

## ABSTRACT

The purpose of the correlation analysis between the metal concentration in water and the metal concentration in the sediment is to examine whether there is a connection between these phenomena and to what extent. The coefficient of linear correlation  $r$  is used to explain the correlation analysis process. Correlation is made for metal ions of Cu, Zn and Pb. The content of Cu, Zn and Pb in water varied depending on the location and seasons, but did not exceed the Maximum Allowable Concentration. Based on the analysis of metals in water and the analysis of metals in the sediment, the calibration curves for dependence of  $\ln C_w$  and  $\ln C_s$  ( $C_w$  metal concentration in water,  $C_s$  metal concentration in sediment) were constructed. The inclination of the dependence direction represents the value of the constant  $1/n$ , and the section on the ordinates is the value of the constant  $K$ . The Freundlich constant  $K$  is about the energy heterogeneity of the surface, is related to the sediment capacity, and the Freundlich exponent  $n$  is related to the free adsorption process energy. The analysis showed that the Freundlich exponent  $n > 1$  for Cu and Zn, while the deviation occurred in Pb where  $n < 1$ .

**KEYWORDS:** Correlation analysis, copper, zinc, lead

## I. INTRODUCTION

Most waters contain very low natural concentrations of dissolved metals, and any contamination threatens the natural balance of the aquatic system that includes sediment and living organisms. In the aquatic systems, sediment is of great importance for the transport and circulation of all elements and matters. (1). Exposure to certain toxic substances in the sediment represents a potentially significant risk to the aquatic organisms' health. Under certain conditions, contaminants from the bottom of the sediment can be returned to water again. The bottom of the sediment is in fact a precursor of pollution in the aquatic environment (2). Heavy metals come into water systems from natural and anthropogenic sources (3-5). Sediment contamination differs from water pollution, since due to its geogenic origin in sediment heavy metals exist much longer than in other parts of the biosphere (6). When the adsorption capacity of the sediment is exhausted, the concentration of metal ions in water increases (7). The concentration of the metal depends on the physical and chemical nature of the sediments and water, because they determine the binding force and the shape of the migration. The occurrence of adsorption of metals in the sediment is spontaneous, which means that at the boundaries of the phases, the components of the system whose presence in the system decreases the specific surface energy of the system will be absorbed (8). In sediments with oxygen deficiency, many metals react with sulfides produced by bacterial and fungal activity forming insoluble metal sulfides, leading to the metal precipitation (9). The process of sorption of heavy metals for sediment makes it possible to remove certain compounds from water (but not from the aquatic system) by binding them to suspended matters and sediments. To describe adsorption processes on solid sorbents, the empirical equation of the Freundlich adsorption isotherm is usually used

$$C_s = K_f \cdot C_w^{1/n} \quad (1)$$

$K_f$  – Freundlich constant or the factor capacity (mg/kg or mol/L)

$n$  – Freundlich exponent

The Freundlich adsorption isotherm is used when the sorbent surface is not homogenous, so the sorption heat depends on the coverage degree of the sorbent surface by the sorbate. The Freundlich constants **K** and **n** can be determined by the regression using a linearized form of the Freundlich adsorption isotherm:

$$\log C_s = n \log C_w + \log K_f \quad (2)$$

The inclination of  $\log C_s$  depending on  $\log C_w$  equals the exponent **n**, and the intercept on the ordinate  $K_f$ . The constant  $K_f$  is associated with the sorbent capacity for the sorbate, and the Freundlich exponent is associated with the free energy of the sorption process. The metal concentrations in water and in sediment presented by the distribution model (using equation 2) are determined in the paper, in order to establish their mutual correlation, and determine the Freundlich constant **K** and **n** which allow the insight in the adsorption capacity of the sediments in the accumulation of Modrac Lake.

## II. MATERIALS AND METHODS

The samples of the water from Modrac Lake and river Bosna were taken from six different locations during four seasons at the depth of 2.5 m, including:

Location 1 – area of the dam “Modrac

Location 2 – the middle of the lake “Modrac”

Location 3 – the mouth of the river Turija into “Modrac”

Location 4 – the mouth of the river Spreča into “Modrac”

Location 5 – the River Bosna upstream from the ironworks

Location 6 – the River Bosna downstream from the ironworks

Water samples for analysis of the heavy metals are sampled in the sterile plastic bottles of 0.33 L. Two samples were taken from each location. Sediment was sampled from the same location from which the water samples were taken. Samples were taken into sterile plastic containers (for the analysis of heavy metals). After the transport into the laboratory, all samples were stored according to the appropriate procedure until the preparation time and were dried in the air in order to prevent the loss of easily volatile elements. In preparation the sediment samples for analysis after drying in the air, drying in the oven at 105°C to constant mass was performed. Then, the dried samples were triturated in an agate mortar. Three samples of 3 g were taken and then annealed at 550°C for 1 h. Evaporation was performed after annealing with the addition of concentrated HNO<sub>3</sub>. This evaporated sample was washed with redistilled water, filtered and added to the mark on the flask.

High purity chemicals (Merck Co and Chemika) were used in the process of preparation and sample analysis for heavy metals, and those were:

- Standard solution of Cu, Zn and Pb concentration 1 g/L from which the working solutions were prepared

- Concentrated HNO<sub>3</sub>, HCl, NaOH p.a. (Merck)

- For determining total metal trace concentration, the electrochemical method of differential pulse voltammetry (DPV) was used by applying potentiostat / galvanostat, PAR, model 303A, with the software program Model 270/250 Research Electrochemistry Software, version 4.3. for the control and monitoring of voltametric measurements and the device for thermostating and the method of inductively coupled plasma (ICP-ES) by using Optical emission spectrometer “Perkin-Elmer” ICP OPTIMA 2100 DV.

The use of electrochemical methods was carried out by using the standard additive method, since it is suitable for determining low concentration of elements in traces in small sample volumes. The trace concentrations of heavy metals (Cu, Zn, Pb) in samples of water and sediment were determined by using this method.

## III. RESULTS AND DISCUSSION

The obtained values of the linear regression analysis of the metal distribution between the solid ( $\ln C_s$ ) and the liquid phase ( $\ln C_w$ ) are shown in diagrams 1, 2 and 3. The regression analysis was performed by using the equation of linearized form of Freundlich adsorption isotherm (equation 1).

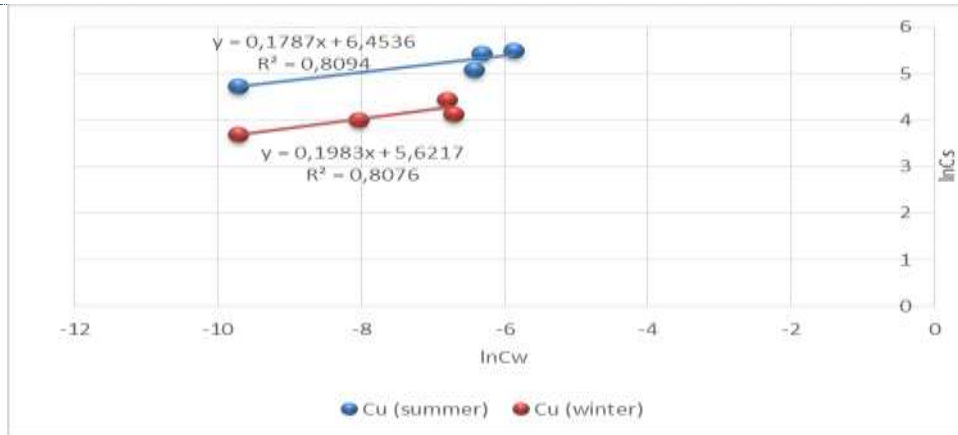


Diagram 1 Correlation dependence of lnCw and lnCs for copper – winter/summer

The results of the linear regression analyses between the experimentally obtained values lnCw and lnCs for copper (winter and summer) are shown in diagram 1. The correlation between the observed phenomena is positive and direct with the coefficient of the simple linear correlation  $r = 0.8986$  and  $r = 0.8996$ . The one-parameter linear regression analysis between the metal concentration in water and the metal concentration in sediment for copper winter-summer resulted in the following dependence:

$$\ln C_s = (5.04)\ln C_w + \ln(276.35) \quad (\text{winter})$$

$$\ln C_s = (5.5)\ln C_w + \ln(638) \quad (\text{summer})$$

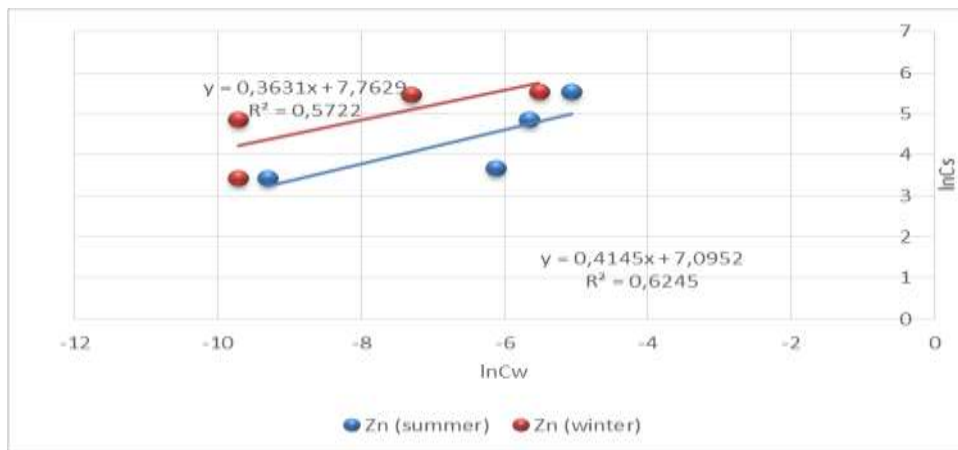


Diagram 2 Correlation dependence of lnCw and lnCs for zinc – winter/summer

The results of the linear regression analysis between experimentally obtained values of lnCw and lnCs for zinc (winter and summer) are presented in the diagram 2. The correlation between the observed phenomena is highly positive and significant with the coefficient of the simple linear correlation  $r = 0.756$  and  $r = 0.79$ . The one-parameter linear regression analysis between the metal concentration in water and the metal concentration in sediment for zinc winter-summer resulted in the following dependence:

$$\ln C_s = (2.27)\ln C_w + \ln(2351) \quad (\text{winter})$$

$$\ln C_s = (2.41)\ln C_w + \ln(1206) \quad (\text{summer})$$

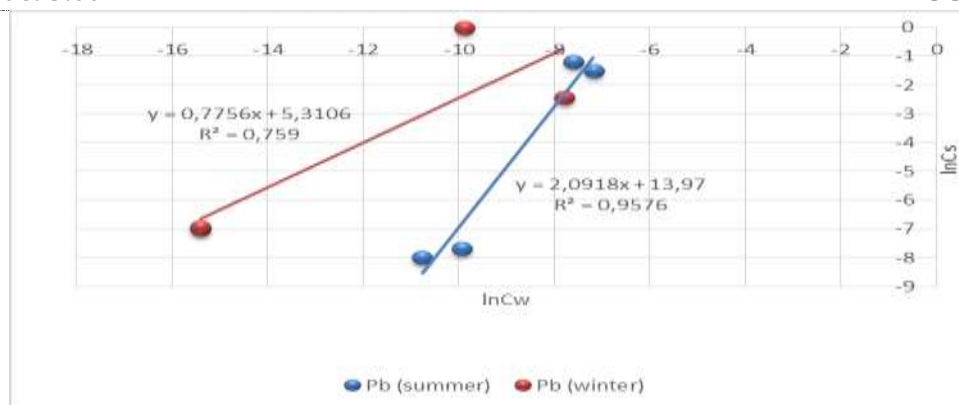


Diagram 3 Correlation dependence of lnCw and lnCs for lead – winter/summer

The one-parameter linear regression analysis between the metal concentration in water and the metal concentration in sediment for lead winter – summer resulted in the following dependence:

$$\ln C_s = (1.28)\ln C_w + \ln(202.4) \quad (\text{winter})$$

$$\ln C_s = (0.47)\ln C_w + \ln(1.1 \cdot 10^6) \quad (\text{summer})$$

By analyzing the results of metal distribution between the two phases (sediment-water), it was generally determined that the Freundlich exponent  $n > 1$  for ion metals of copper and zinc, meaning that the isotherm is convex, and with the increase of the adsorbate concentration increases the free energy for further adsorption. The deviation occurred in lead for the summer period where the Freundlich coefficient is  $n < 1$ , which can be explained by physical-chemical and biochemical processes which occur as a result of eutrophication, high temperature and reduced water volume, which is more expressed in the summer period. All this affects the metal distribution between the solid and liquid phase, determine the shape of finding and behavior of the metal in the system water/sediment.

#### IV. CONCLUSION

1. Distribution of heavy metal traces of Cu, Zn and Pb at six different locations during two seasons in water and sediment, is followed by the application of differential pulse anodic stripping voltammetry. The method has proven to be very selective for determining the content of very low concentrations in water and very high concentrations in sediment.
2. The obtained analysis results of metals Cu, Zn and Pb are significant for the revitalization of the River Bosna and Modrac Lake, because they indicate the appropriate presence of the metals and provide information on sediment quality as evidence of the need to prioritize the application of the recovery measures.
3. By the correlation linear regression analysis of the results of the metal distribution between the solid and liquid phase, the experimentally obtained values lnCw and lnCs are highly positive and direct, generally with high correlation coefficient.
4. The obtained values of the Freundlich exponent ( $n$ ) were greater than 1, which means that the isotherm is convex, and that with the increase of the adsorbate concentration increases the free energy for further adsorption. It means that the value of constant  $K$  increases, and the value  $n$  decreases with time.
5. The results have shown that the deviation occurred with lead for the summer period where the Freundlich coefficient is  $n < 1$ , which can be explained by numerous physical-chemical and biochemical processes, expressed eutrophication and high temperature in this period.

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