

Comparative Study of Heavy Metals from Rivers Around Ramnicu Valcea and Craiova Chemical Platforms from Romania

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In this paper, the analysis of heavy metals from Olt river around Ramnicu Valcea chemical platform and from Jiu river around Craiova chemical platform during three months before and after industrial zone are presented.

Key Words: Heavy metals, Chemical platforms, Industrial zone, Inductively coupled plasma mass spectroscopy.

INTRODUCTION

In previous years, water quality in Romania has slightly improved only because industry and agricultural water consumption has decreased as a direct result of poor economic conditions and therefore their quantity of wastewater¹ discharged into surface waters (lakes, rivers and streams) has decreased. The quality of surface water in Romania is most impacted by its wastewater². Most of the wastewater requiring treatment and discharged by local utilities is either insufficiently treated or untreated, due to the lack of wastewater treatment capacity and/or its ineffective operation.

Olt river flows through Valcea county: The main stationary sources of pollution within this hydrographical basin, area Valcea are the following industries: Oltchim Ramnicu Valcea, Uzinele Sodice Govora through chemical pollution and Ramnicu Valcea communal economy activities.

Since 1968, the Oltchim Rm Valcea plant has been an important source for many types of pollutants due to a wide range of produced chemicals, both inorganic and organic substances³. Heavy metals and organic compounds, such as pesticides, HCH, chlorine residues of various types are the main types of pollutant. Even though, during the recent years, this plant has diminished or even stopped the production of hazardous products and also switched to non pollutant technologies, remnant effects of historical pollutant accumulation exist.

Jiu river flows through Dolj county: *Substantial critical areas in terms of poor water quality (pollution intensive areas):* Jiu river downstream city of Craiova is the critical area caused by discharges from Isalnita platform and industrial city of

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Craiova. Downstream industrial Isalnita groundwater ground water are affected by discharges of wastewater ammonia from Doljchim and Craiova. The area became critical, especially since there is abstraction of groundwater Breasta of RA water Craiova. Doljchim Craiova plant, which is located 7 km from the city of Craiova, in the village Isalnita, Dolj county. Platform chemical Doljchim Craiova is situated around the Jiu river area, north of the confluence with Amaradia. Activity of Doljchim Craiova plant consists in producing and marketing the following products: chemical fertilizers (urea, ammonium nitrate and nitrocalcar), inorganic base (ammonia) and organic products (methanol).

EXPERIMENTAL

Inductively coupled plasma mass spectroscopy (ICP-MS) was developed in the late 1980's to combine the easy sample introduction and quick analysis of ICP technology with the accurate and low detection limits of a mass spectrometer. The resulting instrument is capable of trace multielement analysis, often at the part per trillion levels⁴. ICP-MS has been used widely over the years, finding applications in a number of different fields including drinking water, wastewater, natural water systems/hydrogeology, geology and soil science, mining/metallurgy, food sciences and medicine⁵.

Liquids can be analyzed directly, sometimes with prior dilution. Water samples were collected manually into polyethylene bottles. Before the analysis, the sample was filtrated and it was not mineralized. The distance from the river side is about 2.00-2.50 m and the depth was about 0.20-0.50 m.

RESULTS AND DISCUSSION

The studies presented the analysis of heavy metals from Olt river around Ramnicu Valcea chemical platform and from Jiu river around Craiova chemical platform during three months before and after industrial zone.

It determined the concentrations of five heavy metals *i.e.*, copper, chromium, iron, manganese and zinc. The results obtained are compared with the concentration from the Romanian standard. Table-1 presented the concentrations of heavy metals according to the Romanian standard.

TABLE-1
CONCENTRATIONS OF HEAVY METALS ($\mu\text{g/L}$)
FROM THE ROMANIAN STANDARD

| Metals | Values regulated by the Romanian standards | | | | |
|-----------|--|-----|-----|------|--------|
| | I | II | III | IV | V |
| Chromium | 25 | 50 | 100 | 250 | > 250 |
| Copper | 10 | 20 | 40 | 100 | > 100 |
| Iron | 200 | 500 | 700 | 1000 | > 1000 |
| Manganese | 50 | 100 | 300 | 500 | > 500 |
| Zinc | 50 | 100 | 200 | 500 | > 500 |

The concentrations of heavy metals in Ramnicu Valcea industrial area were measured at Raureni and Tatarani points during 3 months: February, April and July in 2009 year. These represent three seasons: winter, spring and summer⁶.

The samples are taken from 2 points: Raureni and Tatarani. Raureni point is situated before the industrial zone and Tatarani point is situated in downstream of evacuation of chemical platform Ramnicu Valcea and the brook Govora.

This Tatarani point is selected because it is considered like a critical zone by the waters pollution: sewage waters, industrial waste waters, detergents. The results are presented in Table-2.

TABLE-2
RESULTES OF OLT RIVER WATER SAMPLES

| Sample period | Cr (µg/L) | | Cu (µg/L) | | Fe (µg/L) | | Mn (µg/L) | | Zn (µg/L) | |
|---------------|-----------|-----|-----------|----|-----------|-----|-----------|-----|-----------|----|
| | R | T | R | T | R | T | R | T | R | T |
| January 2009 | 20 | 130 | 95 | 30 | 230 | 215 | 30 | 75 | 60 | 5 |
| April 2009 | 25 | 25 | 70 | 70 | 260 | 490 | 51 | 265 | 40 | 10 |
| July 2008 | 10 | 40 | 60 | 80 | 110 | 300 | 120 | 153 | 40 | 60 |

R: Raureni, T: Tatarani.

The same metals were also analyzed from Jiu river water. The samples are taken from 2 points: Isalnita and Podari. Isalnita point is situated before the industrial zone and Podari after industrial zone. The concentration of heavy metals were measured in these points during 3 months: February, April and July in 2009 year. The results are presented in Table-3.

TABLE-3
RESULTES OF JIU RIVER WATER SAMPLES

| Sample period | Cr (µg/L) | | Cu (µg/L) | | Fe (µg/L) | | Mn (µg/L) | | Zn (µg/L) | |
|---------------|-----------|----|-----------|-----|-----------|-----|-----------|----|-----------|-----|
| | I | P | I | P | I | P | I | P | I | P |
| January 2009 | 10 | 15 | 7,5 | 8,2 | 220 | 210 | 32 | 37 | 4,3 | 3,5 |
| April 2009 | 20 | 30 | 8 | 8 | 210 | 270 | 20 | 23 | 3 | 4 |
| July 2008 | 18 | 15 | 6,5 | 8 | 320 | 210 | 25 | 38 | 4 | 8,5 |

I: Isalnita, P: Podari.

The concentration of chromium in Ramnicu Valcea industrial zone is between 10-130 mg/L and in Craiova industrial zone is between 10-30 mg/L. In Tatarani point in January, the concentration of chromium is big, but in both zones is situated under the Romanian standard concentration.

The concentration of copper in Ramnicu Valcea industrial zone is between 30-95 mg/L. This difference of concentration is presented in January month. In April month the concentration of copper is same in both points, it is 70 mg/L and in July month it is 60 mg/L copper in Raureni point and 80 mg/L copper in Tatarani point. The concentration of copper in Craiova industrial zone is smaller than in Ramnicu Valcea industrial zone. It is between 6.5-8.2 mg/L copper.

The concentration of iron is between 110-490 mg/L in Ramnicu Valcea industrial zone. It was more in April month, 490 mg/L iron in Tatarani point, but under the Romanian standard concentration. In Craiova industrial zone, the concentration of iron was between 210-320 mg/L.

The concentration of manganese in Ramnicu Valcea industrial zone is between 30-265 mg/L and the concentration of manganese in Craiova industrial zone is between 20-38 mg/L. It is smaller in Craiova industrial zone than in Ramnicu Valcea industrial zone. In Craiova industrial zone the concentration is in first class by Romanian standards during all months.

In Ramnicu Valcea industrial zone, the concentration of zinc is between 5-60 mg/L and in Craiova industrial zone, it is between 3-8.5 mg/L zinc. Also, as in anterior cases, the concentration of zinc in Craiova industrial zone is small.

Conclusion

The concentration of chromium in water, in Ramnicu Valcea industrial zone, in April and July months is situated by Romanian standard in class I-II and in January month, in Tatarani point is situated in class III. In Craiova industrial zone, the concentration of chromium in water is situated by Romanian standard in class I-II. The concentration of copper in water in Ramnicu Valcea industrial zone is situated by Romanian standard in class IV and in Craiova industrial zone, it is in class I.

The concentration of iron in water in Ramnicu Valcea industrial zone and in Craiova industrial zone is situated in class II.

The concentration of manganese in water in Craiova industrial zone is situated by Romanian standard, in class I. This concentration in Ramnicu Valcea industrial zone is situated in class II and III. The biggest concentration of manganese was in Tatarani point in April month.

The concentration of zinc in water in Craiova industrial zone is situated by Romanian standard, in class I. In Ramnicu Valcea industrial zone the concentration of zinc in water is situated in class I-II.

From these results, it is observed that in Ramnicu Valcea industrial zone, the concentration of heavy metals is higher than the concentration of heavy metals in Craiova industrial zone. It is possible because of the industrialization in Ramnicu Valcea is more active than in Craiova. But, in both places, the concentration of heavy metals is under the Romanian standard concentration.

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