"ALEXANDRU IOAN CUZA"
UNIVERSITY OF IAŞI
FACULTY OF GEOGRAPHY AND GEOLOGY

HYDROGEOCHEMICAL CHARACTERISTICS OF SOME STORAGE LAKES FROM JIJIA CATCHMENT

- DOCTORAL THESIS SUMMARY -

Scientific adviser:
Prof. univ. dr. OVIDIU GABRIEL IANCU

Doctoral student:
Engineer ALINA DRACINSCHI (DUGHILĂ)

-IAŞI-
2012

CONTENTS

Summary of the thesis contains relevant information from each chapter and selective bibliography. In the summary were kept the same notations for chapters, paragraphs, figures and tables used in the text of the thesis.

INTRODUCTION

Ubiquitous hydrological alterations such as dam construction and associated water diversion, stream channelization and intercatchment water transfer are producing global scale effects on the environment. The building of these water infrastructures in many regions of the world, especially hydroelectric and freshwater drinking reservoirs, have sharply increased in the 20th century as part of the efforts to address water scarcity and increased water and energy demands from industrial, agricultural, and municipal activities. The environmental impacts of artificial lakes (reservoirs) include eutrophication, reduced downstream biodiversity, and increased cycling of trace metals (Rosenberg et al. 2000).

The water quality from the studied lakes is essential for drinking water supply, irrigation, fishing, etc. These purposes are clearly in conflict with water degradation induced by agricultural and industrial practices or municipal waste disposal. According to EU regulations required by the Water Framework Directive - 60/2000/EC, lakes quality management is focused on solving these conflicts.

The ***fundamental objective*** of this thesis is to characterize the physicochemical overall quality of six dams from the Jijia catchment as well as the levels of content and distribution of chemical elements (Cd, Cr, Cu, Ni, Pb, Zn etc.) from water and sediments.

In order to achieve the proposed goal the following ***specific objectives*** have resulted:

- systematization and interpretation of the data resulted from analysis;
- assessment and framing of ecological and chemical status of the monitored quality indicators in corresponding quality classes according to current Romanian legislation;
- framing the hydrogeochemical features of the studied lakes as a whole for the water of Jijia catchment lakes;
- identifying the levels of content and distribution of trace and major elements in water and sediment samples;

- comparing the obtained results with those from sediment quality standards with sediment quality guidelines for each contaminant or to those normally found in Earth's crust;
- identifying sources of anthropogenic and / or natural contamination.

The importance of this study stems from the fact that the Jijia basin waters stretch across two counties, Botoşani and Iaşi and investigated reservoirs were built to supply water to various cities and towns in this area or river flow regulation, flood mitigation, irrigation, recreation.

II. GEOLOGICAL AND GEOGRAPHICAL SETTING

II.2. Geological setting

From a geological point of view the region of the Jijia catchment falls within the Moldavian Platform, the oldest platform dating from the Middle Proterozoic located in front of the Oriental Carpathians, overlapping the Hilly Plain of Moldova.

The study area (Fig. 1.1) is constituted at the surface only of Sarmatian deposits (Buglovian + Volhynian in north and Basarabian + Chersoniene in south) and Quaternary, southeastern part of the study region.

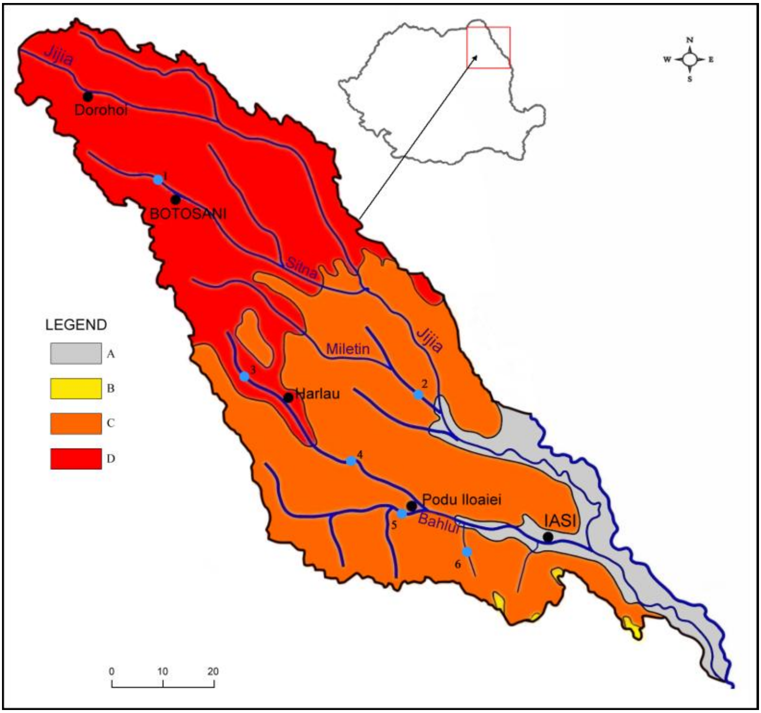


Fig. 1.1. Studied lakes located on the geological map of Jijia catchment (modified after Ionesi et al., 2005)
A. Quaternary; B. Chersonian; C. Basarabian; D. Buglovian + Volhynian
1. Cătămărăşti Lake; 2. Hălceni Lake; 3. Pârcovaci Lake; 4. Tansa Lake; 5. Podu-Iloaiei Lake; 6. Cucuteni Lake.

III. METHODS OF SAMPLING, PREPARATION AND ANALYSIS

III.1. Sampling and storage of water and sediment samples

For **hydrogeochemical assessment** and **framing into quality classes** of the six lakes included in this study, **water samples** were taken from:

- three sections: *middle lake, upstream dam* and *dam outtake* for the lakes used for drinking water supply - Hălceni, Tansa and Pârcovaci;
- two sections: *middle lake, upstream dam* for Cucuteni, Podu-Iloaiei and Cătămărăşti Lakes;
- and with a sample from the rivers that feeds these lake.

Sampling campaigns were scheduled to cover at least three of the four seasons.

Sediment samples were collected with a frame system with tubes, Eijkelkamp. Nine sediment cores were collected from the study lakes.

To determine the **levels of content and distribution of trace and major elements, water and sediment** were sampled from two sections: *middle lake* and *upstream dam*.

IV. HYDROGEOCHEMICAL CHARACTERISTICS OF SOME STORAGE LAKES FROM JIJIA CATCHMENT

IV.1. Hălceni Lake

- The main purpose is drinking water supply for the Vlădeni village, fisheries, flood protection and irrigation.
- It is located on the Miletin River in Hălceni village, Vlădeni, Iaşi county, 18 km upstream of the confluence with the Jijia River.
- It has a surface on normal retention level of 315 ha.
- It was put into service in 1986.

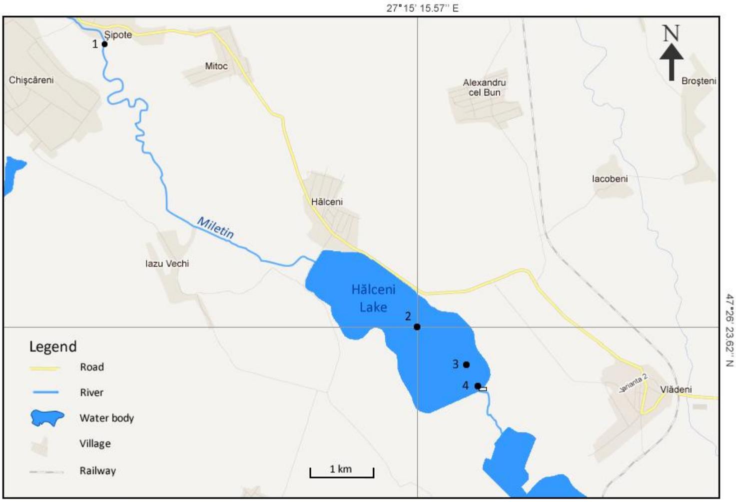


Fig. 4.1. Location of Halceni Lake, with sampling points:
1 - *River*, 2 - *middle lake*, 3 - *upstream dam*, 4 - *dam outtake*
(modified after Google Maps, 2012)

IV.1.1. Quality indicators from oxygen group

a. Dissolved oxygen

Dissolved oxygen (DO) plays a key role in the development of aquatic life and also as a key indicator in assessing the water quality of lakes and rivers.

The DO content in the Hălceni Lake varied between 7.47 mg $O_2 \cdot L^{-1}$ in August and 13.4 mg $O_2 \cdot L^{-1}$ in February, with a mean value of 9.63 mg $O_2 \cdot L^{-1}$ framing the water quality within the 1st quality class (Fig. 4.3).

The lowest oxygen content is recorded during the warm period when high temperatures have a negative effect on its solubility favoring the growth of bacteria, large consumers of oxygen.

b. Biochemical oxygen demand (BOD_5)

BOD_5 represent the concentration of dissolved oxygen consumed in different conditions by biochemical oxidation of organic and/or inorganic matter contained in water, in a 5 day incubation period.

In Hălceni Lake the BOD_5 varied between 5.3 - 15.4 mg $O_2 \cdot L^{-1}$ for the sections across the lake and 4.7 - 12.8 mg $O_2 \cdot L^{-1}$ on the *River* section, framing the water quality within the 4th class for the year 2010 (Fig. 4.4). The poor chemical status of the Hălceni Lake is dictated by the discharge of insufficiently treated wastewater into the Miletin River as well as the use of nitrogen-containing chemical fertilizers.

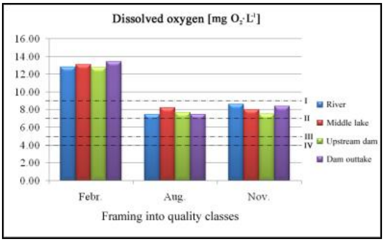


Fig. 4.3. Dissolved oxygen values in the monitored sections of the Hălceni Lake

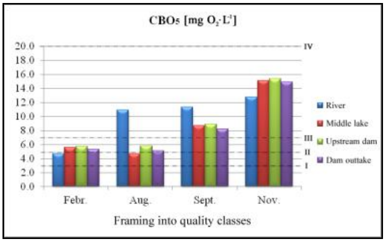


Fig. 4.4. Biochemical oxygen demand values in the monitored sections of the Hălceni Lake

IV.1.2. Quality indicators from nutrient group

c. Nitrate (N calculated from NO_3^-)

The presence of nitrates in water is due to diffuse pollution from agriculture (use of chemical fertilizers), livestock and other anthropogenic activities.

The nitrate content recorded throughout 2010 for the Halceni Lake reveals a growth during the winter period (due to a lower rate of organic decomposition) and a decrease during the warm period (due to intensified biogenic processes) (Fig. 4.8). However, this natural evolution is conditioned by water drainage systems including anthropogenic activity.

The mean values recorded for this parameter (1.1 mg N/L) place the lake water in the 2nd quality class. For the *River* section the levels remain high throughout the year (as a result of the use of nitrogen fertilizers in agriculture and the discharge of wastewater from commercial companies and from wastewater treatment plants) corresponding to the 2nd quality class.

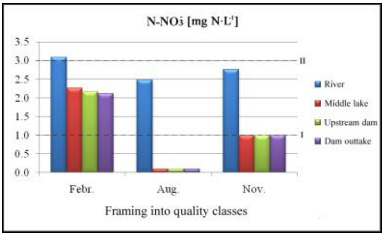


Fig. 4.8. Nitrate values in the monitored sections of the Hălceni Lake

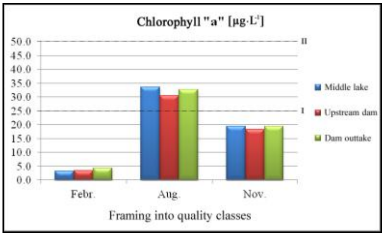


Fig. 4.12. Chlorophyll "a" values in the monitored sections of the Hălceni Lake

g. Chlorophyll "a"

Chlorophyll "a" is the essential photosynthetic pigment of green algae and its determination provides information regarding biomass and potential photosynthetic activity of algae. The chlorophyll "a" content of a water body is an indicator of its trophic status (Oprean & Poplăcean, 2008).

Chlorophyll "a" ranges from 3,3 $\mu g \cdot L^{-1}$ to 33,6 $\mu g \cdot L^{-1}$ with a mean value of 18,4 $\mu g \cdot L^{-1}$, placing the water of the Hălceni Lake in the 1st quality class; in terms of trophicity the lake classifies as eutrophic (Fig. 4.12).

IV.1.3. Quality indicators from salinity group

b. Total suspended matter (TSM)

Knowledge about the content of suspended materials and fixed residue is necessary in the design of reservoirs, in desanding and treatment facilities, in order to function at optimum parameters (Zaharia, 1999).

Overall, the rivers of the Jijia catchment have a high content of suspended matter. Also, the contents of MTS (Fig. 4.14.) measured for the Miletin river (between 301 to 778 $mg \cdot L^{-1}$) are very high compared to the values recorded in the three sections of the Hălceni Lake (22 to 34 $mg \cdot L^{-1}$).

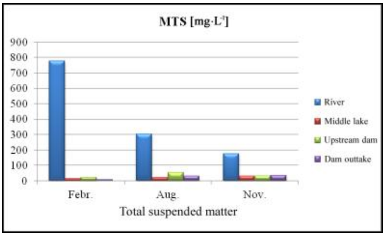


Fig. 4.14. Total suspended matter in the monitored sections of the Hălceni Lake

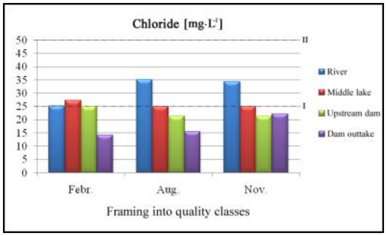


Fig. 4.15. Chloride values in the monitored sections of the Hălceni Lake

c. Chloride

Chlorides are compounds (salts of hydrochloric acid) contained in almost all natural waters and wastewaters. Chlorides in water come from soil (when present in constant concentration) or from wastewater pollution (when the concentration varies over time).

Chloride concentrations range from 14 $mg \cdot L^{-1}$ in *dam outtake* in February and 27 $mg \cdot L^{-1}$ in the *middle lake* section, same month. Mean values for this indicator allows framing Hălceni Lake in the first quality class (Fig. 4.15.).

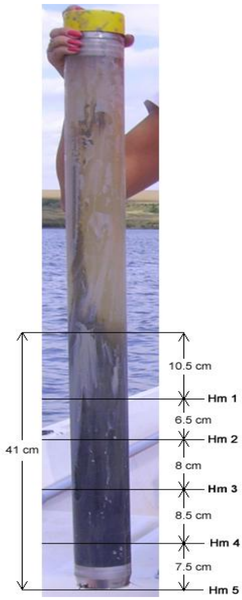
V. TRACE AND MAJOR ELEMENTS FROM WATER AND SEDIMENT OF SOME STORAGE LAKES FROM JIJIA CATCHMENT

V.2. Results obtained through atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS)

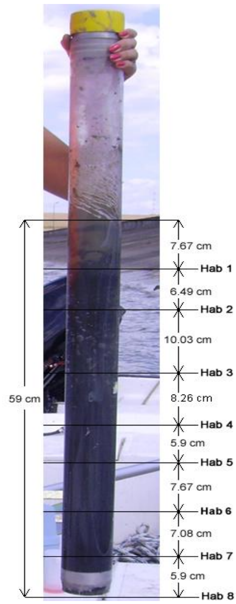
V.2.1. Hălceni Lake

V.2.1.1. Sediments

For the Hălceni Lake were collected two sediment cores (Fig. 5.1. a, b).



a)
Lake depth at sampling point:
4 m



b)
Lake depth at sampling point:
3,5 m

Fig. 5.1. Hălceni Lake, sediment cores from sections: a) *middle lake*, b) *upstream dam*

b. Upstream dam

Trace elements variation on depth in upstream dam section of Lake Hălceni is presented in figure 5.3.

Concentrations ranged from: 0.38 to 0.91 $mg{\cdot}kg^{-1}$ with an average of 0.53 $mg{\cdot}kg^{-1}$ for Cd; 44.8 to 68 $mg{\cdot}kg^{-1}$ with an average of 63 $mg{\cdot}kg^{-1}$ for Cr; 33.8 to 68 $mg{\cdot}kg^{-1}$ with an average of 44.4 $mg{\cdot}kg^{-1}$ for Cu; 56 to 64 $mg{\cdot}kg^{-1}$ with an average of 59 $mg{\cdot}kg^{-1}$ for Ni; 9.7 to 31.5 $mg{\cdot}kg^{-1}$ with an average of 21.4 $mg{\cdot}kg^{-1}$ for Pb; 96 to 114 with an average of 108 $mg{\cdot}kg^{-1}$ for Zn.

Trace elements variation in the *upstream dam* sediment core of Hălceni Lake is relatively uniform with a peak at the water-sediment interface for cadmium.

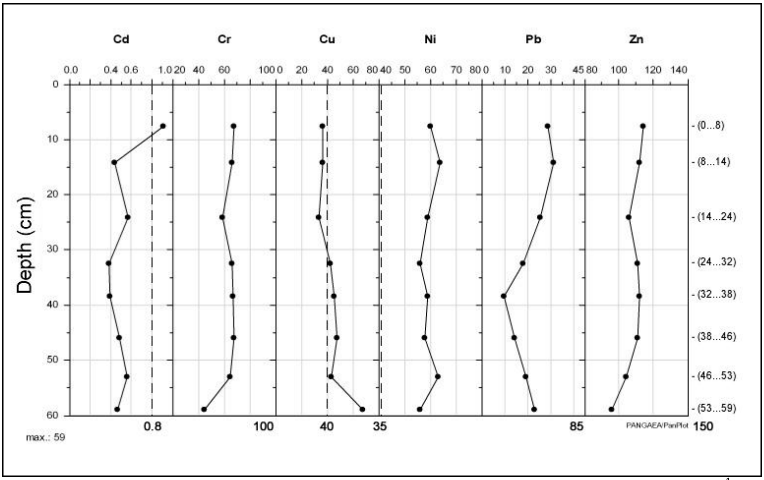


Fig. 5.3. Trace element variation for *upstream dam* section, Hălceni Lake ($mg \cdot kg^{-1}$)
- - - maximum limit under current legislation

The correlation matrix (Table 5.4) shows a strong correlation for Cr and Zn (0.9), indicating a common source of these elements and a slightly poor correlations for Cd and Pb (0.5). The relationship between chromium and zinc can also be seen in Figure 5.3 in the similar distribution of the two elements along the sediment core. Trace elements showed no significant correlation with organic carbon.

Tabel 5.4. Correlation matrix, (*n=8*)

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**TOC**
Cd	1						
Cr	0.2	1					
Cu	-0.3	-0.7	1				
Ni	0.2	0.4	-0.6	1			
Pb	**0.5**	-0.2	-0.3	0.4	1		
Zn	0.2	**0.9**	-0.7	0.3	0.0	1	
TOC	0.0	0.1	0.4	0.3	-0.1	-0.1	1

VI. FINAL CONSIDERATIONS
VI.1. Group and global characterization of water quality indicators for the studied lakes from Jijia catchment
VI.1.1. Hălceni, Tansa and Pârcovaci Lakes

Studying the measured indicators by the mean values for the five groups of indicators shows that of all three reservoirs, used for water supply purposes, two of them, Hălceni and Tansa were classified as 3rd quality class for oxygen regime and 2nd quality class for salinity regime. Nutrients maintain the water from the three reservoirs in 1st quality class and specific toxic pollutants in 2nd quality class (Fig. 6.2).

The *amount of oxygen* required for the organic matter oxidation in the case of **Hălceni, Tansa and Pârcovaci Lakes** indicates an oxygen deficiency above the allowable limits, consumption exceeding aeration by diffusion from the atmosphere.

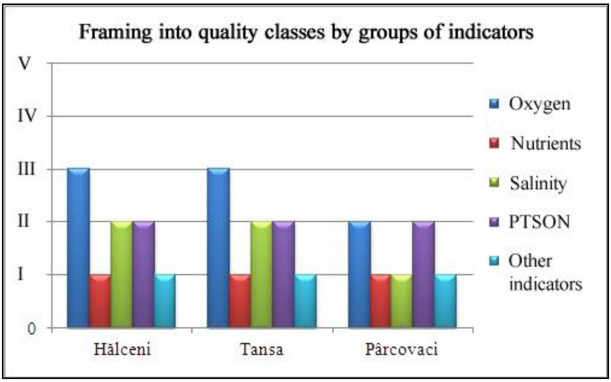


Fig. 6.2. Classification by groups of indicators for Hălceni, Tansa and Pârcovaci Lakes

The *nutrient regime* (especially phosphorus) for **Hălceni and Tansa Lakes** is good, the latter being found in quantities that indicate a positive development, the organic matter being sufficient to absorb it within the biomass. **Pârcovaci Lake** has a reduced nutrient regime determined by the emplacement conditions, forested area with specific vegetation load, therefore natural nutrient intake.

The intake of organic matter and nutrients as well as specific toxic pollutants contained in salts is high, being of both natural and anthropogenic origin.

VI.1.2. Cucuteni, Podu-Iloaiei and Cătămărăşti Lakes

Studying the measured indicators by the mean values for the three groups of indicators it shows that two of them, Cucuteni and Podu-Iloaiei were classified as class III quality for oxygen regime and all three reservoirs in class II for salinity regime. Nutrients fit the water from the Cucuteni and Podu-Iloaiei Lakes in 2nd quality class while Cătămărăşti Lake maintains the water in 1st quality class (Fig. 6.3).

The amount of *organic matter* exceeds the ecosystem capacity of natural regeneration especially for **Cucuteni and Podu-Iloaiei Lakes**.

Sharp decrease in dissolved oxygen during the warm season , with significant diurnal variations due to plant photosynthesis, triggers almost every year specific eutrophication events (in particular for **Podu-Iloaiei Lake**) which results in fish mortality due to sediment entering the anaerobic fermentation and transition through water mass of toxic gases NH_3 and H_2S.

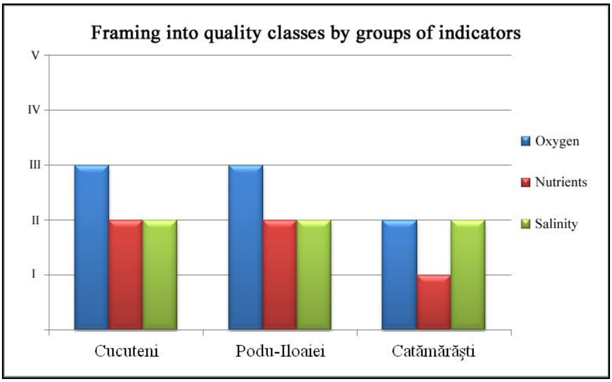


Fig. 6.3. Classification by groups of indicators for Cucuteni, Podu-Iloaiei and Cătămărăşti Lakes

VI.1.3. Global water quality indicator

The general classification of water quality has been carried out by taking into consideration the following five groups of indicators: *(1) oxygen regime, (2) nutrients, (3) salinity, (4) specific toxic pollutants of natural origin (PTSON), and (5) other relevant indicators.*

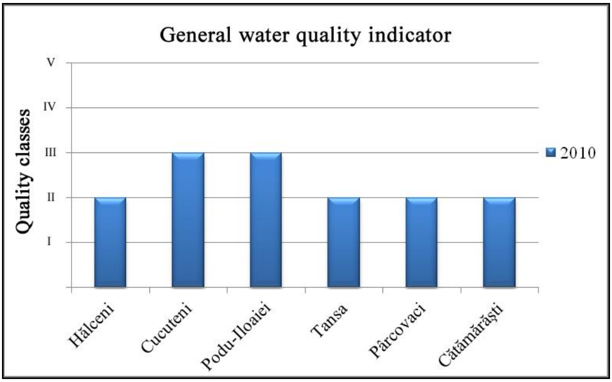


Fig. 6.4. Global characterization of the studied lakes water quality

Global characterization (Fig. 6.4) of the studied lakes indicates the classification in the 3rd water quality class for Cucuteni and Podu-Iloaiei Lakes and 2nd quality class for Hălceni, Tansa, Pârcovaci and Cătămărăşti.

VI.2. Results and discussion

VI.2.1. Trace elements detected by atomic absorption spectrometry (AAS)

The mean concentrations of trace elements resulted from atomic absorption spectrometry (AAS) analysis of the studied lakes were compared (Table 6.2.) with those of other lakes, each with different purposes such as drinking water supply, hydropower, fisheries, flow regulation, irrigation and so on, from different geological regions.

Mean concentrations of Cu, Pb and Zn found in L. Ontario sediments were much higher than those in the studied lakes. Marvin et al. (2004) reported that Lake Ontario was impacted by point sources (e.g., anthropogenic sources). High concentrations of Cu in the studied lakes also come from point sources of pollution.

Tabel 6.2. Comparison of mean concentrations of trace elements ($mg{\cdot}kg^{-1}$) determined by AAS in the studied lakes with those from different lakes

Lacul	Cd	Cr	Cu	Ni	Pb	Zn
L. Hălceni	0.46	61	**42**	**58**	24.4	120
L. Cucuteni	0.41	61	33.2	**45.2**	61	113
L. Podu-Iloaiei	0.37	65	36.3	**43.7**	51	118
L. Tansa	0.31	55	32.7	**38.9**	30.1	106
L. Pârcovaci	0.29	46.3	33.2	**69.1**	69	81
L. Cătămărăşti	0.27	67	**49.1**	**78**	33.6	82
L. Izv. Muntelui [a]	NA	185	75	105	8	80
L. Sambe [b]	NA	31	28	19	34	143
L. Simbi [c]	NA	53.4	44.6	NA	17.4	153
L. Kanyaboli [c]	NA	42	30	NA	11.3	87
L. Sare [c]	NA	16	12.6	NA	5.9	60
L. Namboyo [c]	NA	24	16.3	NA	5	108
L. Ontario [d]	NA	NA	59	NA	72	260
L. Gulshan [e]	NA	118	44	92	38	252
L. Chapala [f]	NA	66	29	39	82	260
C.C. [g]	**0.09**	**92**	**28**	**47**	**17**	**67**
LEL [h]	**NA**	**26**	**16**	**16**	**31**	**120**
SEL [i]	**NA**	**110**	**110**	**50**	**110**	**270**
Ord.161/2006 [j]	**0.8**	**100**	**40**	**35**	**85**	**150**

**NA* – not available; [a] Izvorul Muntelui Lake (Apetroaei, 2003); [b] Sambe Lake, Japonia (Bibi et al., 2010); [c] different lakes of the Victoria Lake (Kenya) basin (Mwaburi, 2009); [d] Ontario Lake, Canada (Marvin et al., 2004); [e] Gulshan Lake, Bangladesh (Ahmed et al., 2005); [f] Chapala Lake, Mexic (Rosales-Hoz et al., 2000); [g] Upper continental crust (Rudnick & Gao, 2003); [h] LEL (Lowest Effect Level) - (NYSDEC-New York State Department of Environmental Conservation, 1999); [i] SEL (Severe Effect Level) (NYSDEC, 1999); [j] *Order no. 161/2006* of the Romanian Ministry of Environment and Forests

VII. CONCLUSIONS

Abundances of As, Cd, Cu, Mo, Ni, Pb, U, V and Zn found in the sediments were greater than average **upper continental crust**, indicating that metal enrichment has occurred in the lake sediments.

According to NYSDEC guidelines, sediments of the studied lakes are slightly contaminated with Zn (L. Hălceni) and moderately contaminated with respect to Cr (all lakes), Cu (all lakes), Pb (L. Cucuteni, L. Pd-Iloaiei, L. Pârcovaci, L. Cătămărăşti) while enrichment with Ni (L. Hălceni, L. and L. Pârcovaci Cătămărăşti) is significant. Concentrations of Cr, Cu and Pb in studied lake sediments exceed the limit of lowest effect level (LEL) which may have a moderate impact on aquatic life, while nickel exceeds the severe effect level (SEL) which can result in a severe impact on the lives of aquatic ecosystems.

Water quality of the investigated lakes in terms of quality indicators:

- Water collected from the Hălceni, Tansa and Pârcovaci Lakes does not meet the criteria for drinking water. It appears that the water evacuated from these lakes as servitude debits correspond qualitatively to the classification **“in a good state” (B) but they are not suitable for drinking.**

- For **Cucuteni and Podu-Iloaiei Lakes** it appears that the water evacuated from these lakes as servitude debits correspond qualitatively to the classification in a “**moderate”** (M) ecological potential, but not for fishing.
- **Cătămărăşti Lake** corresponds qualitatively to the classification **“in a good state”** (B).

Water quality criteria recommended by EPA is significantly exceeded for **copper** and **lead** for almost all studied lakes (except Cătămărăşti Lake). Also cadmium exceeds the EPA reference value for Cătămărăşti Lake.

Concentrations significantly exceeded for the two media of investigation, water and sediment, suggests that a potential source of **nickel** in sediments may be occurring naturally, mainly because they were not found in water samples taken from the the same points (only on a small scale). The concentrations of **copper** occurred predominantly at the water-sediment interface, being also found in water samples taken from the same point, suggesting an anthropogenic intake of copper in lakes (sulfate copper is often used to control the formation of green shore and similar green algae deposits as well as contact fungicide in gardens and orchards).

Selected references

Bai, J., Cui, B., Chen, B., Zhang, K., Deng, W., Gao, H., Xiao, R., 2011. *Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland, China.* Ecological Modelling, Elsevier, 222, 301–306 p.

Bibi, M.H., Ahmed, F., Ishiga, H., 2007. *Assessment of metal concentrations in lake sediments of southwest Japan based on sediment quality guidelines*. Environ Geol., Springer-Verlag, 52, 625–639 p.

Chakrapani, G.J., 2002. *Water and sediment geochemistry of major Kumaun Himalayan Lakes, India.* Environ. Geol., 43, 99–107 p.

Dughilă, **A**., Crețescu, I., Iancu, O. G., 2010. *Water quality monitoring in key reservoirs from Jijia Basin*. The Danube River – Environment and Education, 9, VI, 23-34 p.

Dughilă, **A**., Iancu, O.G., Râşcanu, I.D., 2012 a. *Geochemical evaluation of quality indicators for the water of the Tansa Lake from the Jijia Catchment, Romania.* Carpathian Journal of Earth and Environmental Sciences, Ed. Univ. de Nord Baia Mare, 7, 3, 79 - 88 p.

Dughilă, **A**., Iancu, O.G., Romanescu G., 2012 b. *Trace element distribution in the water and sediments of certain storage lakes from the Jijia catchment, (Romania).* Geophysical Research Abstracts (GRA), 9th EGU General Assembly, Ed. Copernicus GmbH (Copernicus Publications), 496-497 p.

Fetter, C.W., 1994. *Applied Hydrogeology. Third Edition*. Macmillan College Publishing Company, Inc., USA, 691 p.

Gâştescu, P., 1971. *Lakes of Romania*. Romanian Academy Publishing House, Bucureşti, 372 p. (In Romanian).

Iancu, O.G., Buzgar, N., 2008. *The geochemical atlas of heavy metals in the soils of the municipality of Iaşi and its surrounding areas*. Univ. "Al. I. Cuza" Publishing House, Iaşi, 33 p.

Ionesi, L., Ionesi, B., Lungu, A., Roşca, V. & Ionesi, V., 2005. *Upper and Middle Sarmatian from the Moldavian Platform.* Romanian Academy Publishing House, 558 p. (In Romanian).

Nasir Din, S. M., 1999. *A geochemical survey and water quality modelling study of the Lake St. Claire water system.* Master of science thesis, University of Windsor, Ontario, Canada, 124 p.

Stoeppler, M.,1992. *Hazardous metals in the environment*. Vol. 12, Elsevier, Amsterdam, 541 p.