SURFACE WATER POLLUTION WITH HEAVY METALS IN THE LOWER CATCHMENT OF JIU RIVER BASIN, ACCORDING TO THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)

ADINA SANDA ŞERBAN[1]

ABSTRACT. – **Surface water pollution with heavy metals in the lower catchment of Jiu river basin, according to the Water Framework Directive (2000/60/EC).** The Water Framework Directive establishes a single transparent, effective and coherent water policy by defining a strategy to combat pollution by requiring specific action programs.

Chemical pollution of surface water presents a threat to the aquatic environment with acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a threat to human health (art.1 from Directive 2008/105/EC regarding the environmental quality standards for water policy).

The purpose of this study is to evaluate the chemical status for surface water bodies in the lower catchment of Jiu river basin. The assessment was made taking into account the water impact of four heavy metals: cadmium (Cd), nickel (Ni), mercury (Hg) and lead (Pb).

Keywords: Water Framework Directive (WFD), chemical status, heavy metals.

1. INTRODUCTION

Heavy metals occur naturally in the environment and their chemistry differs significantly from that specific organic pollutants. Heavy metal can also appear in the wastewater discharges from point sources or diffuse sources of emissions that may contain besides heavy metals, synthetic pollutants (organic pollutants).

From legal perspective, the impact of dangerous substances, including the heavy metals on aquatic ecosystems was taken into consideration since the early 70 when one of the first water related directive, (76/464/EEC) concerning the pollution caused by certain dangerous substances discharged into the aquatic environment was adopted. The Directive introduced the concept of list I and list II substances, which were listed in the Annex to the Directive, with the purpose to eliminate pollution from list I substances and to reduce pollution from list II substances. From the heavy metals assessed in this study, mercury and cadmium are part of list I and lead, nickel of list II.

Water Framework Directive (Directive 2000/60/EC), which is the most comprehensive and integrated piece of water legislation ever adopted in Europe,

[1] Bucharest University, Faculty of Geography, 010041, Bucharest, Romania, e-mail: adinaserban22@yahoo.com

assesses the pollution with heavy metals by establishing the chemical status. According to WFD, all member states are required to achieve good water status for all water (continental, estuarine, subterranean and coastal water bodies) by 2015. Surface water quality is assessed taking into account the ecological and chemical status.

Water Framework Directive defines the "Good surface water chemical status" as the chemical status achieved by a surface water body in which concentrations of pollutants do not exceed the environmental quality standards (EQS) established in Annex IX, under Article 16(7) and under other relevant Community legislation setting environmental quality standards at Community level (Article 2, Water Framework Directive).

Environmental Quality Standards (EQS) are defined as concentrations of pollutants that should not be exceeded in order to ensure protection of the environment and human health. The list of these EQS is aproved by the 2008/105/EC Directive *(Annex I)* concerning environmental quality standards in the field of water policy and includes 33 substances and groups of substances. The environmental quality standards for the four heavy metals assessed in this study are presented in the next table (table no.1.)

Table 1. ***Environmental Quality Standards (EQS) for priority substances***

No	***Name of substances***	***CAS number (1)***	***AA-EQS (2) Inland surface waters***	***MAC-EQS (3) Inland surface waters***
1.	Nickel and its compounds	7440-02-0	20	Not applicable
2.	Mercury and its compounds	7439-97-6	0.05	0.07
3.	Lead and its compounds	7439-92-1	7.2	Not applicable
4.	Cadmium and its compounds (depending on water hardness classes) ***(4)***	7440-43-9	≤0.08(class 1) 0.08 (class 2) 0.09 (class 3) 0.15 (class 4) 0.25 (class 5)	≤0.45 (class 1) 0.45 (class 2) 0.6 (class 3) 0.9 (class 4) 1.5 (class 5)

(1) CAS: Chemical Abstracts Service.
(2) This parameter is the EQS expressed as an annual average value (AA-EQS). (3) This parameter is the EQS expressed as a maximum allowable concentration (MAC-EQS).
(4) For cadmium and its compounds the EQS values vary depending on the hardness of the water as specified in five class categories (Class 1: < 40 mg CaCO3/l, Class 2: 40 to < 50 mg CaCO3/l, Class 3: 50 to < 100 mg CaCO3/l, Class 4: 100 to < 200 mg CaCO3/l and Class 5: ≥ 200 mg CaCO3/l).

Source: *2008/105/EC Directive of the European Parliament and of the Council on environmental quality standards in the field of water policy.*

2. DATA AND METHODS

The chemical status of surface water bodies can be assessed using two approaches:

(a) following the principle of *one out, all out* as established by the Water Framework Directive, meaning that any metal in waters over the EQS (environment quality standard according to 2008/105/CE Directive) will determine the whole water body to fail in achieving the chemical status;

(b) using a combined analysis of the metals in water and in sediment.

By considering both water and sediment analysis in determining the status of water quality, resources could better be targeted at those water bodies where levels of pollution have a greater negative effect on the biological elements. However, some researchers say further research is needed on EQS measurements in water and in the interpretation of chemical concentrations of contaminants in sediments.

The chemical status is classified in:

(1) Good chemical status, which is an objective for the Water Framework directive.
(2) Bad chemical status (when the water body is failing in achieving the chemical good status).

The chemical status is assessed for each surface water body which include at least one monitoring station.

"Body of surface water" is a discrete and significant element of surface water such as a lake, a reservoir, a stream, river or canal, part of a stream, river or canal, a transitional water or a stretch of coastal water (art. 2, Water Framework Directive) .

There is still relatively little comprehensive information about the overall impact of most hazardous chemicals, particularly concerning the effects of combinations of chemicals on human health and the environment. The increasing number of man-made substances present in the environment is a matter of great concern, and calls for the application of the precautionary principle.

The first approach above mentioned was used in this study.

Due the fact that heavy metals can be found naturally in the environment, first it is calculated the background level of each metal by calculation the ratio between the average concentration in water and the assigned value of each metal (Cd, Hg, Ni and Pb). The assigned values are common concentration values found in inland waters, estimated as: 0.050 μg/ for cadmium, 0.010 μg/l for mercury, 4.7 μg/l for nickel and 0.43 μg/l for lead.

Heavy metal concentrations are expressed in dissolved fraction which means the proportion of substance to be found as dissolved after separation of suspended solids in the water column;

So, if $X = \frac{annual\_average\_concentration}{assigned\_value}$ is ≤ 1.0 *(1)* ,

in the assessment will be used the Environmental Quality Standards from 2008/105 Directive.

If the ratio ”X” is > 1.0, the Specific Environmental Quality Standard for each metal is calculated.

Y = annual average concentration – assigned value.(2)

$EQS_{specific}$ *=EQS (from 2008/105 Directive) + Y. (3)*

This Specific Environmental Quality Standard will be used to assess the chemical status for the downstream monitoring stations.

For each heavy metal is calculated the next evaluation ratio in order to assess the chemical status:

$$Q_1 = \frac{annual\_average\_concentration}{EQS_{average\_concentration}} \quad (4)$$

$$Q_2 = \frac{annual\_average\_concentration}{EQS_{\max imum\_concentration}} \quad (5)$$

If $Q_1 \leq 1.0$ and $Q_2 \leq 1.0$ the chemical status in that monitoring station is good.

If $Q_1 > 1.0$ sau $Q_2 > 1.0$ that monitoring station fail to achieve the chemical good status.

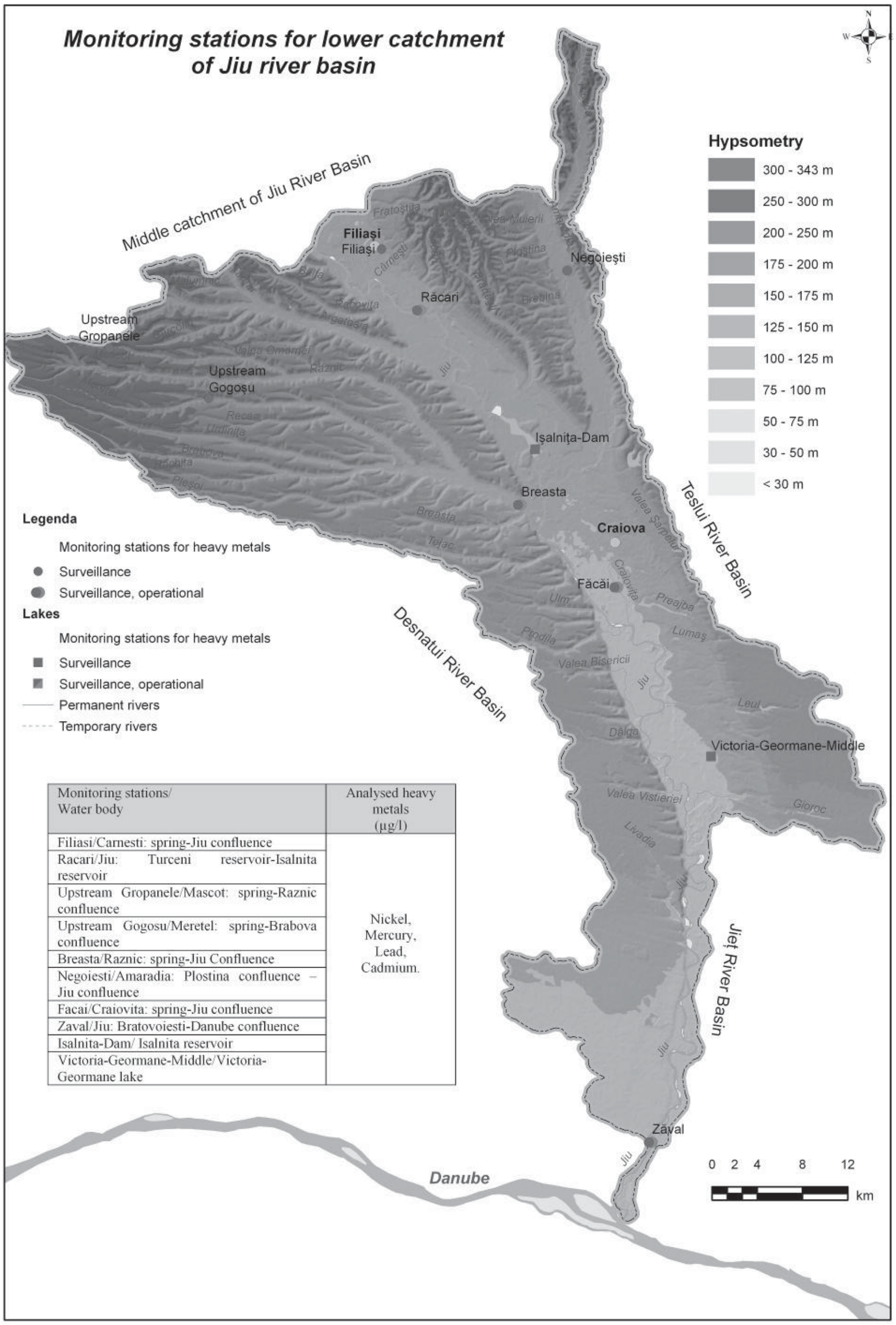
3. STUDY AREA

The chemical status was assessed for the lower catchment of Jiu river basin with a surface of 2215 skm and a river network of 357 km which included: Jiu river between Racari until Danube confluence, Carnesti river, Amaradia between Plostina confluence and Jiu confluence, Meretel, Mascot, Raznic, Craiovita river, Isalnita reservoir (surface of 1,8 skm) and Victoria-Geormane lake (0,59 skm). The assessment was made using the average concentration of heavy metals for 2007, in ten monitoring stations as it can be seen in the next figure (Fig.1.Monitoring stations for lower catchment of Jiu river basin).

The analysis took into account the data confidence level, which can be:

a) High, when the frequency of heavy metal monitoring is according to the Water Framework Directive (12 measurements/year).
b) Medium, when the frequency of heavy metal monitoring is less than12 measurements/year.
c) Low, when there are no monitoring data for the reference year that is used in the establishing of chemical status. In this case it is made a risk assessment analysis.

In this study, the chemical status of the water bodies was assessed with a medium confidence level.



Monitoring stations/ Water body	Analysed heavy metals (µg/l)
Filiasi/Carnesti: spring-Jiu confluence	Nickel, Mercury, Lead, Cadmium.
Racari/Jiu: Turceni reservoir-Isalnita reservoir	
Upstream Gropanele/Mascot: spring-Raznic confluence	
Upstream Gogosu/Meretel: spring-Brabova confluence	
Breasta/Raznic: spring-Jiu Confluence	
Negoiesti/Amaradia: Plostina confluence – Jiu confluence	
Facai/Craiovita: spring-Jiu confluence	
Zaval/Jiu: Bratovoiesti-Danube confluence	
Isalnita-Dam/ Isalnita reservoir	
Victoria-Geormane-Middle/Victoria-Geormane lake	

Fig.1. ***Monitoring stations for lower catchment of Jiu river basin***

4. RESULTS AND DISCUSSIONS

By using the first approach, the study reveals the chemical status for the lower catchment of Jiu river basin.

As it can be seen in the figure no.2 (Chemical status for lower catchment of Jiu river basin), after the evaluation of the ten water bodies (Carnesti: spring-Jiu confluence, Jiu: Turceni reservoir-Isalnita reservoir, Mascot: spring-Raznic confluence, Meretel: spring-Brabova confluence, Raznic: spring-Jiu confluence, Amaradia: Plostina confluence – Jiu confluence, Craiovita: spring-Jiu confluence, Jiu: Bratovoiesti-Danube confluence, Isalnita reservoir and Victoria-Geormane lake), eight water bodies achieved the good chemical status and the rest of two were failing in achieving this status.

Table 2. *The mean heavy metal concentrations in 2007*

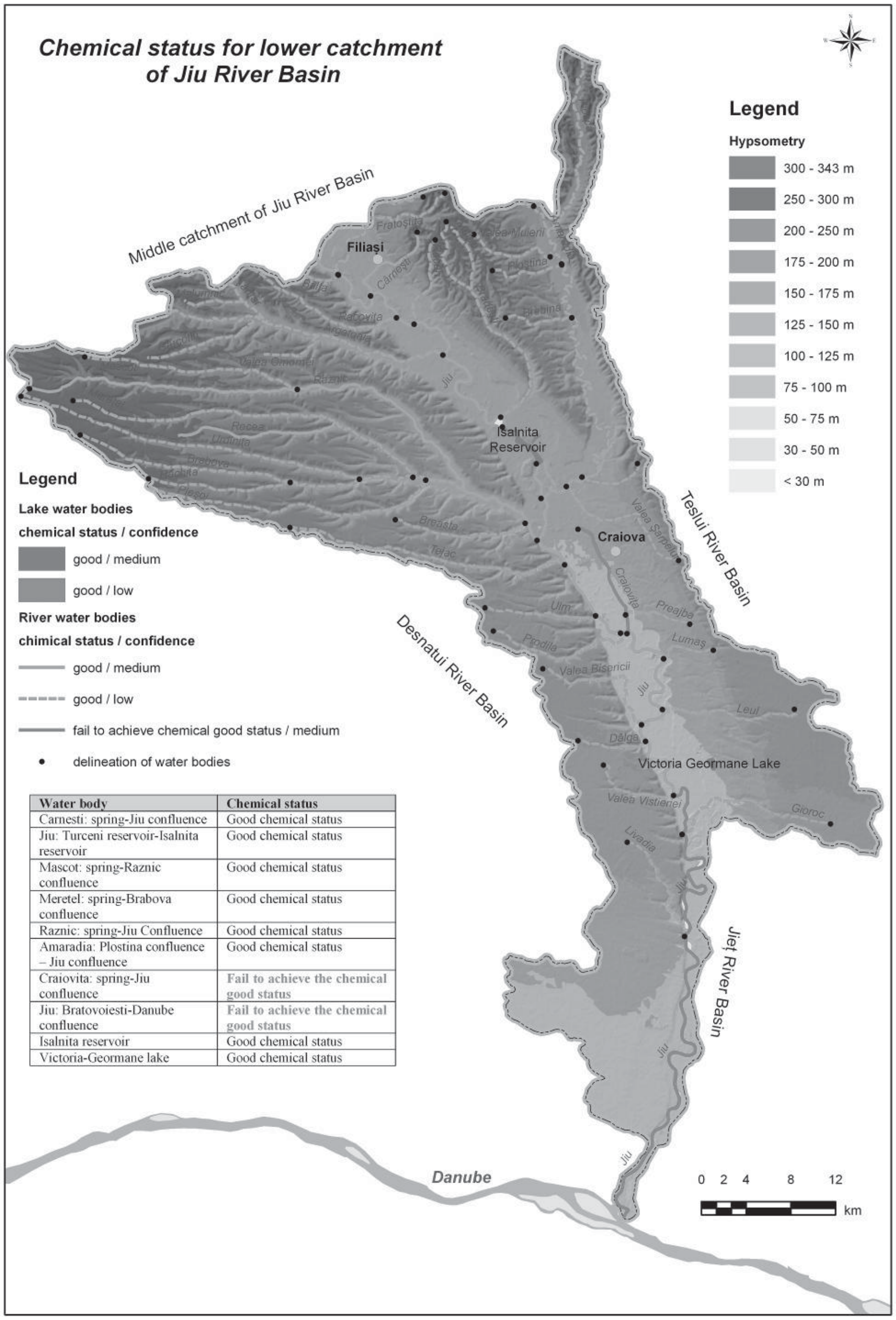
Monitoring Station/Water body	Nickel (µg/l)	Mercury (µg/l)	Lead (µg/l)	Cadmium (µg/l)	Hardness (mg $CaCO_3$)
Filiaşi /Carnesti: spring-Jiu confluence	2,26	0,09	0,83	0,06	387,4
Răcari/ Jiu: Turceni reservoir-Isalnita reservoir	0,99	0,11	0,61	0,035	100,5
Upstream Gropanele/ Mascot: spring-Raznic confluence	2,3	0,04	0,75	0,03	151,5
Upstream Gogosu/ Meretel: spring-Brabova confluence	1,9	0,04	1,1	0,03	321
Breasta/ Raznic: spring-Jiu confluence	3,1	0,16	0,54	0,04	339,7
Negoieşti/ Amaradia: Plostina confluence – Jiu confluence	1,7	0,133	0,56	0,044	284,4
Facai/ Craiovita: spring-Jiu confluence	3,01	0,23	1,69	0,35	310
Zaval/ Jiu: Bratovoiesti-Danube confluence	1,34	0,25	0,808	0,40	98,5
Dam/ Isalnita reservoir	1,51	0,1	0,73	0,05	91
Baraj/ Victoria-Geormane lake	0,55	0,14	0,3	0,023	215

The two water bodies that have failed in achieving the chemical good status are situated downstream from Craiova waste water discharge point, which did not have a waste water treatment plant until December 2010 and also from the Doljchim Chemical Plant, situated at about 10 km north-west of Craiova city.

5. CONCLUSION

These Hazardous substances which have been assessed in this study can harm ecosystems and human health. Due to their intrinsic properties, they can be accumulated in the food chain to such levels that can become toxic to organisms, also can remain in the environment for a very long time and may cause toxicity, persistence and bioaccumulation in the aquatic environment.

In the lower catchment of Jiu river basin (Jiu: Bratovoiesti-Danube confluence and Craiovita: spring-Jiu confluence water bodies), the concentration of cadmium and mercury exceeded the environmental quality objectives.



Water body	Chemical status
Carnesti: spring-Jiu confluence	Good chemical status
Jiu: Turceni reservoir-Isalnita reservoir	Good chemical status
Mascot: spring-Raznic confluence	Good chemical status
Meretel: spring-Brabova confluence	Good chemical status
Raznic: spring-Jiu Confluence	Good chemical status
Amaradia: Plostina confluence – Jiu confluence	Good chemical status
Craiovita: spring-Jiu confluence	**Fail to achieve the chemical good status**
Jiu: Bratovoiesti-Danube confluence	**Fail to achieve the chemical good status**
Isalnita reservoir	Good chemical status
Victoria-Geormane lake	Good chemical status

Fig.2. ***Chemical status for lower catchment of Jiu river basin***

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