MONITORING OF PRIORITY HAZARDOUS SUBSTANCES FROM AN INDUSTRIAL PLATFORM AREA

Mihaela IORDACHE¹, Aurelia MEGHEA², Luisa Roxana POPESCU³, Nicoleta Georgeta DOBRE⁴, Georgeta ȚOȚEA⁵

This paper aims to establish the degree of pollution with priority hazardous substances in soil, water and sediments on the complex industrial platform Râmnicu Vâlcea. The studied area is a section of 20 km long in the lower basin of the Olt River. For the study were collected soil samples inside the platform, in the areas where they used priority hazardous substances and water and sediment samples from the Olt River and Govora River (tributary of the Olt River). The following priority hazardous substances have been determined: copper, nickel, lead, mercury, cadmium, zinc, chromium, cobalt, manganese, 1,2- dichloroethane, 1,1,2trichlorethylene, perchlorethylene and 1,2,4- trichlorobenzene. The heavy metal content has been determined by inductively coupled plasma-mass spectrometry), while organochlorinated substances by chromatography coupled with mass spectrometry. These values are analyzed by comparing with admitted limits imposed by the regulations in force and the possible origin of pollution sources is discussed.

Keywords: heavy metals, organochlorinated substances, surface waters, sediments, soils

1. Introduction

Water quality protection is a complex and difficult problem that requires an extensive data collection program on the physical, chemical and biological characteristics of rivers and lakes. Knowing the current state permanently on the trends in water quality of courses is essential for making decisions, being necessary to analyze fundamental and increasingly more careful to their quality.

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Chemical pollution of surface waters presents a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a threat to human health [1].

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].

In order to achieve "good chemical status" the environmental quality standards must be monitored for the priority pollutants in all water bodies before 2015 [2,3]. Crucial aspects in the evaluation of the chemical status of a water body are: the quantification of the influence of environmental conditions on toxicant bioavailability, the identification of key toxicants causing impairment of biological communities, the prediction of possible additive or synergic action of a mixture of toxicants and the characterization of hot spots in relation to their particular pollution patterns [4].

GD 1038/2010 on approving "Program of the gradual elimination of discharges, emissions and losses of priority hazardous substances" establishes the legal frame work, unitary and institutional resources necessary to prevent pollution of inland surface waters, territorial sea, coastal waters and groundwater with families and groups of hazardous substances in lists I and II.

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. [5].

Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Copper also does essential work in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death. Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis. Moreover, it is known that nickel is human carcinogen [6].

In addition, heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Therefore, their presence in the environment, in particular in water, should be carefully controlled [5].

Halogenated compounds and of them especially chlorinated hydrocarbons have been obtained in recent years at large scale synthesis. They are obtained as main or secondary products in some industrial processes and are used as solvents, refrigerants, fire extinguishing agents, lubricants and pesticides. Important amounts of chlorinated hydrocarbons are obtained during the process of chlorination of drinking water and waste water [7]. Although over 200 natural halogenated hydrocarbons have been found [8], most chlorinated compounds released into the environment or existent in the environment are of anthropogenic origin. These products manufactured by humans have led to contamination of air, soil and water [9]. Such cases have attracted attention because some of these xenobiotics were found as being harmful agents against certain forms of life. Other xenobiotics proved detrimental effects to humans and animals. Specific norms aiming to assess the risk of accidentally or intentionally released xenobiotics into environment and biota, have pursued the following aspects: acute toxicity of the compound, the effects on long term, especially in low concentrations, the fate of the environment.[10]

2. Experimental 2.1. About the studied area

The studied area was a section of 20 km long in the lower basin of the Olt River. This area is located at 12 km South of Ramnicu Valcea city and in a closer vicinity of the industrial platform. 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 purpose of the present study was to evaluate the status of priority hazardaous substances in soil, water and sediments. The sampling points have been selected for this study at the above mentioned zone 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 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 $140 \text{ m}^3/\text{s}$.

2.2. Samples collection and handling

The surface water and sediments samples were collected in 6 points, distributed upstream and downstream of the industrial platform. The soil samples were collected in five sites, on two levels deep, level I (10 cm) and level II (30 cm) respectively, from the industrial area (platform) of Râmnicu Vâlcea. Nickel, copper, cadmium, chromium, manganese, cobalt, zinc, mercury, 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.

2.3. Metals determination

The concentrations of metals have been determined with inductively coupled argon plasma spectrometer VARIAN 82.

The main principle of ICP-MS is the generation of positively charged ions using a high temperature plasma discharge. A liquid sample is pumped into the instrument's sample injection system, which comprises a nebulizer and spray chamber. The sample is transformed into an aerosol and is brought to the base of the plasma by means of a sample injector. The sample undergoes drying, vaporizing, atomizing and ionizing in the various heating zones of the plasma. At the 6000-7000° K zone in the plasma, excited atoms and ions exist and the elemental composition of the sample is represented. The plasma has enough energy to remove an outer electron from the orbital of these atoms in order to generate ions. These generated positive ions are then transported and detected [11].

2.3.1. Metals determination in water samples

All samples were filtered through a $0.45-\mu m$ filter and were then acidified at the time of collection with HNO₃ (5mL/L).

It was transferred to a 100 ml aliquot of the sample well mixed in a beaker. For the metals that were analyzed were added 2 ml the concentrated HNO_3 and 5 ml the concentrated hydrochloric acid. 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.

It was removed and the flask was allowed to cool. We washed the sides. The final volume was adjusted to 100 ml with ultra pure water.

2.3.2. Metals determination in sediments and soil samples

The sample was mixed thoroughly to achieve homogeneity and was sieved if necessary. For each digestion procedure were weighed to the nearest 0.01 g and was transferred to a 1-2 g sample (wet weight) and 1.0 g sample (dry weight) in a digestion vessel. For the digestion the sample for analysis by ICP-MS were added 10 ml of 1:1 HNO₃ was mixed and covered with a watch glass or a vapor recovery device. The sample was heated to 95 ° C and reflux for 10 to 15 minutes with boiling. The sample was allowed to cool, it was added 5 ml of concentrated HNO₃, to put the cover, and reflux for 30 minutes. If brown smoke was generated, indicating oxidation of the sample of HNO₃, to repeat this step (to adage 5 mL concentrated HNO₃) until smoke emanated not been brown. After it has cooled, were added 2 ml of water and 3 ml of H₂O₂ 30%. Was covered the beaker with a watch glass or vapor recovery device and covered dish to put the heat source for heating and begin peroxide reaction. Was continued to add 30% H₂O₂ until effervescence was minimal or until the general sample appearance was unchanged. Sample was covered with a ribbed watch glass or vapor recovery device and heating was continued until the volume was reduced to about 5 ml. After cooling, it was diluted to 100 ml with water.

2.4. Organochlorine compounds determination

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

Gas chromatography applied to separation of volatile and easily volatilizable at temperatures below 400°C. Chromatography coupled with mass spectrometry is a coupled analytical technique used for the following purposes: a. confirmation and identification of volatile and semi-volatile analyses from a complex mixture; b. determine the molecular weight and / or the basic structure of volatile / semi volatile unknown; c. structural determination of volatile / semi volatile / semi volatile unknown; a spectral matching and spectral interpretation [12].

2.4.1. Organochlorine compounds determination in water samples

Determination of highly volatile halogenated hydrocarbons

Samples were collected and stored in water in clean glass bottles. A normal sample was collected by diving bottle or ampoule filling completely

discarded this water, refilled and off so as to leave no headspace. A sample was taken and discarded glass bottle filled with enough water so that there was no residual sample volume of 200 ml. It was glass and sample weight to determine the exact volume of the sample. Was added to the extraction solvent (pentane), close to the sample and vigorously mixed 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.

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, to adjust the pH immediately after collection to be within the range of from 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 extraction was used sample volume equal to one liter. Were added to 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. It was 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.

2.4.2. Organochlorine compounds determination in sediments and soil samples

For samples that contain volatile components which no pre-treatment was not necessary. They weigh 30 grams of wet soil in a glass beaker iodometrical. Were added 50 ml of methanol and stirred 30 min., were added 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. With glass filter was washed and soil with 10 ml of pentane. The funnel was stirred 5 min. allowing separation and discard the organic phase. The organic layer was passed through a filter with anhydrous Na₂SO₄ into a hermetic closed glass. The funnel and the layer with Na₂SO₄ and was rinsed with 5 ml of pentane were added to the organic layer.

3. Results and discussion

3.1. Content of priority hazardous substances in surface water

Wastewaters from industrial platform Râmnicu Vâlcea are discharged into the Olt River after specific treatment.

In order to assess water quality of the Olt River, (upstream and downstream of the discharge industrial platform Ramnicu Valcea), water samples were collected from six sampling points. From the Olt River samples were collected from four points, two points upstream of the industrial platform (AM-PO, PO) and other two points downstream of the industrial platform (C, M). The points Rg-Am and Rg-Av were collected from the Govora River, a tributary of the Olt River. In the Govora River, are discharged wastewaters from Waste Water Treatment Plant (WWTP). The distribution of those points was conditioned by hydro-geographical characteristic of the Olt River basin in above mentioned area: flow, effluents, dams, etc.

Table 1 shows the concentrations of priority hazardous substances in these six collecting points. The results were compared with the limits imposed by the National legislation [13].

3.1.1. Content of heavy metals in surface water

For various heavy metal ions the different water quality classes have been assessed. For instance, chromium concentrations were within the limits for the 1st Class, 2nd Class, 3rd Class of quality, manganese concentrations were within the limits 1st Class, 2nd Class, 3rd Class, 4th Class of quality, cobalt, nikel, zinc and hercury concentrations were within the limit 1st Class of quality in majority points, except the point Rg-AM that was within the limit 2nd Class, 3rd Class, 4th Class of quality. Moreover, copper and lead concentrations were within the limits 1st Class, 3rd Class, 4th Class of quality, while cadmium concentrations were within the limits 1st Class, 3rd Class, 2nd Class, 4th Class of quality.

The highest heavy metal concentrations were found for chromium in the point PO, manganese in the points PO and M, cobalt in the point Rg-AM, nickel in the point Rg-AV, cooper in the point M, zinc in the point Rg-AM, cadmium in the points AM-PO and Rg-AV, mercury in the points PO and Rg-AV, lead in the point M.

From these data registered on metal distribution in surface water one may conclude that the dominant metals are chromium, manganese, copper, zinc, and lead.

3.1.2. Content of organochlorine substances in surface water

The results observed for organochlorine substances in surface water were as follows: 1,2-dichloroethane took values between 0.24 - 5.34 μ g / L as compared to limit of 10.0 μ g/ L from the National legislation, 1,1,2-trichlorethylene, perchlorethylene and 1,2,4-trichlorobenzene having values below the detection limit.

3.2. Content of priority hazardous substances in sediments

To evaluate the degree of sediment contamination in the studied area sediments from the upper layer have been sampled.

From data collected in Table 2 can be observed that the concentrations of heavy metals from sediments in the upstream point (PO and AM-PO) are higher as compared with the downstream points (C, M).

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 loocated 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.

It was also observed that in all the points, 1,2-dichloroethane, 1,1,2-trichlorethylene, perchlorethylene, 1,2,4-trichlorobenzene were below the detection limit.

3.3. Content of priority hazardous substances in soil

In order to investigate soil pollution with priority hazardous substances samples from industrial area of Râmnicu Vâlcea the samples have been collected from five sites on two levels deep, level I (10 cm) and level II (30 cm) (Table 3).

For comparison purpose, the authors also present in Table 4 the reference values imposed by environmental legislation [14].

By analysis of the obtained values one can observe that chromium, cobalt, nickel, zinc, cadmium and lead were within the normal values and alert thresholds types / less sensitive use, while cooper was within thresholds the alert / less sensitive types of use.

The higher concentrations of the nickel, chromium and lead were found in the depth, while higher concentrations of manganese, cobalt and mercury were found on the soil surface. These higher concentrations of metals in the second level than in the first level can be attributed to historical pollution. This was probably caused by faulty operation of facilities, improper storage and by the lack of environmental legislation in the past.

Method of	analysis	SR ISO 10390:1999					SR EN ISO 17294- 2:2005					S	R EN ISO 10301:200 2	n	SR EN ISO 6468:2000
t value	5 th Class		>250	>1.0	>100	>100	>100	>1000	~5	~	>50				
	4 th Class	6.5 - 8.5	250	1.0	100	100	100	1000	S	-	50				
ard limi	3 rd Class		100	0.3	50	50	50	500	2	0.5	25	10	10	10	
Standa	2 nd Class		50	0.1	20	25	30	200	1	0.3	10				
	1 st Class		25	0.05	10	10	20	100	0.5	0.1	5				
Rg-AV	(9)	11.2	14.9	0.19	8.26	61.13	13.0	26.0	0.93	1.13	1.1	5.34	3.41	<0.05*	<0.002*
Rg-AM	(5)	8.1	67.76	0.74	10.5	28.72	44.5	110.1	0.41	0.13	11.92	0.67	<0.05*	<0.05*	<0.002*
М	(4)	7.33	12.2	0.086	0.1	<0.5*	54.6	52.25	<0.05*	<0.5*	35.9	0.24	<0.05*	<0.05*	<0.002*
С	(3)	7.33	33.7	0.13	2.42	8.07	8.1	23.9	0.43	1.75	0.54	0.52	<0.05*	<0.05*	<0.002*
PO	(2)	7.41	74.32	0.086	1.03	1.02	32.08	39.5	<0.05*	<0.5*	14.32	0.32	<0.05*	<0.05*	<0.002*
-MA-	P0	7.4	48.0	0.044	0.13	0.38	49.7	43.14	0.93	1.46	4.25	ı			
MU		Unit.pH	µg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Indicators analyzed		Hq	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Cadmium	Mercury	Lead	1,2- Dichoroethane	1,1,2- Trichlorethylene	Perchlorethylene	1,2,4- Trichlorobenzene
Ľ.	crt.	1	5	3	4	5	6	7	~	6	10	11	12	13	14

Concentrations of priority hazardous substances in surface water

* LOD

Table 1

Concentrations of priority bazardous substances in sediments												Та	ble 2	
Method of analysis	SR ISO 10390:1999	SR EN ISO 17294-2:2005 SR EN ISO 10301:2003												SR EN ISO 6468:2000
Standard limit value	ı	100		ı	35	40	150	0.8	0.3	85	ı		ı	I
RG-AV (6)	10.4	13.32	283.97	3.64	12.97	7.23	22.13	0.3	1.13	1.84	<0.05*	<0.05*	<0.05*	<0.002*
RG-AM (5)	7.7	15.88	285.71	4.89	12.61	8.88	35.42	0.18	0.35	0.2	<0.05*	<0.05*	<0.05*	<0.002*
M (4)	7.36	62.2	226.4	1.70	3.79	1.01	50.9	*20.05*	<0.05*	10.0	<0.05*	<0.05*	<0.05*	<0.002*
C (3)	7.58	13.78	187.55	4.06	12.97	9.74	28.37	0.08	<0.05*	6.95	<0.05*	<0.05*	<0.05*	<0.002*
PO (2)	7.47	15.55	145.9	4.92	12.82	12.22	31.41	<0.05*	<0.05*	9.87	<0.05*	<0.05*	<0.05*	<0.002*
AM-PO (1)	7.32	97.2	125.92	2.88	29.55	4.78	17.95	0.15	0.4	3.13			ı	I
NM	Unit.pH	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg/kg D.W	mg / kg D.W.
Indicators analyzed	Hq	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Cadmium	Mercury	Lead	1,2 -Dichoroethane	1,1,2- Trichlorethylene	Perchlorethylene	1,2,4- Trichlorobenzene
Nr. crt.	1	2	ю	4	5	9	7	8	6	10	11	12	13	14

*LOD

Method of analysis		SR ISO 10390:1999					SR EN ISO 17294-2:2005						SR ISO 14507:2000	SR ISO 11423 -2:2000	
S5	II	7.86	37.53	253.6	17.62	33.32	50.08	55.10	0.1	<0.05*	52.04	<1.0*	<1.0*	<1.0*	<1.0*
	I	7.76	40.51	269.6	84.1	37.22	90.41	61.0	0.11	<0.05*	52.04	<1.0*	<1.0*	<1.0*	<1.0*
S4	II	7.67	28.0	509.2	9.49	53.22	39.68	119.3	0.4	1.07	24.12	<1.0*	<1.0*	<1.0*	<1.0*
	Ι	7.19	34.52	423.8	8.0	32.1	103.3	213.8	0.91	1.41	93.1	<1.0*	<1.0*	<1.0*	<1.0*
S3	Π	7.40	29.9	528.8	10.47	71.53	84.1	401.1	0.94	0.17	78.17	<1.0*	<1.0*	28,6	<1.0*
	Ι	6.91	17.23		11.85	27.25	26.5	128.8	0.71	0.825	76.17	<1.0*	<1.0*	<1.0*	<1.0*
5	II	7.65	21.44	489.4	8.27	36.8	28.3	64.6	0.395	1.96	8.8	<1.0*	<1.0*	<1.0*	<1.0*
S	Ι	7.10	16.15	465.7	8.17	25.4	45.33	80.4	1.07	1.32	30.3	<1.0*	<1.0*	<1.0*	<1.0*
_	Π	7.61	32.11	391.3	7.34	41.06	196.7	132.7	0.56	0.83	70.0	<1.0 *	<1.0 *	<1.0	<1.0 *
S	I	7.04	15.93	396	7.2	20.0	98.7	158.1	0.03	1.33	86.17	<1.0*	<1.0*	<1.0*	<1.0*
MU		Unit.pH	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.				
Indicators analyzed		Hq	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Cadmium	Mercury	Lead	1,2- Dichoroethane	1,1,2- Trichlorethylene	Perchlorethylene	1,2,4- Trichlorobenzene
Nr. crt.		1	2	3	4	5	9	7	8	6	10	11	12	13	14

Concentrations of priority hazardous substances in soils collected from the area studied

* LOD

Table 3

Reference values imposed by the Order no. 756/1997															
ervention es /.)	Less sensitive	1	600.0	4000.0	250.0	500.0	500.0	1500.0	10.0	10.0	1000.0				30.0
Thresholds for int (P/I) Types of us (mg/kg D.V	Sensitive		300.0	2500.0	50.0	150.0	200.0	600.0	5.0	2.0	100.0				10.0
lds alert (P/A) es of uses /kg D.W.)	Less sensitive	-	300.0	2000.0	100.0	200.0	250.0	700.0	5.0	4.0	250.0			ı	10.0
Thresh Ty (m	Sensitive	I	100.0	1500.0	30.0	75.0	100.0	300.0	3.0	1.0	50.0				5.0
Limits outlet		ı	30.0	0.006	15.0	20.0	20.0	100.0	1.0	0.1	20.0				<0.1
MU		Unit.pH	mg/kg D.W.	mg / kg D.W.	mg/kg D.W.	mg / kg D.W.	mg / kg D.W.	mg / kg D.W.	mg/kg D.W.	mg/kg D.W.	mg / kg D.W.	mg/kg D.W.	mg / kg D.W.	mg/kg D.W.	mg / kg D.W.
I Parameter		Hq	Chromium	Manganese	Cobalt	Nickel	Copper	Zinc	Cadmium	Mercury	Lead	1,2- Dichoroethane	1,1,2- Trichlorethylene	Perchlorethylene	1,2,4- Trichlorobenzene
Nr. crt.		1	2	3	4	5	9	7	8	6	10	11	12	13	14

Table 4

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It was also observed that in all points, 1,2-dichloroethane, 1,1,2trichlorethylene, perchlorethylene, 1,2,4-trichlorobenzene have values below the detection limit.

4. Conclusion

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Regarding the distribution of metals in surface water from industrial platform Râmnicu Vâlcea area, the dominant metals are chromium, manganese,

copper, zinc, and lead. The highest heavy metal concentrations were found in the next points: chromium to Priza Olt, manganese to Priza Olt and Marcea, cobalt upstream to Waste Water Treatment Plant, nickel downstream to Waste Water Treatment Plant, cooper to Marcea, zinc, downstream to Waste Water Treatment Plant, cadmium upstream to Priza Olt and downstream of the Waste Water Treatment Plant, mercury to Priza Olt and downstream of the Waste Water Treatment Plant, and lead to Marcea. The organochlorine substances analyzed had values that fall within the limits imposed by the current legislation.

The obtained data indicate that the concentrations of heavy metals from sediments in the upstream point are higher as compared with the downstream points. An important amount of heavy metal pollutants is coming from upstream of industrial platform.

As referring to soil pollution, higher concentrations of the nickel, chromium and lead were found in the depth, while higher concentrations of manganese, cobalt and mercury were found on the soil surface. This situation can be attributed to historical pollution caused by faulty operation of facilities, improper storage and by the lack of environmental legislation in the past.

In the next studies adequate mathematical models will be used in order to examine the distribution of the priority hazardous substances among the environmental compartments.

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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] A. Bouzas, A. Seco, D. Aguado, N. Marti and L. Segovia-Martínez," Occurrence of priority pollutants in WWTP effluents and Mediterranean coastal waters of Spain", Marine Pollution Bulletin, vol.62, 2011, pp. 615–625
- [3] J. Gasperi, R. Moilleron, S. Garnaud, V. Rocher, "Priority pollutants in surface waters and settleable particles within a densely urbanised area: Case study of Paris (France)", Science of the Total Environment, vol. 407, 2009, pp. 2900–2908
- [4] A. Ginebreda, A. Munne, H. Guasch, L. Faggiano, L. Tirapu, M. Flo, M. Real, P.Carsten von der Ohe and R. Carafa, "Water toxicity assessment and spatial pollution patterns identification in a Mediterranean River Basin District. Tools for water management and risk analysis", Science of the Total Environment, vol. 409, 2011, pp. 4269 – 4279

- [5] A.Faz, J.A.Acosta and S.Martinez-Martinez, "Identification of heavy metal sources by multivariable analysis in a typical Mediterranean city (SE Spain)", Environ Monit Assess, vol.169, (1-4), 2010, pp. 519-30
- [6] F.Fu and Q.Wang,"Removal of heavy metal ions from wastewaters: A review", Journal of Environmental Management, vol.92, 2011, pp. 407-418
- [7] J.E. J.Henderson and W.H.Glaze, "Water Pollt. Control Fed., vol.47, 1975, pp. 2511-2515
- [8] J.F. Debernardis and J.F. Siuda, Lloydia, vol.36, 1973, pp.107-143
- [9] *M.J. Schneider*, "Persistent Poisons: Chemical Pollutants in the Environment", The New York Academy at Sciences, N.Y., 1979
- [10] C.A.Fewson, in Leisinger et al. (ads.), "Microbial Degradation of Xenobiotics and Recalcitrant Compounds", Academic Press, London, 1981, 141-179
- [11] S.J. Hill, "Inductively Coupled Plasma Spectrometry and its Applications"- Blackwell Publishing, 2007
- [12] A.M. Iordache, C. Mesaros, I. Stefanescu, M. Culea, "Aplicatii biomedicale si ecologice prin spectrometria de masa, Cluj-Napoca, 2012
- [13] Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 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.
- [14] MESDR, (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.