respectively. In samples S-PO/I and S-C/II the Cd concentration was 3.0 and 2.5 times higher than standard value, respectively.

Also notice that in all three points, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene taking values below the detection method.

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Table no. 1. Concentrations of hazardous pollutants in effluents of industrial area

Nr. crt.	Indicators analyzed	UM	Effluent 1 (mixing chamber)		Effluent 2 (Biological Treatment Plant)		Limits outlet mg / l	Method of analysis
			23.02.	15.06.	23.02.	15.06.		
1	Nickel	mg/l	<0.01*	0.09	0.18	0.31	0.5	SR ISO 8288:2001
2	Copper	mg/l	<0.01*	0.06	0.031	0.09	0.2	
3	Cadmium	mg/l	<0.005*	0.028	0.042	0.084	0.1	
4	pH	U.pH	7.78	10.5	12.5	12.0	6.5 – 8.5	SR ISO 10523:1997
5	1,2 Dichloroethane	mg/l	0,477	0,006	1,666	0,707	2,0	SR EN ISO 10301:2003
6	Trichlorethylene	mg/l	0,0006	<0,00005*	0,008	<0,00005*	0,5	
7	Perchlorethylene	mg/l	0,002	<0,00005*	0,021	<0,00005*	0,5	
8	1,2,4 Trichlorobenzene	mg/l	<0,000005*	<0,000005*	<0,000005*	<0,000005*	0,05	SR EN ISO 6468:2000

* method detection limit

Table No.2. Concentrations of hazardous pollutants in water (Olt River)

No. crt.	Indicators analyzed	UM	PO		C		M		Class I	Class II	Class III	Class IV	Class V	Method of analysis
			PO/I	PO/II	C/I	C/II	M/I	M/II						
1	pH	U.pH	7.51	7.41	7.7	7.44	7.91	7.54	6.5 – 8.5					SRISO105 23 :1997
2	Nickel	mg/l	<0.01*	<0.01*	<0.01*	0.06	<0.01*	<0.01*	0.01	0.025	0.05	0.1	>0.1	SRISO 8288:2001
3	Copper	mg/l	0.031	<0.01*	<0.01*	<0.01*	0.031	0.037	0.02	0.03	0.05	0.1	>0.1	
4	Cadmium	mg/l	<0.005*	<0.005*	<0.005*	<0.005*	<0.005*	<0.005*	0.0005	0.001	0.002	0.005	>0.005	
5	1,2 Dichoroethane	µg/l	0,011	<0,05*	21,0	<0,05*	0,008	<0,05*	10					
6	Trichlorethylene	µg/l	<0,05*	<0,05*	1,6	<0,05*	0,39	<0,05*	10					SR EN ISO 10301:2003
7	Perchlorethylene	µg/l	0,45	<0,05*	3,8	<0,05*	0,6	<0,05*	10					
8	1,2,4 Trichlorobenzene	µg/l	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	-					

* method detection limit

Table No. 3. Concentrations of hazardous pollutants in sediment determined in sections of Olt River

Nr.crt.	Indicators analyzed	Sample name						Standard limit value	Method of analysis
		S-PO		S-C		S-M			
		S-PO/I	S-PO/II	S-C/I	S-C/II	S-M/I	S-M/II		
1	pH	7.69	7.57	8.38	7.59	7.99	7.38	-	SR ISO 10390:1999
2	Nickel mg / kg D.W.	116.36	38.92	41.1	19.3	21.37	10.5	35.0	SR ISO 11466:1999 SR ISO 11047:1999
3	Copper mg / kg D.W.	98.68	43.6	44.3	6.24	18.12	<1.0*	40.0	
4	Cadmium mg / kg D.W.	2.12	2.93	2.1	2.79	<1.0*	<1.0*	0.8	
5	1,2 Dichloroethane mg / kg D.W.	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	-	SR EN ISO 10301:2003
6	Trichlorethylene mg / kg D.W.	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	-	
7	Perchloroethylene mg / kg D.W.	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	-	
8	1,2,4 Trichlorobenzene mg / kg D.W.	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	<0,005*	-	SR EN ISO 6468:2000

* method detection limit

3.3. The content of hazardous pollutants in soils

In order to investigate soil pollution with hazardous pollutants there was collected samples from industrial area of Ramnicu Valcea. The soil samples was collected from eight sites on two levels deep, level I (10 cm) and level II (30 cm), between February and June 2010. The analysis on two level is conditioned by environmental normative and is realized in order to verify the circulation of hazardous pollutants in soil caused by precipitations and migration of the soil microorganisms. The distribution of points was realized in order to cover into a uniform manner all industrial area.

From the information presented is observed that the pollution with heavy metals in both levels (I and II) don't respect a rule form point of view of quantitative concentration, there are points where level I have higher concentration than level II, but also the opposite is true. The same cannot be say about qualitative concentrations, for all situations was observed that if one metal have a higher concentration at one level in comparison with the opposite level, all heavy metal pollutants will respect the same trend. This thing shows that heavy metals have the same manner to migrate in soils.

In order to have good elements of comparison, the authors present in Table No.7 reference values imposed by environment legislation. Table No.6 presents concentrations of hazardous pollutants in soil collected from the studied area. The analyses were performed compared with the environmental legislation (Order No. 756-1997). Nickel concentration was between 1.0 and 250.5 mg/kg D.W., cadmium concentration was between 1.97 to 4.33 mg/kg D.W., copper concentration was between 4.7 to 1088 mg/kg D.W. Those show that are numerous situations where the limits are over fulfilled add the concentration of heavy metals is at the limit of thresholds for intervention. Also notice that in all three points, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchloroethylene taking values below the detection method.

Table no.6. Concentrations of hazardous pollutants in soils collected from the area studied

Nr. crt.	Contaminated	S1		S2		S3		S4		S5		S6		S7		S8		Method of analysis
		I	II	I	II	I	II	I	II	I	II	I	II	I	II	I	II	
1	pH Unit. pH	7.12	7.42	7.62	7.8	7.22	7.65	8.84	8.87	7.59	7.34	7.2	7.48	7.22	7.67	8.5	6.5	SR ISO 10390:1999
2	Nickel mg/kg D.W.	<1.0*	7.56	<1.0*	14.37	48.0	41.4	250.5	124.0	14.8	7.37	<1.0*	7.7	46.8	28.0	76.2	76.4	SR ISO 11466:1999
3	Cadmium mg/kg D.W.	<1.0*	2.0	<1.0*	4.21	<1.0*	<1.0*	<1.0*	<1.0*	4.33	2.0	1.97	<1.0*	<1.0*	<1.0*	<1.0*	<1.0*	SR ISO 11047:1999
4	Copper mg/kg D.W.	9.38	39.7	4.7	39.8	31.0	27.0	196.0	90.0	117.8	30.1	8.8	18.0	78.0	45.0	140.0	1088.0	SR ISO 11047:1999
5	1,2 Dichorethane mg / kg D.W.	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	SR ISO 14507:2000
6	Trichlorethylene mg / kg D.W.	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	
7	Perchlorethylene mg / kg D.W.	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	2,51	0,91	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	
8	1,2,4 Trichlorobenzene mg / kg D.W.	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	<1,0*	

* method detection limit

Reference values imposed by the Order no. 756/1997

Nr.crt.	Contaminated	UM	Limits outlet	Spoiler alert (P/A) Types of uses (mg/kg D.W.)		Thresholds for intervention (P/I) Types of uses (mg/kg D.W.)	
				Sensitive	Less sensitive	Sensitive	Less sensitive
1	pH	Unit. pH	-	-	-	-	-
2	Nickel	mg/kg D.W.	20.0	75.0	200.0	150.0	500.0
3	Cadmium	mg/kg D.W.	1.0	3.0	5.0	5.0	10.0
4	Copper	mg/kg D.W.	20.0	100.0	250.0	200.0	500.0
5	1,2 Dichoroethane mg / kg D.W.	mg/kg D.W.	-	-	-	-	-
6	Trichlorethylene mg / kg D.W.	mg/kg D.W.	-	-	-	-	-
7	Perchlorethylene mg / kg D.W.	mg/kg D.W.	-	-	-	-	-
8	Trichlorobenzene mg / kg D.W.	mg/kg D.W.	<0.1	5.0	10.0	10.0	30.0

Conclusions

This study was realized in order to determine the degree of hazardous pollutants pollution in the closer vicinity of the Ramnicu Valcea industrial area (platform). Samples were collected in two campaigns, between February and June 2010. Nickel, copper, cadmium, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchlorethylene from surface water, soil and sediments were analyzed. The results show that heavy metals in sediments collected from the Olt River, have different concentration depending by the position from industrial area, in ones point there are higher concentrations than in national legislation. Concentrations of heavy metals in water, also, have variations, but were lower than the limits imposed by national legislation. In the points from immediately vicinity of industrial area (PO, C) were found a degree of accumulation of heavy metals higher in comparison with farthestmost point (M), located in downstream of wastewater discharges of chemical platform. For organochlorine substances analyzed in three points, an increase of concentration for 1,2 dichloroethane, trichlorethylene and perchlorethylene in sections downstream of the chemical platform of Ramnicu Valcea (C and M) to the (PO) upstream section of the platform.

The concentrations of nickel, copper and cadmium in soil samples respect the limits by the environmental legislation. Also notice that in all three points, 1,2 dichloroethane, trichlorethylene, 1,2,4 trichlorobenzene and perchloroethylene taking values below the detection method.

References

1. IORDACHE M., POPESCU L.R., TARALUNGA M., *“Assess the degree of accumulation of substances priority/hazardous pollutants in soil and sediment sources around the Olt river, upstream and downstream of wastewater discharges from industrial platform Ramnicu Valcea”* - MEDIND - PN – 2010.