

# Survey of the Concentration of Some Heavy Metals in Waste Waters from Râmnicu Vâlcea Chemical Plant at the Biological Purification Plant Their Impact Over the Natural Water Source, River Govora

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*Heavy metals are natural components of Earth's crust. They cannot be degraded or destroyed. The impurification of water surfaces with heavy metals usually has disastrous effects on the environment. That's why the determination of heavy metals concentrations at levels of ppm or ppb is strictly necessary. Industrial, economical and demographic development generates huge amounts of wastes which have different chemical composition and variable content in toxic heavy metals. A defective management of these wastes leads to environment pollution and then to its degradation. This paper presents a method of determining these heavy metals and their levels in the waste waters from Rm. Valcea Chemical Platform at the "Biological Purification Plant". The following toxic heavy metals were determined: Cr, Zn, Fe., Cu. The concentration of these metals was determined by atomic absorption spectrometry method (AAS) using an analyzer type A ANALYST 700. The final part of this paper presents the impact of these heavy metals on the natural water source the River Govora that is used as the recipient of the waste waters from the "Biological Purification Plant" administered by S.C. Oltchim Rm. Vâlcea.*

*Keywords: water wastes, heavy metals, , pollution, environment*

Water represents a renewable natural resource, vulnerable and limited, an indispensable element for life and society, a raw material for production, a source of energy and a transport route, a determining factor in maintaining the ecologic equilibrium of the environment.

Water pollution is a problem of the modern world with consequences over the well-being of the general population. We call water pollution any kind of physical, chemical or biological alteration of water, above a preestablished limit, including the increase in the natural radioactive levels, produced directly or indirectly by human activities, making it improper for normal usage for the purposes it was put to before the alteration appeared. [1-3]. The effects of pollution of the water sources are complex and vary with the nature and the concentration of the pollutants [4].

The effects of pollution with heavy metals over the health differ with the period of exposure and the nature of the pollutants. Thus, we can be faced with acute effects or the acutization of chronic diseases as a consequence of short term exposure or with chronic effects due to long term exposure [5-7].

Toxic pollutants of the heavy metal type exercise their influence over various bodily organs or systems with effects that are specific to the compound in question. The most important aspect is that they accumulate inside the body with the possibility of producing subtle alterations of the pathological kind [8].

The "Biological Purification Plant" operates the mechano-chemical purification of the biodegradable impure waters from the production processes from S.C. Oltchim Rm. Vâlcea and of the sewage from the chemical plant Rm. Vâlcea (S.C. Oltchim Rm. Vâlcea, CET Govora, US Govora, SC Vilmar SA, ICSI Rm Vilcea)

Considering the high toxicity of the heavy metals over the aquatic flora and fauna, it is necessary to maintain the concentration of heavy metals in the waste waters under the limits mentioned in the legislation.

In order to determine the content of heavy metals in the waste water samples from the "Biological Purification Plant" has been analyzed a set of samples from the first semester of 2006 and the first semester of 2007 using as analytical method the atomic absorption spectrophotometry with electrothermic atomization in a graphite oven.

## Experimental part

The samples have been collected over a period of 6 months (first semester of 2006 and first semester of 2007 from the waste waters from the "Biological Purification Plant" and from the natural water course of River Govora, sampled both up- and down-stream from the point of discharge of the "Biological Purification Plant".

The results of the analysis can be influenced but a deficient sampling or by its incorrect preparation. Consequently, the two stages of the analysis, the sampling and the preparation stage have been performed in accordance with the "Guide to the Programs for the Collection of Samples and the Preparation of Materials for Waste Waters" NTPA 004/1997, Anex 2 to the Order of the Minister for Waters, Forests and Environmental Protection nr 1097/1997. The samples have been collected in polyethylene flasks.

The analysis has been performed using atomic absorption spectrophotometry with electrothermic atomization in a graphite oven.

The absorption spectrophotometry determines the concentration of an element in a sample by measuring the absorption of electromagnetic radiation of a specific wave-

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**Table 1**  
INSTRUMENTAL PARAMETERS

Parameters	Element			
	Cr tot.	Zn	Fe tot.	Cu
Wavelength (nm)	357,9	213,9	248,3	324,8
Maximum lamp voltage (mA)	10	10	15	5
Apperture (nm)	0,3	0,2	0,2	0,2
Calibration range	6,0-15,0 $\mu\text{g}\cdot\text{l}^{-1}$	0,05-0,3 $\text{mg}\cdot\text{l}^{-1}$	0,5-5,0 $\text{mg}\cdot\text{l}^{-1}$	5,0-20,0 $\mu\text{g}\cdot\text{l}^{-1}$

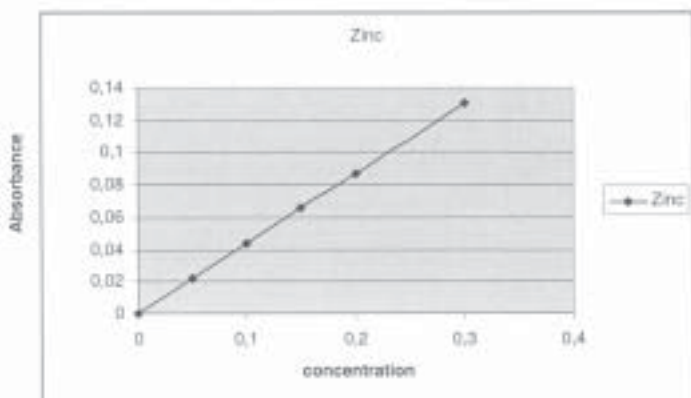


Fig. 1  
Calibration curve specific for zinc 213.9 nm wavelength

length (frequency) passing through a homogenous medium containing the free atoms of the sample to be analyzed as uniformly distributed vapors.

A number of four heavy metals has been analyzed (Cr, Zn, Fe, Cu.) using an atomic absorption spectrophotometer type A ANALYST 700. The parameters of this spectrophotometer are listed in table 1 and the calibration curves have been performed on Merk standard solutions, according to figure 1.

### Results and discussions

Table 2 presents the limit values for pollutant loading of industrial waste waters in the natural sources according to the Romanian standards for various cations of heavy metals. (According to HG 352/2005 regarding the modification and supplementation of HG nr 188/2002, Annex 3, table 1).

The metals analyzed have had normal values, within the permitted limits for industrial waste waters evacuated in natural water streams, according to table 3.

The presence of heavy metals is due to the waste waters released into the Govora River from the purification plant of the Băile Govora City.

**Table 2**

LIMIT VALUES FOR POLLUTANT LOADING OF INDUSTRIAL WASTE WATERS IN THE NATURAL SOURCES ACCORDING TO THE ROMANIAN STANDARDS

Nr. ctr.	Quality criteria	units	Maximum admitted values
1	Cr tot	$\text{mg}/\text{dm}^3$	1,0
2	Zn	$\text{mg}/\text{dm}^3$	0,5
3	Cu	$\mu\text{g}/\text{dm}^3$	100
4	Fe total	$\text{mg}/\text{dm}^3$	5

The heavy metals are known as having reduced mobility, meaning that once released into an ecosystem they are very difficult to eliminate.

*Chromium ( $\text{Cr}^{3+}$ )* is an element that in small quantities helps the human and animal metabolism. The hexavalent chromium ( $\text{Cr}^{6+}$ ) has toxic action. Short term exposure leads to irritations, but long term exposure can lead to the malfunction of the circulatory system and affects the nervous system. The chromium that accumulates in water leads to diseases in aquatic species.

**Table 3**

THE VALUES OF THE CONCENTRATIONS OF HEAVY METALS FROM SAMPLES COLLECTED FROM THE EVACUATION OF THE BIOLOGICAL PURIFICATION PLANT FROM RM. VÂLCEA CHEMICAL PLANT IN THE FIRST SEMESTER OF 2006

criteria	January	February	March	April	May	June
Fe tot ( $\text{mg}/\text{dm}^3$ )	0,542	0,988	0,673	0,655	0,622	0,531
Zn ( $\text{mg}/\text{dm}^3$ )	0,083	0,034	0,045	0,075	0,065	0,065
Cr tot ( $\text{mg}/\text{dm}^3$ )	0,032	0,054	0,071	0,073	0,052	0,043
Cu ( $\mu\text{g}/\text{dm}^3$ )	0,022	0,031	0,015	0,031	0,041	0,041

**Tabelul 4**

THE VALUES OF THE CONCENTRATIONS OF HEAVY METALS FROM SAMPLES COLLECTED FROM THE EVACUATION OF THE BIOLOGICAL PURIFICATION PLANT FROM RM. VÂLCEA CHEMICAL PLANT IN THE FIRST SEMESTER OF 2007

criteria	January	February	March	April	May	June
Fe tot (mg/dm <sup>3</sup> )	0,653	1.	0,873	0,944	0,759	0,657
Zn (mg/dm <sup>3</sup> )	0,161	0,087	0,075	0,122	0,104	0,079
Cr tot (mg/dm <sup>3</sup> )	0,048	0,064	0,076	0,095	0,072	0,054
Cu (µg/dm <sup>3</sup> )	0,035	0,037	0,029	0,039	0,040	0,030

**Table 5**

THE VALUES OF THE CONCENTRATIONS OF HEAVY METALS FROM SAMPLES COLLECTED FROM THE RIVER GOVORA UPSTREAM FROM THE POINT OF DISCHARGE OF THE BIOLOGICAL PURIFICATION PLANT FIRST SEMESTER 2007

criteria	January	February	March	April	May	June
Fe tot (mg/dm <sup>3</sup> )	0,012	0,014	0,022	0,013	0,027	0,016
Zn (mg/dm <sup>3</sup> )	0,001	0,021	0,008	0,031	0,032	0,027
Cr tot (mg/dm <sup>3</sup> )	0,011	0,010	0,014	0,021	0,013	0,009
Cu (µg/dm <sup>3</sup> )	0,006	0,007	0,003	0,001	0,003	0,007

**Table 6**

THE VALUES OF THE CONCENTRATIONS OF HEAVY METALS FROM SAMPLES COLLECTED FROM THE RIVER GOVORA DOWNSTREAM FROM THE POINT OF DISCHARGE OF THE BIOLOGICAL PURIFICATION PLANT FIRST SEMESTER 2007

criteria	January	February	March	April	May	June
Fe tot (mg/dm <sup>3</sup> )	0,423	0,632	0,486	0,833	0,633	0,548
Zn (mg/dm <sup>3</sup> )	0,087	0,067	0,066	0,087	0,072	0,059
Cr tot (mg/dm <sup>3</sup> )	0,031	0,032	0,054	0,065	0,047	0,037
Cu (µg/dm <sup>3</sup> )	0,024	0,027	0,017	0,022	0,031	0,018

*Zinc (Zn)* is a common pollutant of the water streams and sediments and a major component of waste waters. The plants that produce goods containing zinc are the usual pollutants. Over the limit of toxicity, Zn changes the taste of water. The values recorded do not overpass the limit concentration.

*Copper (Cu)* is toxic in high concentrations in water. Germany has a record of human victims due to this metal. It does not bioaccumulate in the human body. The source can be the copper pipes that are vulnerable to mild or acidic waters.

*Iron (Fe)* is an element commonly encountered in nature, high iron concentrations being naturally present in surface waters, soils, sediments, etc. Its widespread use in industry makes it a common component of waste waters.

## Conclusions

The analysis have been performed using atomic absorption spectrophotometry with electrothermic atomization in a graphite oven. The biggest advantage of the method consists in its precision.

This advantage makes atomic absorption spectrophotometry with electrothermic atomization in a graphite oven the optimal analysis method for the evaluation of the quality of waste waters like sewage or industrial waters or for rivers acting as collectors and of residual waters covering large areas.

According to the norms regarding the discharge in aquatic media of waste waters, the quality criteria of the waste waters discharged into the River Govora through the Biological Purification Plant (heavy metals) did not exceed the maximum permitted concentration and the method used has allowed the determination of the following heavy metals at very low concentrations: Cr, Zn, Fe, Cu.

By comparing the results of the samples collected during the first semester of 2006 in the waste waters discharged from the Biological Purification Plant by the Rm. Vâlcea Chemical Plant with the same results from first semester 2007 one can observe lower values recorded in 2006 while the production of the plant has been roughly constant. The differences are due to the higher water flow evacuated during the first semester of 2006 compared with 2007, respectively 6221 cm/h, compared to 4589 cm/h. The impact of these over the River Govora during the first semester of 2007 has been small (see Table 5 and 6) considering that the flow of River Govora has been 536.4 cm/h upstream from the discharge point of the Biological Purification Plant and downstream, after the confluence, 5125.4 cm/h.

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