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# Experimental Modeling of Heavy Metals Concentration Distribution in Rivers

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**Abstract:** Heavy metals in water, cause a certain effect, which may be beneficial or toxic depending on their concentration variation in the aquatic system. The toxicity of heavy metals is due to the fact that they can not be broken or destroyed, but accumulate. Rivers are used both as a source of water supply and as a wastewater receiver, and is very important to know both the concentration of heavy metals and its tendency. In this paper, a case study concerning the analysis and variation of heavy metals concentration in Bazias-Gruia Danube sector was carried out. Based on this study, an evaluation of the water quality from that area was accomplished and some mathematical statistical models which describe the variation of heavy metals in water were elaborated. Experimental data used in this paper were obtained from the monthly monitoring of the Danube water quality.

**Keywords:** heavy metals, rivers, mathematical modeling, black box model.

## 1. Introduction

Heavy metals are considered dangerous substances for aquatic system, providing a significant pollution risk for water resources and human beings [1].

On ppb (µg/L) to ppm (mg/L) concentration, metals as Fe, Mn, Cu, Zn, Mo, Co are nutrients, but on higher ppm concentration becomes toxic [2]. Therefore it is important to know the concentration of heavy metals in water and its tendency.

This paper consists in a study case on the evolution of heavy metals concentration in Danube, in the Bazias Gruia sector.

The measurements performed and the studies carried out allowed the comparison between the values of the heavy metals concentrations measured in 4 different locations of the Bazias Gruia sector and the values of specific toxic pollutants of natural origin, provided for by the standards of chemical and physical-chemical quality [3].

The Danube river is the second largest river in Europe, its length is of 2860 km from the source (Germany) to the river mouth in the Black Sea (Romania) and it is both the water source and the waste water receiver of bordering villages from 13 countries [4].

In the Romanian Bazias – Gruia sector, the Danube presents different flow regimes and flow rates which vary yearly between 2100 mc/s (September-October) and 10400 mc/s (March – April) [5].

The present studies were carried out in order to draw some dependencies between the variation of heavy metals concentration in relation to water parameters (water temperature, flow, pH). Based on these dependencies, a series of statistical mathematical models were elaborated, useful for assessing water quality.

Experimental mathematical modeling is performed when a process is not sufficiently well known or it is too complex. The experimental model has a probabilistic nature because, during experimental data acquisition, statistical processing and results interpretation, errors are not taken into account [6, 7].

In developing the mathematical model we can start from the black box model, skipping the structure or functionality of the system [8]. Impulses received by the system from the environment (input) are taking into account and, after being processed by the system, are transformed into environmental actions (output) [7].

## 2. Experimental

In order to built the necessary database, water samples from four different locations of Danube river ( Bazias – km 1071, Upstream Dr. Tr. Severin – km 932, Pristol – km 851 and Gruia – km 836.7) were analyzed monthly during year 2009. The results of the measurement were provided by the Romanian Water National Administration –Water Management System Mehedinti.

The heavy metal concentration was measured using laboratory analytical methods, such as Graphite Furnace Atomic Absorption Spectrophotometry (VARIAN Spectraa 220 atomic absorption spectrometer), for heavy metals (Zn, Cu, Cr, Cd si Ni) concentration of µg/L and Flame Atomic Absorption Spectrophotometry (Perkin Elmer Aanalyst 700 spectrometer) for iron (Fe) concentrations of mg/L.

The obtained values give the concentration of heavy metals dissolved in water.

## 3. Results and Discussion

Concentrations of heavy metals (Cd, Cr, Cu, Ni, Fe, Zn) in analyzed waters were compared with standard values corresponding to class (III) of water quality : Cr (100 µg/L); Cu (50 µg/L); Fe (1 mg/L); Zn (500 µg/L); Cd

(2 µg/L); Ni (50 µg/L) in order to classify the water from Bazias Gruia sector in one of the five categories : very good (I); good (II), moderate (III); low (IV); poor (V) [3]. In Drobeta Turnu Severin upstream section, at 932 km, the heavy metal concentrations of water were compared with the limit values stipulated by drinking water standards: Cd (5 µg/L); Cr (50 µg/L); Cu (50 µg/L); Ni (50 µg/L); Fe (2 mg/L); Zn (5 mg/L) [9].

In figures 1-6 there are illustrated the variations of heavy metals (Fe, Zn, Cr, Cu, Ni, Cd) concentrations, during year 2009, measured in four measuring points of Bazias Gruia sector and the limit values stipulated by Ord.161/2005 for the chemical and physical-chemical quality standard of surface water and by HG 100/2002 for drinking water quality standard.

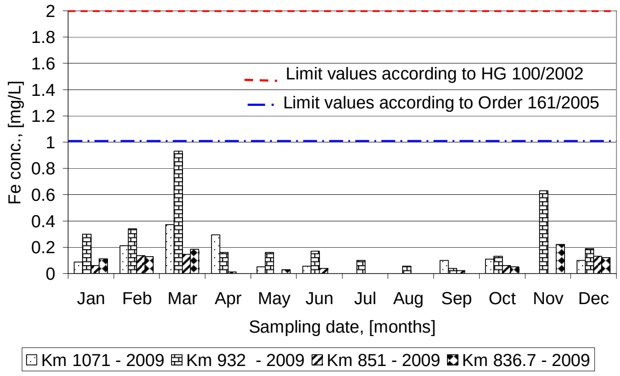


Figure 1. Variation of iron concentration in Bazias Gruia sector (year 2009)

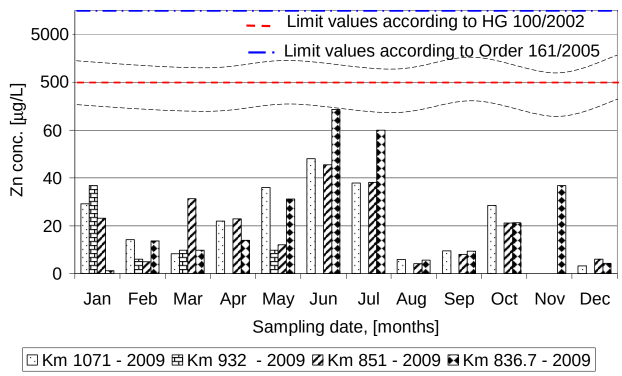


Figure 2. Variation of zinc concentration in Bazias Gruia sector (year 2009)

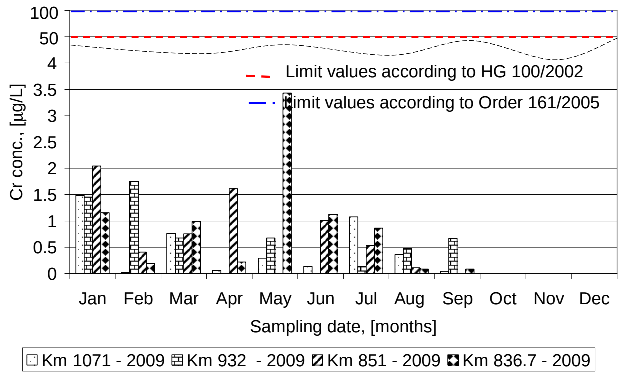


Figure 3. Variation of chrome concentration in Bazias Gruia sector (year 2009)

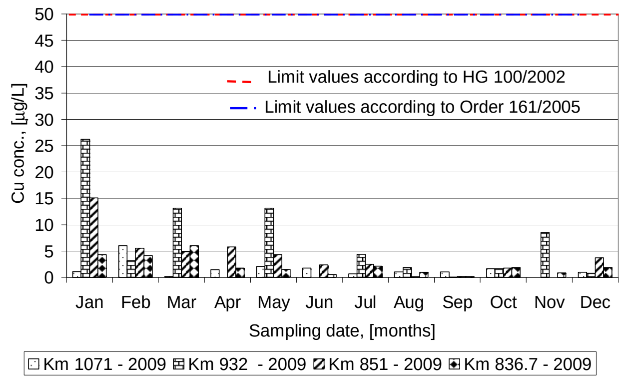


Figure 4. Variation of copper concentration in Bazias Gruia sector (year 2009)

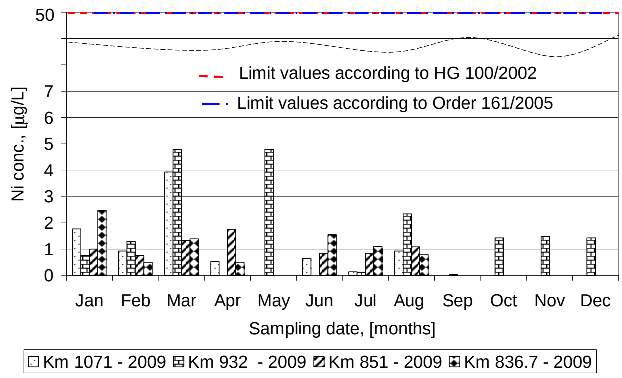


Figure 5. Variation of nickel concentration in Bazias Gruia sector (year 2009)

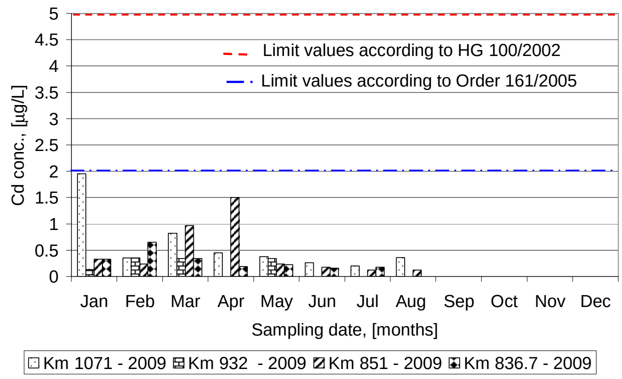


Figure 6. Variation of cadmium concentration in Bazias Gruia sector (year 2009)

From the figures we note that in the Drobeta Turnu Severin Upstream sector, 932 km, the concentrations of heavy metals dissolved in water are lower than the limit provided for by HG 100/2002.

Nevertheless, if we compare the heavy metal concentrations with the limits provided for the third quality class, we find that only Fe and Cd tend to fit in this class. Because the other metals have lower values it can be concluded that, in the Bazias Gruia sector, the Danube belongs to the second quality class, according to a good ecological state from the point of view of the heavy metal content.

For the development of the statistical mathematical models, only iron compound was taking into account because it changes the organoleptic properties of water and its drinking properties [2].

The mathematical models were drawn up starting from the black box model.

Figure 7 illustrates the black box model that describes the emission process of heavy metals in waters.

Knowing the variation of process parameters, empirical models were developed in this work by using the statistical correlation relations, like [10, 11]:

$$y = f(x_1, ..., x_n) \quad (1)$$

x1, …, xn – independent variables of the process - inputs (river flow rate, pH, water temperature, water hardness, etc); y – dependent variable – outputs (concentration of heavy metals in water; quantity of heavy metals in sediments).

There were used correlations between heavy metals concentration and some water parameters like flow rate, water temperature and hardness.

By replacing in equation (1) the numerical sets of values experimentally obtained, a system of m equations is generated; m is the total number of the experiments.

The system coefficients are the unknown elements of a system. In order to choose the correct value of the coefficients for all equations, an optimization criterion is necessary, which is to be minimized.

The most used criterion for the processing of experimental data is the least squares method. This method assumes that the best-fit curve of a given type is the curve that has the minimal sum of the deviations squared (least square error) from a given set of data. The mathematical equation is:

$$S = \sum_{j=1}^{m} (\hat{y}_j - y_j)^2 \quad (2)$$

$\hat{y}_j$ – experimental values of the dependent variable; yj – values calculated with the proposed model for the same values of variables xij, …, xnj; m – total number of experiments.

Experimental data were processed with the STATISTICA 6.0 program. The validation of mathematical model has been done by using the following performance criteria: dispersion ($\sigma^2$), standard deviation ($\sigma$), model accuracy indicator ($R^2$) and correlation coefficient (R) [10, 11, 12].

Moreover, the mathematical model proposed does not have to be a very detailed description of the real mechanisms inside the system, but it should have the minimum complexity level required by the purpose it was built for [13].

In figures 8-10 there is a three-dimensional representation of the dependences between the Iron concentrations and hardness and temperatures of water, between Iron concentrations and flow rates and water temperatures, respectively between Iron concentrations and water temperatures and sampling locations. Both, the experimental data and the surfaces generated by the statistical mathematical models are presented.

The concordance between the results generated by the mathematical model and the experimental ones was checked not only visually, by graphic representation, but also by calculating the following performance criteria: dispersion ($\sigma^2$), standard deviation ($\sigma$), model accuracy indicator ($R^2$) and correlation coefficient (R). In table 1, the equations of mathematical models and the performance criterions for the three studied cases are presented.

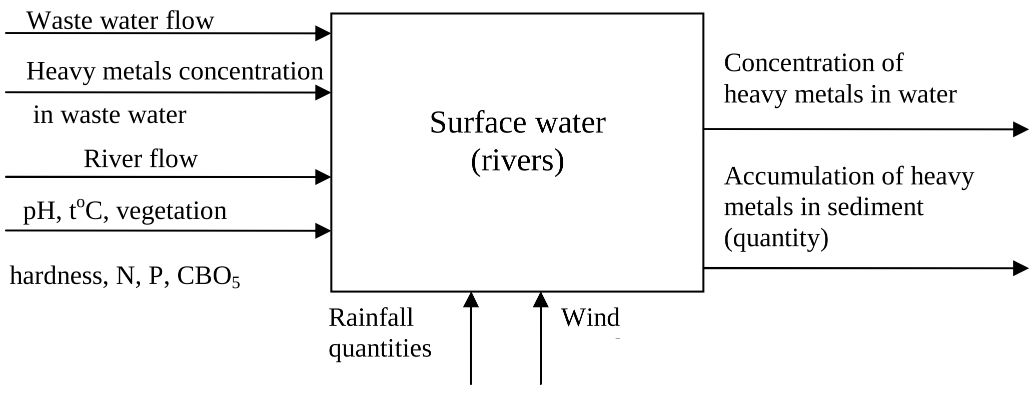


Figure 7. Black box model for heavy metals emissions in water

*TABLE 1. Equations of statistical mathematical models and the values of performance criterions*

| Type of variation | Statistical mathematical model | $\sigma^2$ | $\sigma$ | $R^2$ | R |
|---|---|---|---|---|---|
| Conc Fe, [mg/L]=f(W_Temp [$^0$C], W_Hardness [$^0$G]) | Fe_conc [mg/L] = 4.9155-0.0918* W_Temp -0.733* W_Hardness +0.0009* W_Temp * W_Temp +0.0049* W_Temp * W_Hardness +0.0293* W_Hardness * W_Hardness | 0.0131 | 0.1144 | 0.5583 | 0.7472 |
| Conc Fe, [mg/L]=f(W_Temp [$^0$C], Flow rate [$m^3$/s]) | Fe_conc [mg/L] = 0.0368-8.3159E-6* Flow +0.0134* W_Temp +4.0282E-9* Flow * Flow -2.0972E-6* Flow * W_Temp -0.0003* W_Temp * W_Temp | 0.0034 | 0.0586 | 0.5885 | 0.7671 |
| Conc Fe, [mg/L]=f(W_Temp [$^0$C], Location [km]) | Fe_conc [mg/L] = -12.0729-0.0124* W_Temp +0.0259*Loc+0.0003* W_Temp * W_Temp -8.898E-6* W_Temp *Loc-1.3324E-5*Loc*Loc | 0.0137 | 0.1171 | 0.5376 | 0.7332 |

Analysing the correlation coefficients whose values are higher than 0.7, we note that the mathematical model satisfactorily describes the evolution of Iron concentrations in relation to physico-chemical water parameters taken into account.

The model that describes the relationship between the Iron concentrations and water temperature at different locations was checked by replacing the values in equation (3), generated by the model.

Fe conc, [mg/L] = -12.0729 - 0.0124 * W_Temp + 0.0259 * Loc + 0.0003* W_Temp * W_Temp - 8.898E-6 *W_Temp* Loc-1.3324E-5 *Loc*Loc (3)

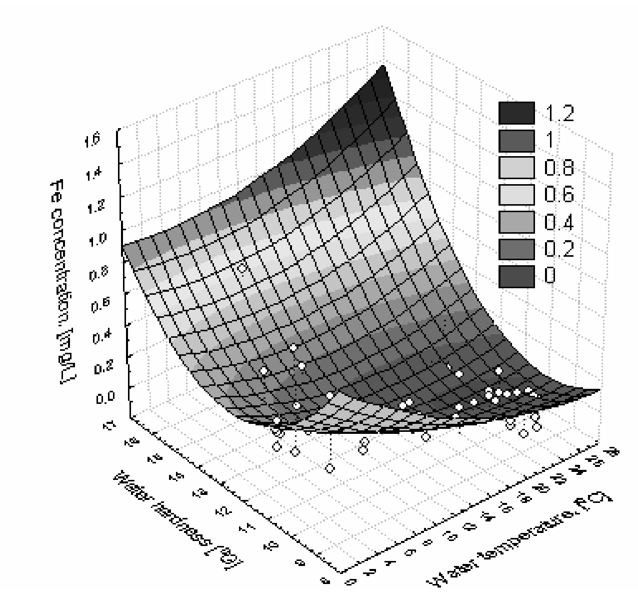


Figure 8 . The variation of iron concentrations depending on water hardness and temperature

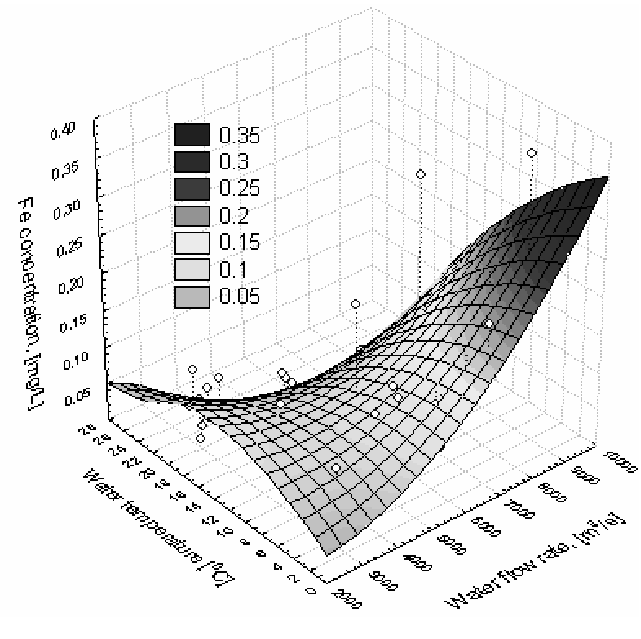


Figure 9. Variation of iron concentrations depending on water temperatures and flow rates

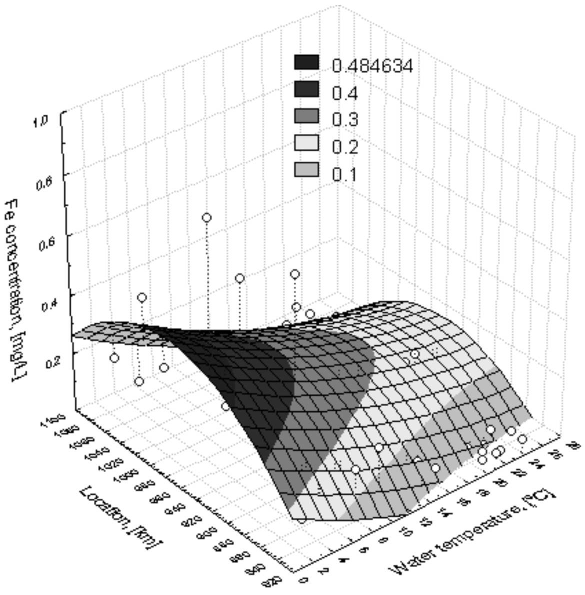


Figure 10. Variation of iron concentrations depending on water temperatures and sampling locations

In figure 11 the graphical representation of the comparison between the values calculated according to the model and the measured values is illustrated.

Analysing fig.11 we may conclude that the proposed mathematical model describes well enough the variation of Iron concentrations function of water temperature and location, taking into account both the dynamic nature of a river and the fact that the heavy metal concentrations was monitored monthly.

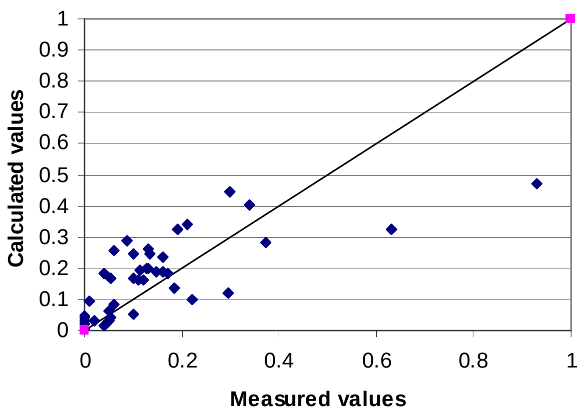


Figure 11. Comparison between the calculated and the measured values of iron concentrations

## 4. Conclusions

After analysing the data and graphics from fig. 1-6 one notices that the concentration values of heavy metals dissolved in water do not exceed the limits provided for by the drinking water standards, showing that the quality of the Danube water in the analyzed sector is good.

From the point of view of the chemical and physico-chemical quality standards, the Danube fits into the second quality category due to a good state from the point of view of the heavy metal contents.

The mathematical model proposed for describing the variation of iron concentration function of 2 characteristic parameters of water (water hardness, water temperature or flow rate) can be considered satisfactory due to the dynamic and inconstant nature of flowing water parameters.

The proposed mathematical model shows that iron concentration in water depend on water temperature. Because the iron concentrations vary with sampling location, we can conclude that in the analyzed sector, a source of iron exists.

The conclusions generated as a result of mathematical models application were validated by the values of performance criterions used.

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