Evaluation of Contamination with Priority Hazardous Substances in Olt River Water and Sediments near the Industrial Platform of Ramnicu Valcea

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This paper aims to establish the pollution degree with priority hazardous substances in water and sediments of the Olt River, near the industrial platform Râmnicu Vâlcea area. The study area was a 20 km long section of the lower basin of the Olt River. Water and sediment samples have been collected from the three sections, distributed to upstream and downstream of the industrial platform. The following priority hazardous substances have been determined: copper, nickel, lead, mercury, cadmium, zinc, chromium, cobalt, 1,2-dichloroethane, 1,1,2-trichlorethylene, perchlorethylene and 1,2,4-trichlorobenzene. Higher concentrations of chromium, copper, zinc and cadmium have been observed in the upstream section of the platform, and nickel, mercury and lead have been found in the upstream section of the platform Ramnicu Valcea, while the concentrations of nickel, mercury and lead have been found in the downstream section. Moreover, in the sediments of Olt river similar heavy meatals are found correspondingly, while the organochlorine compound content was below the detection limit.

Keywords: heavy metals, chloro organic substance, surface waters, sediments

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. 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 European Directive 2000/60/EC is probably the most significant European legislation in force in the field of water in the last years [1]. The proposed 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 aquatic 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 toxic bioavailability, identification of key toxic causing impairment of biological communities, prediction of possible additives or synergic action of a mixture of toxicants and characterization of hot spots in relation to their particular pollution patterns [4]. 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 dangerous to the environment. [5].

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, people 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 stormwater. Metal discharges to the environment not only cause acute toxicity to aquatic organisms, microorganisms, and plants, but also they strongly decrease microbial activity, which adversely affects biological wastewater treatment plants (WTPs) [6].

Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds. The adsorption

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process is influenced by several physico - chemical and chemical parameters such as: pH, oxidative-reductive potential, dissolved oxygen, organic and inorganic carbon content, and the presence in water phase of some anions and cations that can bind or co-precipitate the waterdissolved or suspended pollutants [7].

Adsorbed heavy metals can be desorbed from sediments and cause a secondary pollution when environmental conditions change. Heavy metals are among the most persistent pollutants due to their resistance to decomposition in natural conditions. Such elements tend to accumulate in the surface sediments, and may affect population health if the contents reach levels at which they constitute toxic pollutants [8, 9].

Heavy metals are ubiquitous and hazardous contaminants in the aquatic environments showing a strong biomagnification effect along the food chain. The most common transfer path to the human body is the consumption of contaminated fish. The poisoning with heavy metals may lead to damage in the central nervous system. Thus, it is important to examine current and past contamination levels in aquatic media [10].

Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms. Many heavy metal ions are known to be toxic or carcinogenic [11]. The presence of heavy metals at high concentrations has been shown to adversely affect microbial activities in soils [12].

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

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.

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

Article complements the recent concerns of the scientific community from Romania related to the presence of pollutants in various rivers. It is a useful exercise to make a comparison of the indicators of other rivers from the same geographic region, such as the Danube [13] or Dambovnic [14], and data from this study.

Experimental part

Description of studied area

The studied area was a section of 20 km lengthwise 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 surface water and sediments samples were collected in three points, one point upstream the industrial platform (PO) and other two points downstream the industrial platform (C, M).

Metals determination in water samples

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

All the samples were filtered through a $0.45-\mu m$ filter and were acidified at the time of collection with HNO₃ diluted solution (5mL/L). Then, a 100 mL well mixed aliquot of the sample 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.

Metals determination in sediment samples

The sample was stirred 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, were added, stirred and covered with a watch glass or a vapour 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, solution, and refluxed for 30 minutes. If brown smoke was generated, this is and indication of oxidation of the sample by HNO₃; this step is repeated (addition of $5 \,\mathrm{mL}$ concentrated HNO^{\circ}) and refluxed until smoke emanated is not being brown. After cooling, 2 mL of water and 3 mL of 30% H₂O₂ solution 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.

Determination of organochlorine compounds in water samples

The contents of organochloride compounds were determined by gas 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.

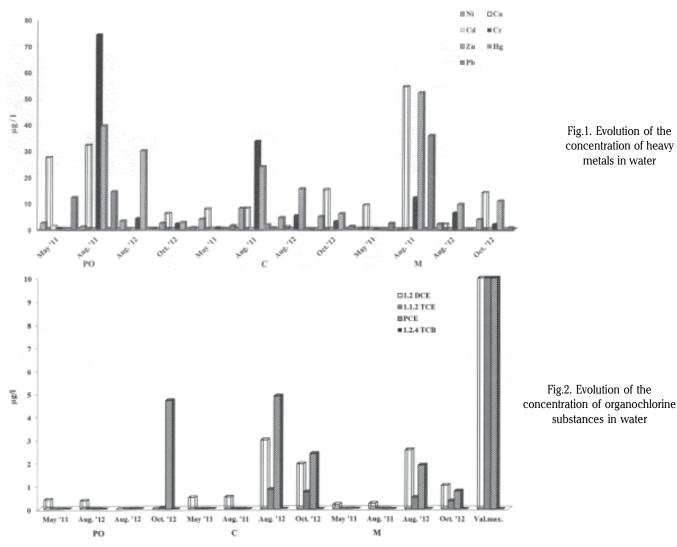
Determination of 1,2,4 -trichlorobenzene

Samples of water were taken in a brown glass bottle. The pH was verified and, if necessary, adjusted 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 h).

The sample volume was one liter. A volume of 30 mL of extraction solvent (heptane) was added and the solution was stirred for at least 10 min and transferred to a separating funnel with adequate capacity and standing to allow phase separation.

Organochlorine compounds determination in sediment samples

For samples that contain volatile components no any pre-treatment was necessary. Amount of 30 g of wet soil was weighed in a glass iodometrical beaker. 50 mL of methanol were added and stirred 30 min., then a volume of 50 mL pentane was added and stirred for another 30 min. The liquid phase was filtered through a filter paper with medium porosity and was introduced into a 500 mL separator funnel together with 250 mL distilled water. The soil was washed 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 Na₂SO₄ into a hermetic closed vessel. The



funnel and the layer with Na_2SO_4 was rinsed with 5 mL of pentane and added to the organic layer.

Results and discussions

Content of priority hazardous substances in surface water

Figures 1 and 2 shows the evolution of the concentrations of priority hazardous substances in the sections denoted as (PO), (C) and (M), during the period 2011-2012. The results were compared with the limits imposed by the national legislation [15].

The highest heavy metal concentrations were found for chromium, copper, zinc, lead and cadmium in upstream section of the platform, and nickel and mercury in downstream section of the platform.

It may observed from these data registered on metal distribution in surface water that the dominant metals are chromium, copper, zinc, and lead. The concentrations determined for organochlorine substances in surface water were as follows: 1,2-dichloroethane with values between $0.24 - 2.99 \,\mu\text{g} / \text{L}$ as compared to limit of $10.0 \,\mu\text{g} / \text{L}$ according to the national legislation, 1,1,2-trichlorethylene with values between $0.06 - 0.85 \,\mu\text{g} / \text{L}$, perchlorethylene with values between $0.78 - 4.9 \,\mu\text{g} / \text{L}$ and 1,2,4-trichlorobenzene having values below the detection limit.

Content of priority hazardous substances in sediments

From data indicated in table 1 it can be observed that the concentrations of all heavy metals from sediments in the upstream points are higher compared with the downstream points

In sediment of the Olt River, higher concentrations of nickel, copper, zinc and lead have been found in the

| Sampling Sites | Period | рН | Cr | Ni | Cu | Zn | Cd | Hg | Pb |
|----------------|--------------|------|-------|-------|--------|--------|--------|---------|-------|
| PO | May 2011 | 8.73 | 59.9 | 35.5 | 34.975 | 175.79 | 0.748 | 3.14 | 51.19 |
| | August 2011 | 7.47 | 15.55 | 12.82 | 12.22 | 31.41 | <0.05* | <0.05* | 9.87 |
| | March 2012 | 7.33 | 13.5 | 10.31 | 55.57 | 81.8 | 0.026 | < 0.05* | 0.38 |
| | August 2012 | 7.52 | 9.52 | 35.58 | 58.95 | 146.52 | 0.047 | 0.08 | 14.79 |
| | October 2012 | 7.90 | 19.82 | 26.06 | 36.68 | 103.68 | 0.234 | 0.0556 | 11.31 |
| C | May 2011 | 8.17 | 18.19 | 14.22 | 12 | 37.07 | 1.13 | 0.76 | 8 |
| | August 2011 | 7.47 | 13.78 | 12.97 | 9.74 | 28.37 | 0.08 | <0.05* | 6.95 |
| | March 2012 | 7.60 | 8.64 | 1.22 | 25.85 | 39.82 | 0.03 | <0.05* | 0.47 |
| | August 2012 | 7.62 | 11.14 | 17.29 | 19.82 | 41.47 | 0.093 | 0.139 | 9.129 |
| | October 2012 | 8.12 | 7.7 | 9.62 | 5.9 | 15.07 | 0.1 | <0.05* | 1.847 |
| M | May 2011 | 8.05 | 5.2 | 3.75 | <0.05* | 95.5 | 0.75 | 0.775 | 15.65 |
| | August 2011 | 7.38 | 5.79 | 3.79 | 10.1 | 50.9 | <0.05* | <0.05* | 10 |
| | March 2012 | 7.40 | 3.54 | 0.56 | 30.73 | 31.41 | 0.03 | <0.05* | 0.48 |
| | August 2012 | 7.38 | 3.187 | 2.44 | 2.27 | 4.7 | <0.05* | <0.05* | 1.74 |
| | October 2012 | 8.05 | 1.88 | 2.53 | 5.8 | 8.41 | 0.031 | <0.05* | 2.28 |

Table 1CONTENT OF PRIORITYHAZARDOUS SUBSTANCESIN THE SEDIMENTS FROMRIVER OLT (mg/kg DRYWEIGHT)

| Sampling Sites | Period | pН | 1.2-DCE | 1.1.2-TCE | PCE | 1.2.4-TCB |
|----------------|--------------|------|----------|-----------|---------|-----------|
| PO | May 2011 | 8.73 | <0.05* | <0.05* | < 0.05* | < 0.002* |
| | August 2011 | 7.47 | <0.05* ~ | <0.05* | <0.05* | <0.002* |
| | March 2012 | 7.33 | <0.05* | <0.05* | < 0.05* | < 0.002* |
| | August 2012 | 7.52 | <0.05* | <0.05* | <0.05* | <0.002* |
| | October 2012 | 7.90 | <0.05* | <0.05* | < 0.05* | <0.002* |
| С | May 2011 | 8.17 | <0.05* | <0.05* | < 0.05* | <0.002* |
| | August 2011 | 7.47 | <0.05* | <0.05* | < 0.05* | <0.002* |
| | March 2012 | 7.60 | <0.05* | <0.05* | < 0.05* | <0.002* |
| | August 2012 | 7.62 | <0.05* | <0.05* | < 0.05* | < 0.002* |
| | October 2012 | 8.12 | <0.05* | <0.05* | <0.05* | <0.002* |
| M | May 2011 | 8.05 | <0.05* | <0.05* | <0.05* | <0.002* |
| | August 2011 | 7.38 | <0.05* | <0.05* | <0.05* | <0.002* |
| | March 2012 | 7.40 | <0.05* | <0.05* | <0.05* | <0.002* |
| | August 2012 | 7.38 | <0.05* | <0.05* | <0.05* | <0.002* |
| | October 2012 | 8.05 | <0.05* | <0.05* | < 0.05* | < 0.002* |

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

upstream section (PO) of the Ramnicu Valcea platform, while higher concentrations of cadmium and mercury have been found in the downstream section (C) of the Ramnicu Valcea platform.

This means that an important amount of heavy metal pollutants is coming from upstream the industrial platform. The sources of pollution can be the city of Ramnicu Valcea and industrial activities located in upper part of 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.

In sediments it was also observed, (table 2), that in all the points, the concentrations of 1,2- dichloroethane, 1,1,2trichlorethylene, perchlorethylene, 1,2,4- trichlorobenzene are below the detection limit of the method.

Assessment of the metal pollution degree of sediments in Olt River

For assessment of the pollution degree with heavy metals in sediment four parameters have been used:

| 05* | <0.002* |] |
|-------|--------------|----------------|
| 05* | <0.002* | |
| .05* | <0.002* | |
| | | |
| | Table 3 | |
| NTAMI | NATION LEVEL | S OF SEDIMENTS |

Table 2CONTENT OF PRIORITYHAZARDOUS SUBSTANCESIN THE SEDIMENTS FROMRIVER OLT (mg/kg DRYWEIGHT)

 Table 3

 CONTAMINATION LEVELS OF SEDIMENTS

 ACCORDING TO VALUES OF CONTAMINATION

 FACTOR

Contamination factor (CF), Geo-accumulation index (I_{geo}), Ecological risk index (Ef) and Pollution load index (PLI).

The contamination factor (CF) was used to determine the contamination status of Olt River sediments and it is calculated as the ratio between the heavy metal concentration in the sediment sample (C_{metal}) and the maximum admitted value in sediments ($C_{background}$). Depending on its value the sediment pollution degree is classified as shown in table 3.

Contamination factor is calculated as the following equation (1):

$$CF = \frac{C_{metal}}{C_{background}} \tag{1}$$

According to the contamination factor (CF), in the sediments of Olt River, it was found, generally, a low level of heavy metals contamination (table 4). However, a moderate contamination with nickel, lead, zinc and copper was found in the section (PO), situated upstream the

| Sampling | Period | | Cr | | NI | | Cu | Zn | | |
|----------|--------------|---------|--|---------|--|------|--|------|-------------------------|--|
| Sites | | CF | Level | CF | Level | CF | Level | CF | Level | |
| PO | May 2011 | 0.59 | <1 | 1.01 | 1.01 1 <cf<3< td=""><td><1</td><td>1.17</td><td>1<cf<3< td=""></cf<3<></td></cf<3<> | | <1 | 1.17 | 1 <cf<3< td=""></cf<3<> | |
| | August 2011 | 0.15 | <1 | 0.36 | <1 | 0.30 | <1 | 0.20 | <1 | |
| | March 2012 | 0.13 <1 | | 0.29 | <1 | 1.38 | 1 <cf<3< td=""><td>0.54</td><td><1</td></cf<3<> | 0.54 | <1 | |
| | August 2012 | 0.09 | | | 1 <cf<3< td=""><td>1.47</td><td>1<cf<3< td=""><td>0.97</td><td><1</td></cf<3<></td></cf<3<> | 1.47 | 1 <cf<3< td=""><td>0.97</td><td><1</td></cf<3<> | 0.97 | <1 | |
| | October 2012 | 0.19 | <1 | 0.74 | <1 | 0.91 | <1 | 0.69 | <1 | |
| С | May 2011 | 0.18 | <1 | 0.40 | <1 | 0.3 | <1 | 0.24 | <1 | |
| | August 2011 | 0.13 | <1 | 0.37 | <1 | 0.24 | <1 | 0.18 | <1 | |
| | March 2012 | 0.08 | <1 | 0.03 | <1 | 0.64 | <1 | 0.26 | <1 | |
| | August 2012 | 0.11 | <1 | 0.49 | <1 | 0.49 | <1 | 0.27 | <1 | |
| | October 2012 | 0.07 | <1 | 0.27 | <1 | 0.14 | <1 | 0.10 | <1 | |
| M | May 2011 | 0.05 | <1 | 0,10 | <1 | 0.00 | <1 | 0.63 | <1 | |
| | August 2011 | 0.05 | <1 | 0.10 | <1 | 0.25 | <1 | 0.33 | <1 | |
| | March 2012 | 0.03 | <1 | 0.01 | <1 | 0.76 | <1 | 0.20 | <1 | |
| | August 2012 | 0.03 | | | <1 | 0.05 | <1 | 0.03 | <1 | |
| | October 2012 | 0.01 <1 | | 0.07 <1 | | 0.14 | <1 | 0.05 | <1 | |
| | | | Cd | | Hg Pb | | | | | |
| PO | May 2011 | 0.93 | <1 | 10.4 | CF>6 | 0.60 | <1 | | | |
| | August 2011 | 0.06 | <1 | 0.16 | <1 | 0.11 | <1 | | ć. | |
| | March 2012 | 0.03 | <1 | 0.16 | <1 | 0.00 | <1 | 1 | | |
| | August 2012 | 0.05 | <1 | 0.26 | <1 | 0.17 | <1 | 1 | | |
| | October 2012 | 0.29 | <1 | 0.18 | <1 | 0.13 | <1 | | | |
| С | May 2011 | 1.41 | 1 <cf<3< td=""><td>2.53</td><td>1<cf<3< td=""><td>0.09</td><td><1</td><td></td><td></td></cf<3<></td></cf<3<> | 2.53 | 1 <cf<3< td=""><td>0.09</td><td><1</td><td></td><td></td></cf<3<> | 0.09 | <1 | | | |
| | August 2011 | 0.1 | <1 | 0.16 | <1 | 0.08 | <1 | | | |
| | March 2012 | 0.03 | <1 | 0.16 | <1 | 0.00 | <1 | | | |
| | August 2012 | 0.11 | <1 | 0.46 | <1 | 0.10 | <1 | | | |
| | October 2012 | 0.12 | <1 | 0.16 | <1 | 0.02 | <1 | | | |
| М | May 2011 | 0.93 | <1 | 2.58 | 1 <cf<3< td=""><td>0.18</td><td><1</td><td></td><td></td></cf<3<> | 0.18 | <1 | | | |
| | August 2011 | 0.06 | <1 | 0.16 | <1 | 0.11 | <1 | | | |
| | March 2012 | 0.03 | <1 | 0.16 | <1 | 0.00 | <1 | | | |
| | August 2012 | 0.06 | <1 | 0.16 | <1 | 0.02 | <1 | | | |
| | October 2012 | 0.03 | <1 | 0.16 | <1 | 0.02 | <1 | | | |

Table 4CONTAMINATION FACTOR (CF)FOR THE HEAVY METALSOF OLT RIVER SEDIMENTS

| l _{geo} value | Class relative to I _{geo} | Pollution level | | | | | |
|------------------------|---------------------------------------|----------------------------------|--|--|--|--|--|
| ≤0 | 0 | No polluted | | | | | |
| 0-1 | 1 | No polluted to moderate polluted | | | | | |
| 1-2 | 2 | Moderate polluted | | | | | |
| 2-3 | 3 | Moderate to strong polluted | | | | | |
| 3-4 | 4 | Strong polluted | | | | | |
| 4-5 | 5 | Strong to very strong polluted | | | | | |
| >5 | 6 | Very strong polluted | | | | | |

| Sampling | Period | | Cr | | Ni | | Cu | Zn | | |
|----------|--------------|-------|-------|-------|-------|------------------|---------|-------|-------|--|
| Sites | | Igeo | Class | Igeo | Class | I _{geo} | Class | Igeo | Class | |
| PO | May 2011 | -1.32 | 0 | -0.56 | 0 | -0.77 | 0 | -0.73 | 0 | |
| | August 2011 | -3.26 | 0 | -2.03 | 0 | -2.29 | 0 | -2.84 | 0 | |
| | March 2012 | -3.47 | 0 | -2.34 | 0 | -0.11 | 0 | -1.45 | 0 | |
| | August 2012 | -3.97 | 0 | -0.56 | 0 | -0.02 | 0 | -0.61 | 0 | |
| | October 2012 | -2.91 | 0 | -1.01 | 0 | -0.70 | -0.70 0 | | 0 | |
| С | May 2011 | -3.04 | 0 | -1.88 | 0 | -2.32 | 0 | -2.60 | 0 | |
| | August 2011 | -3.44 | 0 | -2.01 | 0 | -2.62 | 0 | -2.98 | 0 | |
| | March 2012 | -4.11 | 0 | -5.42 | 0 | -1.21 | 0 | -2.49 | 0 | |
| | August 2012 | -3.75 | 0 | -1.6 | 0 | -1.59 | 0 | -2.43 | 0 | |
| | October 2012 | -4.28 | 0 | -2.4 | 0 | -3.34 | 0 | -3.90 | 0 | |
| Μ | May 2011 | -4.85 | 0 | -3.80 | 0 | -10.2 | 0 | -1.23 | 0 | |
| | August 2011 | -4.69 | 0 | -3.79 | 0 | -2.57 | 0 | -2.14 | 0 | |
| | March 2012 | -5.40 | 0 | -6.55 | 0 | -0.96 | 0 | -2.84 | 0 | |
| | August 2012 | -5.55 | 0 | -4.42 | 0 | -4.72 | 0 | -5.58 | 0 | |
| | October 2012 | -6.31 | 0 | -4.37 | 0 | -3.37 | 0 | -4.74 | 0 | |
| | | Cd | | Hg | | Pb | | | | |
| PO | May 2011 | -0.68 | 0 | 2.80 | 3. | -1.31 | 0 | 1 | | |
| | August 2011 | -4.58 | 0 | -3.16 | 0 | -3.69 | 0 | - | | |
| | March 2012 | -5.52 | 0 | -3.16 | 0 | -8.39 | 0 | - | | |
| | August 2012 | -4.67 | 0 | -2.49 | 0 | -3.10 | 0 | 1 | | |
| | October 2012 | -2.35 | 0 | -3.01 | 0 | -3.49 | 0 | 1 | | |
| С | May 2011 | -0.08 | 0 | 0.75 | 1 | -3.99 | 0 | 1 | | |
| | August 2011 | -3.90 | 0 | -3.16 | 0 | -4.19 | 0 | 1 | | |
| | March 2012 | -5.32 | 0 | -3.16 | 0 | -8.08 | 0 | - | | |
| | August 2012 | -3.68 | 0 | -1.69 | 0 | -3.80 | 0 | | | |
| | October 2012 | -3.58 | 0 | -3.16 | 0 | -6.10 | 0 | - | | |
| М | May 2011 | -0.67 | 0 | 0.78 | 1 | -3.02 | 0 | 1 | | |
| | August 2011 | -4.58 | 0 | -3.16 | 0 | -3.67 | 0 | 1 | | |
| | March 2012 | -5.32 | 0 | -3.16 | 0 | -8.05 | 0 | 1 | | |
| | August 2012 | -4.58 | 0 | -3.16 | 0 | -6.19 | 0 | 1 | | |
| | October 2012 | -5.27 | 0 | -3.16 | 0 | -5.80 | 0 | 1 | | |

platform, with cadmium in the section (C), located downstream the platform, and the mercury in the sections situated downstream of the platform (C and M). In May 2011 it was found a very high contamination with mercury in the upstream section (PO).

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

$$I_{geo} = \log_2 \left[\frac{C_n}{1,5B_n} \right]$$
(2)

Where: C_n is the concentration of element n^n and B_n is the standard value.

From the I_{geo} calculation in the points analyzed generally was not observed any pollution by heavy metals, except for mercury on May 2011, fall within Class 1, with a level of pollution "unpolluted to moderate polluted" (table 5, 6).

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 7, 8) [16].

The index is calculated as the following equations (3), (4), (5), (6):

$$C_f^i = \frac{C_D^i}{C_R^i} \tag{3}$$

Table 5RELATION BETWEEN I
GEOPOLLUTION LEVEL

 Table 6

 GEO-ACCUMULATION INDICES

 (I_{GEO}) OF HEAVY METALS IN OLT

 RIVER SEDIMENTS

 $C_H = \sum_{i=1}^m C_f^i \tag{4}$

$$E_f^i = T_f^i \times C_f^i \tag{5}$$

$$RI = \sum_{i=1}^{m} E_f^i \tag{6}$$

where C_{f}^{i} is the pollution coefficient of single metal; C_{D}^{i} is the measured concentration of sample; C_{R}^{i} is the background concentration of sediments; C_{H} is the polluted coefficient of many metals; E_{f}^{i} is the potential ecological risk factor of single metal; T_{f}^{i} is the biological toxicity factor of different metals; RI is the potential ecological risk index of many metals.

From the data presented in Table 9 it is noted that for the sediments of Olt River there is not a significant ecological risk with regard to heavy metals. However, it was noted that in May 2011 there was a strong ecological risk in the point PO, situated the upstream of the industrial platform.

Pollution load index (PLI) is calculated as the following equation (7):

$$PLI = (CF1 \ x \ CF2 \ x \ CF3 \ x \ ... \ CFn)^{1/n}$$
(7)

where, n^{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

| | Parameter | | Cd | С | r | Cu | Pb | Z | Zn | | Table 7 | | | |
|-------------------|---|--------|--------------------------|----------------------|---------------------------|----------------------|----------------------|---------|------|--------|--------------------------|---|-----|--------------------|
| Pre-indus | trial back | ground | I, C_R^i | 0.2 | 9 | 7 | 32 | 20 | 1: | 29 | | ALUATED PARAMETERS FOR ECOLOGICAL RISK INDEX | | |
| Toxic r | esponse f | actor, | T_f^i | 30 | 2 | 2 | 5 | 5 | | 1 | CALCULATION | | | |
| | Pollution Pollution Coefficient Ef | | lution (RI) | index | Ecological risk | | | | |] | | Table 8 | | |
| 40-7 80-1 | <pre><40 <15 40-79 150-2 80-159 300-6</pre> | | <150 150-29 300-60 | 99 00 | Low Moderate Strong | | | | | | | PARAMETERS OF ECOLOGICAL RISK | | |
| 160-3 >32 | | | >600 |) | | | ry stron mely str | | | | | | | |
| Sampling Sites | Perio | d | Cr E _f | Cu E _f | Zn E _f | Cd E _f | Hg E _f | Pt E | | RI | Grade Hakanson (1980) | | | |
| PO | May 20 | 11 | 1.19 | 4.37 | 1.17 | 28.0 | 418.6 | 3.0 | | 456.46 | Strong | 1 | | |
| | August 2 | | 0.31 | 1.52 | 0.20 | 1.87 | 6.66 | 0.5 | | 11.17 | Low | | | |
| | March 20 August 20 | | 0.27 | 6.94 | 0.54 | 0.97 | 6.66 | 0.0 | 2 | 15.42 | Low | 1 | | |
| | | | 0.19 | 7.36 | 0.97 | 1.76 | 10.66 | 0.8 | 7 | 21.83 | Low | 1 | | |
| | October 2 | 012 | 0.39 | 4.58 | 0.69 | 8.77 | 7.41 | 0.6 | 6 | 22.52 | Low | T IL 0 | | |
| С | May 20 | 11 | 0.36 | 1.5 | 0.24 | 42.3 | 101.3 | 0.4 | | 146.28 | Low | Table 9 | | |
| | August 2 | | 0.27 | 1.21 | 0.18 | 3 | 6.66 | 0.4 | | 11.75 | Low | ECOLOGICAL RISK INDEX | | |
| | | | March 2012 | | 0.17 | 3.23 | 0.26 | 1.12 | 6.66 | 0.0 | | 11.48 | Low | (EF) FOR THE HEAVY |
| | August 2 | | 0.22 | 2.47 | 0.27 | 3.48 | 18.53 | 0.5 | 3 | 25.53 | Low | METALS OF OLT RIVER | | |
| | October 2 | | 0.15 | 0.73 | 0.10 | 3.75 | 6.66 | 0.1 | 0 | 11.51 | Low | SEDIMENTS | | |
| м | May 20 | 11 | 0.10 | 0.00 | 0.63 | 28.1 | 103.3 | 0.9 | 2 | 133.12 | Low | J SEDIWERTS | | |
| | August 2 | | 0.11 | 1.26 | 0.33 | 1.87 | 6.66 | 0.5 | | 10.84 | Low | 1 | | |
| | March 20 | | 0.07 | 3.84 | 0.20 | 1.12 | 6.66 | 0.0 | | 11.94 | Low | _ | | |
| | August 2 | | 0.06 | 0.28 | 0.03 | 1.87 | 6.66 | 0.1 | | 9.02 | Low | | | |
| | October 2 | .012 | 0.03 | 0.72 | 0.05 | 1.16 | 6.66 | 0.1 | 3 | 8.78 | Low |] | | |
| Sampling Sites | Per | iod | I | PLI | Lev | el of p | ollution | | | | | | | |
| PO | May | 2011 | 1 | .19 | | Pollut | ed | | | | | | | |
| | Augus | t 2011 | |).17 | Unpolluted | | | | | | | | | |
| | March | | |).13 | | Unpollu | | | | | | | | |
| | Augus | | | 0.33 | | Unpollu | | | | | | | | |
| | Octobe | | | 0.35 | | Unpollu | | | | | | | | |
| С | May | | |).41 | | Unpollu | | | | | | | | |
| Ŭ | August | | |).17 | | Unpollu | | | | | Table 10 | | | |
| 1 | March | | | 0.08 | | Unpollu | | | | | | LUTION LOAD INDEX (PLI) | | |
| 1 | Augus | | |).24 | | Unpollu | | | | | VALUES | FOR HEAVY METALS IN OLT | | |
| | Octobe | | |).24 | | | | | | | | RIVER SEDIMENTS | | |
| M | | | | | | | npolluted | | | | | | | |
| | May 2 | | |).16 | | Unpollu | | | | | | | | |
| | Augus | | |).13 | | Unpollu | | | | | | | | |
| | March | | | .06 | | Unpollu | | | | | | | | |
| | Augus | | | 0.05 | | Unpollu | | | | | | | | |
| | Octobe | r 2012 | 0 |).06 | | Unpollu | uted | | | | | | | |

pollutants are presented and PLI > 1 would indicate deterioration of site quality.

Regarding the pollution load index (PLI) at all points analyzed all the values are below 1, therefore apparently there is no deterioration in the quality of sediments with heavy metals. The exception is also the point (PO) when in May 2011 PLI > 1, which means that there was a deterioration of the quality of sediments with heavy metals (table 10).

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 2011-2012.

Regarding Olt River water, generally, it 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, except for mercury and cadmium which have had higher concentrations downstream the platform, in the point situated about 10 kilometers far from the platform. The organochlorine substances analyzed had concentration values that are situated within the limits imposed by the current legislation.

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

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