Mathematical Models Describing the Emission and Distribution of Heavy Metals in Surface Waters

MARILENA FAIER CRIVINEANU1*, DELIA PERJU 2, GABRIELA-ALINA DUMITREI3, DANA SILAGHI PERJU4

1 Environmental Protection Agency Mehedinti, 3 Baile Romanie Str., 220234, Drobeta Turnu Severin, Romania
2 Politehnica University of Timisoara, Industrial Chemistry and Environmental Engineering Faculty, Timisoara, 2 Victoriei Square, 300006, Timisoara, Romania
3 Politehnica University of Timisoara, Mechanical Faculty, 1 Mihai Viteza, 300222, Timisoara, Romania

In this paper are presented: the possibility to identify, through cause-effect diagram, the phenomena that determine the presence of heavy metals in surface water the elucidation of the structure and functional connection between the water body components, using systems theory as well as a mathematical model as a heavy metals balance equations and its validation with experimental data obtained for Arsenic.

Keywords: heavy metals, mathematical model, mass balance, causes-effect diagram, Danube river

Heavy metals (those metals with a density higher than 5 g/cm²: Zn, Hg, Fe, Cu, Cr, Pb, Cd, Os) normally present in nature, are not dangerous for the environment [1] but they may become pollutants, i.e. they may alter the balance of environmental components, when they exceed a certain threshold value set by the laws.

Ppm concentrations of heavy metals in water have a toxic effect on the aquatic environment due to bioaccumulation - living organisms take them over and concentrate them [1, 2].

The presence of heavy metals in water is due to emission processes, to direct or indirect discharges of such substances into the environment [3], to human activities and to natural causes respectively [4-6].

The most common sources of heavy metals which end up in rivers are: discharges of untreated or inefficient treated wastewater from various activity fields, atmospheric emissions of combustion gas generated by industrial activity or transportation and uncontrolled waste [4,7].

Once they get into water, heavy metals cannot decompose or be destroyed [1], part of them being found dissolved in water, another part being assimilated by aquatic plants and beings, some settling on the bottom of the bed, and most of them being transported along the water course as suspensions [7, 8].

The water body, defined as a discrete and significant element of the surface waters [9] such as a river sector, may be taken to be, from the perspective of systems theory, a complex system consisting of a multitude of entities with a certain organization and between which there occur a number of interactions. These interactions within the system and between system and environment are in fact flows of mass, energy and information [10].

In the specific case of a flowing water sector, the system is considered a real physical system, with imaginary boundaries between two villages bordering the water course and it is open, since it interacts with the environment. An imaginary interface may be taken into account, for the purpose of setting limits to the system [11,12].

For the purposes of a simplified approach, we may assume that the elements of the system do not depend on spatial coordinates, but only on time; thus, we obtain a system with concentrated parameters [13].

This oriented system may be described by the following equations:

\[ R(u_1, u_2, \ldots, u_q, y_1, y_2, \ldots, y_p) = 0 \]
\[ R_1 (u_1, u_2, \ldots, u_q, y_1, y_2, \ldots, y_p) = 0 \]
\[ \ldots \]
\[ R_r (u_1, u_2, \ldots, u_q, y_1, y_2, \ldots, y_p) = 0 \]  \quad (1)

where: \( R \) represents the dependency relationships between cause and effect variables reflecting the operation of the system; \( q \) is a number of cause variables and \( p \) is a number of effect variables [13].

By means of a systemic approach to those factors relevant for a water sector, the causes leading to a significant effect on the water body may be seen and logically structured, with the help of the cause-effect diagram.

This diagram offers the possibility to identify weaknesses, vulnerable points in a sector of activity, considered to be a potential generator of heavy metals; an intervention on them may take place, by triggering selective actions for the reduction of pollutant emissions in the investigated watercourses [14].

In this paper were studied the following objectives: identifying the causes of the presence of arsenic in the surface waters through causes-effect diagram; description of the distribution of heavy metals in the water body components by a block scheme, using systems theory; developing a balance equations to describe the process of distribution of arsenic in the aquatic environment.

The case study considered was a 31 km segment from Danube river, between Bazias – km 1071 (entrance of the Danube in Romania) and Coronini – km 1040.

Checking and testing the mathematical model developed (the material balance equation) was performed using experimental data obtained from monitoring the Danube River in September 2007, for the case study approach.

For developing causes effect diagrams for the case study in question, and for determining a mathematical model as a material balance equation we chose Arsenic, a chemical element with a highly toxic effect on water, even at very low levels [15,16] and which is distributed in all parts of the water body [8].

* email : marifaier@gmail.com; Tel.: +40-252-320396

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Arsenic toxicity is highly dependent on chemical form in which it is in water; it is known that the inorganic forms of Arsenic are harmful, in comparison with the organic ones, which can be tolerated by aquatic organisms [17].

The theme addressed in this paper is of great interest, considering the ecological accident from aluminum factory in Korontar, Hungary, which has raised large concerns about heavy metals pollution of inland rivers of this country, pollution which has reached the Danube River.

**Experimental part**

For the deduction of balance equation, samples of water, sediments, suspended solids and fish (especially benthic species - such as the bream - which feed on the bottom of the bed and accumulate high concentrations of heavy metals [15]) were collected from Danube River.

Surface water samples were filtered through a porous membrane with a pore size of 0.45 µm, treated with nitric acid to pH values < 2 and temporarily stored in plastic bottles.

For the analysis of suspended solids and sediments, the wet samples were first frozen and then dried by forced removal of water vapour, i.e. lyophilisation.

The fish samples collected were analyzed as frozen samples. The analytical laboratory method used for determining Arsenic in different samples was atomic absorption spectrophotometry (AAS) with hydride generation [8].

**Results and discussions**

From the many factors that contribute to the emission of heavy metals in water, those causing the occurrence of Arsenic in streams have been selected. The causes-effect diagram [14], shown in figure 1, was developed taking into account the dynamic nature of flowing waters.

The diagram shows that, besides the natural factors determining the occurrence of heavy metals in the environment, human activities are mainly responsible for their growing concentrations [4-6].

By comparing the activities in the diagram in figure 1 with those carried out on the Bazias - Coronini river sector, the following potential Arsenic sources were identified: 3 decantation ponds from the copper ore exploitation and processing at Moldova Noua (now closed), the agricultural holdings in the area, 5 settlements (Divici, Belobresca, Pojejena, Macesti, Moldova Noua) and naval, air or road transportation activities.

Arsenic can be obtained only as a by-product of the processing of copper ores and it is also the basic component of insecticides and raticides, extensively used in agriculture [18].

Pollutants - heavy metals included - once in streams, they are carried downstream by convection and spread in the water body by dispersal mechanisms, according to the diffusion theory [19].

In order to determine the distribution of heavy metals among the water system components, a block scheme was imagined and illustrated in figure 2, whose main entities: water, aquatic plants, fish, sediments and suspended matter are interconnected.

The block scheme system components are the following:

- M1 - mass of heavy metals in water in dissolved form, upon system entry
- M2 - mass of heavy metals in plants
- M3 - mass of heavy metals in fish
- M4 - mass of heavy metals in sediments, upon system entry
- M5 - mass of heavy metals on the surface of suspended particles, upon system entry
- M6 - mass of heavy metals in water, upon system exit

![Fig. 1. Causes-effect diagram for the study of Arsenic emission processes in water](image-url)
M7 - mass of heavy metals retained on the surface of suspended particles, upon system exit

Figure 2 shows that there is a combined connection of system elements, namely two connections in series, one between M1, M5, M6, M7 and one between M3, M4, M2, 2 parallel connections between M2 with M3 and M4 with M5 and three connections in opposition with feedback: M4 with M2, M4 with M5 and M4 with M3.

The parallel connection between M2 and M3 is accounted for by the fact that aquatic plants (which can retain in their tissue, by means of leaves, roots or rhizomes [20] heavy metal concentrations that can exceed the concentration of metals in water 10 to up 100 times [21]) may provide food for fish. In turn, lifeless fish or plants get to the bottom of the river, as sediments.

The three feedbacks in the block scheme emphasize that the heavy metals from sediments can get into the bodies of fish, plants or they may be reabsorbed on suspended solids, due to resuspension phenomena.

For a system in which processes take place, with or without a chemical reaction, in a certain period of time, [22] the mass balance equation may be written; it is, at the same time, a mathematical model describing system operation, with the following form:

\[ \Delta M2 + \Delta M3 + \Delta M4 = (M1+M5) + (M2+M3+M4) - (M6+M7) \] (3)

Where, for a certain period of time
\[ \Delta M2 \] - the amount of heavy metals accumulated in the body of aquatic plants;
\[ \Delta M3 \] - the amount of heavy metals accumulated in the fish bodies;
\[ \Delta M4 \] - the amount of heavy metals accumulated in the sediment.

Equation 3 is the material (heavy metals) balance equation, which is both an ideal mathematical model of the system block scheme shown in figure 2.

In order to determine the mathematical expression of a real model [23, 24] for the same system in figure 2, were considered the following:

- terms of the mathematical model have been calculated for one day; reasons of monitoring techniques (samples require several days of harvest) were considered so that the material balance to be calculated for a month.
- the values for the current sediment volume in the Danube bed (table 1) were provided by the Iron Gates Hydropower and Navigation SHEN System. These were calculated in 2006 and were considered valid for 2007 also [25];

- in order to estimate the amount of benthic fish in Danube, during the monitoring period, we are taking into account the quantity of fish caught in the Danube in August 2007, i.e. 165.6 kg [26]. This value was provided by National Agency for Fisheries and Aquaculture - Timis Branch. Considering that this amount represents 1% of the existing benthic fish in the Danube sector analysed, we obtained the total amount shown in table 1.

The simplifying assumptions adopted are:

- in flowing waters, the largest proportion of heavy metal concentration is equally found in sediments and suspended materials [7]. So, the heavy metal accumulations in plants and fish, in one month, are quantitatively insignificant; therefore \( \Delta M3 \) and \( \Delta M2 \) were considered to be null.

- thus, in September, plants undergo a decomposition process, remaining on the bottom of the bed, it was considered that the concentration of arsenic in plants, M2 is null;
- after analyzing the on-site situation, along the distance under scrutiny, it was considered that there are no diffuse or punctual Arsenic sources other than those on 10 km upstream of Coronini, a sector with agricultural holdings and copper mining from Moldova Noua.

Considering the above, equation 3 becomes:

\[ (M1+M5) + (M2+M3+M4) = (M6+M7) + \Delta M4 \] (4)

The terms of equation 4 are calculated using the following expressions, for the selected time interval:

\[ M_i = c_{i,water} \cdot Q_{water} \cdot t \]
\[ M_f = m_{fish} \cdot c_{as,fish} \]
\[ M_s = c_{as, sediments} \cdot V_{sediments} \cdot rsediments \cdot d \]
\[ M_f = c_{as, suspension} \cdot Q_{suspension} \cdot t \]
\[ M_f = c_{as, suspension} \cdot Q_{suspension} \cdot t \]

\[ \Delta M4 = (c_{as, sediments} - c_{as, sediments}) \cdot V_{sediments} \cdot rsediments \cdot d \]

where:
\( c_{as, water} \) - As concentration in water, entering the system, [mg/L];
\( Q_{water} \) - water flow, [L/s];
\( t \) - time, [s];
\( m_{fish} \) - amount of benthic fish, [kg];
\( c_{as,fish} \) - As concentration in fish, [mg/kg];
\( c_{as, sediments} \) - As concentration in sediments, entering the system [mg/kg];
\( V_{sediments} \) - sediment volume, [m³/m/day];
\( rsediments \) - the density of sediments assimilated to sand with a granulation of 0-3 mm, 1300 [kg/m³];
\( d \) - sedimentation distance, [m];
\( c_{as, suspension} \) - As concentration retained on the suspended particles entering the system, [mg/kg];
\( Q_{suspension} \) - flow of silt in suspension, entering the system, [kg/s];
ceAs-water – As concentration in water, exiting the system, [mg/L];
ceAs-suspension - As concentration retained on the suspended particles exiting the system;
Qe-suspension – flow of silt in suspension, exiting the system, [kg/s];
ceAs-sediments - As concentration in sediments, exiting the system, [mg/kg].

Equation 4 represents the real mathematical model of the system shown in figure 2

Experimental data obtained for Arsenic concentrations in water, suspended matter, sediments and fish are presented in table 1 [8].

The values for water flows [27] and silt in suspension [28] were taken legally from the Mehedinti Water Management System database.

Based on data from table 1 the terms of eq. 4 were computed and the values are presented in table 2.

By replacing these values into the eq. 4, we obtain a 23.27% deviation of a real mathematical model compared with the ideal mathematical model.

By analyzing these balance equations can be observed that mass of heavy metals out of the system is higher than the mass of heavy metals from entering the system.

This fact shows that there it was a supplemental source of Arsenic in the system, contributing to the accumulation of this pollutant in the studied sector.

A possible explanation could be the existence of decantation ponds from the former copper mine at Moldova Noua, located upstream of Coronini, where Arsenic is obtained as a byproduct in copper ore processing.

Another explanation could be the existence of farms along the river and the use of Arsenic-based insecticides.

Conclusions

In this study has been analysed the possibility to determine the pollution with heavy metals (As) of the surface and flowing waters.

Thus causes-effect diagram was constructed for the case study approach.

Using this diagram was developed a block scheme which gives, in terms of systems theory, the number of components in the system, their interconnection and possible interactions that occur.

Based on the block scheme developed were determined the mathematical expressions for the ideal model (3) and the real model (4), after being issued a series of simplifying assumptions.

Adequacy and accuracy of real model in relation to the ideal model was verified using the experimental database (table 1 and table 2) for the case study approach.

Following calculations it was observed that between ideal and real model of the system shown in block scheme from figure 2 there is a 23.27% deviation, acceptable, taking into account simplifying assumptions allowed.
By analyzing real mathematical model revealed that in the studied section of the Danube, between Bazaia and Coronini, there has been a source or more of arsenic, which led to an increase in its concentration in water, sediments and suspensions, to exit the system.

These can be identified as tailings from copper mining from Moldova Noua and farm using arsenic-based insecticides.

Also to be noted that in the case study approach arsenic concentrations in water did not exceed the value of 2.48 mg / L, falling to the maximum extent permissible standard of 20 mg / L [29].

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