EVALUATION OF LONGITUDINAL AND TEMPORAL DIFFERENTIATION IN HEAVY METALS CONCENTRATIONS AS PRIORITY HAZARDOUS SUBSTANCES IN THE WATER OF MOARA DOMNEASCA LAKE

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ABSTRACT

The European Water Framework Directive (WFD-2000/60/EC) was implemented in order to improve and protect water quality (for surface water, coastal water, and groundwater) and to prevent further deterioration across Europe by the year 2015 [1]. Also, this directive stipulated that Priority Hazardous Substances are a subset of Priority Substances considered extremely harmful. Heavy metals are listed in the first category as they may accumulate to very high toxic levels and cause severe impact on the aquatic organisms without any visible signs. During the period 2008-2010 National Research and Development Institute for Environmental Protection was involved in the project SAFAR [2]. One of the main objectives of this project was the determination of heavy metals content (Pb, Cd, Hg, Ni) [3] and risk assessment for water and sediments. Another objective of the project was to establish the variation of environmental factors in respect to the heavy metal content upstream and downstream from the Moara Domneasca Lake.

This paper presents part of the most relevant results concerning the heavy metals content and the hazard of the heavy metals in the water samples. The results obtained were interpreted according with the Romanian quality standards Order 2006/161 [4] and Governmental Decision 2010/1038 based on the 2008/105/EC Directive with the W.F.D. amendment [5].

INTRODUCTION

According to the Water Framework Directive (2000/60/EC) enforced in Romania by the Law no 310/2004 regarding the surface waters, the processing and interpretation of analytical data (obtained in the field and in laboratory) represents two essential aspects of the ecological and chemical status. To assess the chemical status, according to The European Water Framework Directive (WFD-2000/60/EC and EU Directive 105/2008), in respect to the hazardous substances content, especially in the case of the priority hazardous substances (such as heavy metals), it is necessary to evaluate the natural background. Because the EQS (Environmental Quality Standard) values include the natural background, we used this alternative in the research study.

This paper refers to investigations on the concentration of hazardous substances and priority hazardous substances in the water column of Moara Domneasca Lake, in order to establish the action / protection priorities.

EXPERIMENTAL

Pretreatment of the water samples - Water samples were sampled according to ISO 5667-4:1987 and ISO 5667-6:1991. Samples in the initial state were brought to the laboratory in iceboxes, at a temperature of 2 – 4°C, and were preserved by bringing them at an acid pH.

The determination of the priority hazardous and hazardous substances (Cd, Pb, Ni and Hg) from the water samples was carried out using various methods of analysis, following the existing ISO standards and methods specified in Table 1.

Table 1 – Methods of analysis used to determine Cd, Pb, Ni si Hg

Indicator	UM	Analysis method	ISO Standard
Cadmiu (Cd)	µg/l	AAS – GF*	ISO 15586:2003
Plumb (Pb)	µg/l	AAS - GF	ISO 15586:2003
Nichel (Ni)	µg/l	AAS - GF	ISO 15586:2003
Mercur (Hg)	µg/l	FIMS**	SR EN 1483:2003

* AAS – GF – Atomic Absorption Spectrometry – Graphite Furnace
** FIMS – Flow Injection System for Mercury Analysis

RESULTS AND DISCUSSIONS

Being a lake of transition, Moara Domneasca Lake, could have a "trap" effect for heavy metals, retaining them in sediments. This would correspond in an initial approximation to the fact that small concentrations of heavy metals were found downstream of the lake compared to those determined upstream. Figure No. 1 shows the obtained values of the hazardous and priority hazardous substances in the water column, for the 2008-2010 period.

With the exception of the lead and nickel content, cadmium and mercury levels were below detection limit for the duration of the study, so the following data and interpretations refer exclusively to lead and nickel. Monitoring sections (1) – upstream of the lake and (2) – input of the lake, are not particularly relevant for the statistical processing of the data since the process occurs "remuu", meaning that a mixing of the entering lake water with the existing lake water occurs, the process being depending on the hydrological conditions.

The significant sections for highlighting the spatial differentiations is (3) – the middle of the lake, where concentrations (in the water column) are lower than the concentrations at the entrance of the lake (especially for Ni). Taking into account the fact that the longitudinal differences in concentrations are not relevant, and also considering the errors from the analysis, it can be concluded that the Moara Domneasca Lake has no retention effect (trap) for heavy metals in sediments. This observation also reflects the fact that the determined values

were in over 80% of the situations the concentrations of the dissolved fraction of heavy metals.

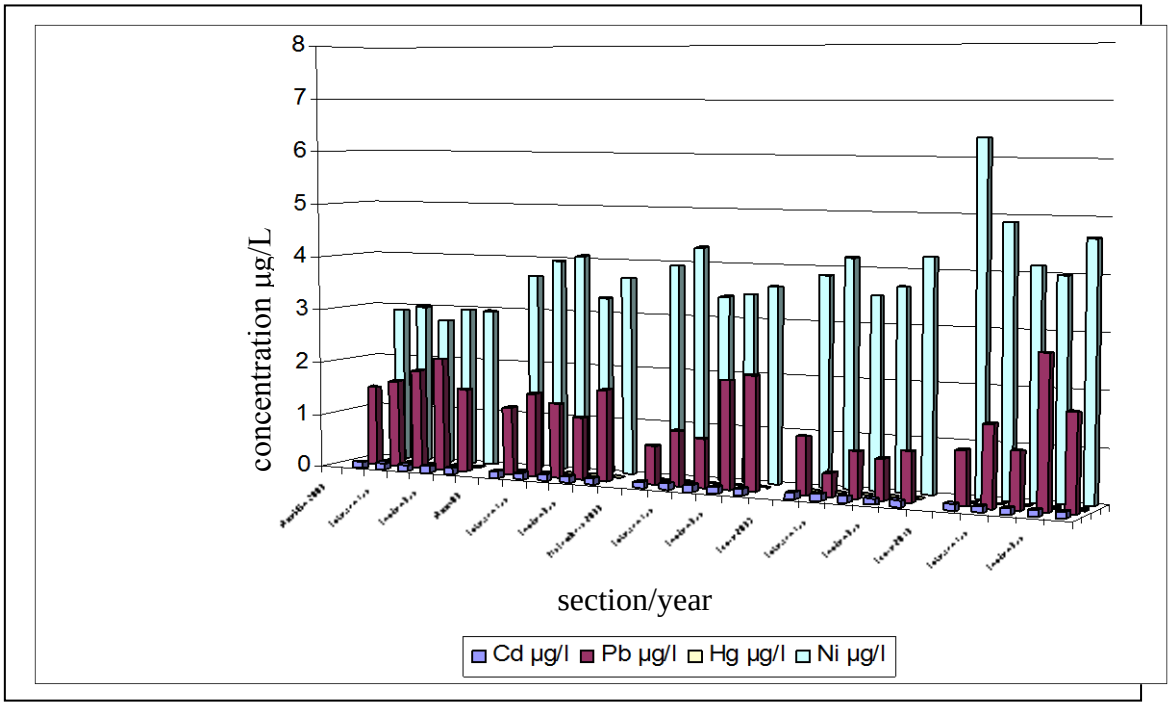

Figure 1 - The variation of the heavy metals concentration in the water column for the sections in the monitoring period 2008-2010

The Table 2 shows the ratios between hazardous and priority hazardous substances content and EQS values.

Table 2 –The ratio between the metals concentration in water and the quality standard (EQS)

Monitoring section	Cd µg/L	Hg µg/L	Pb µg/L	Ni µg/L
Upstream	<0.8	<0.014	0.15	0.21
Lake entrance	<0.8	<0.014	0.18	0.20
Middle of the lake	<0.8	<0.014	0.17	0.18
Lake exit	<0.8	<0.014	0.24	0.17
Downstream	<0.8	<0.014	0.22	0.19
Average	<0.8	<0.014	0.19	0.19

To ensure congruence within the parameters specified in the Directive 105/2008, we used the multiannual average and the maximum values detected. For cadmium and mercury, according to EU safety procedures, LOD values (limit of detection) were used. The analysis of standard ratio values R shows that the chemical state in terms of heavy metals and priority hazardous substances is appropriated, illustrating that anthropogenic pressures specific to industrial activities are not relevant for the Moara Domneasca Lake.

Interesting to note is that both R values for lead and nickel are close (0.19 average value), which may be caused by the fact that they are at the background levels. The Table 3 shows the background values adopted in the EU (referential EAF/7/06/01), 90% percents FOREGS database values (Hg, Ni) and 50% percents for Cd and Pb. Note that except for Pb, the other concentrations values are very close to the background, confirming the hypothesis mentioned above.

Tabel 3 – Comparison between monitored and background concentrations

Metal	µg/l multiannual average	Background values
Cd	< 0.12	0.05
Hg	< 0.01	0.01
Pb	1.38	0.43
Ni	3.81	4.7

CONCLUSIONS

In respect to the spatial-temporal differences of the heavy metals concentrations in the water column, the following conclusions can be draw:

- Moara Domneasca Lake does not have the "trap" effect (retention) for the heavy metals analyzed on longitudinal profile, differences being irrelevant during 2008-2010 monitoring period;
- The statistical analysis of the primary parameters shows that small temporal oscillations of the concentration occurs, but caused by the hydrological regime; the small increases of lead and nickel concentrations in the 2009-2010 period are similar with the fluctuations recorded in April / November 2008.

Regarding the comparisons of the results obtained with EQS (EU Directive 105/2008), we concluded that the chemical state in respect to heavy metals content (dangerous - Ni, Pb and priority hazardous - Cd, Hg) is appropriate, illustrating that the anthropogenic pressures specific to industrial activities are not relevant for the Moara Domneasca Lake. Generally, the heavy metals concentrations are very close (with some exceptions regarding lead) to the natural background values at European level.

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