Volume 7, Issue 3, 2017, 2048 - 2052 ISSN 2069-5837

Biointerface Research in Applied Chemistry

www.BiointerfaceResearch.com

Original Research Article **Open Access Journal**

Received: 20.03.2017 / Revised: 25.04.2017 / Accepted: 05.05.2017 / Published on-line: 15.05.2017

Statistical correlations between physical and chemical indicators in order to assess the water quality of artificial lakes in south Romania, Bucharest-Ilfov area

Ana-Maria Anghel [1,*], Elena Diacu [2], Mihaela Ilie [1], Cristina Cimpoeru [1], Florica Marinescu[1], Ecaterina Marcu [1], Carmen Tociu [1]

[1]National Institute for Research and Development in Environmental Protection Bucharest, 294 Splaiul Independenței, 6th District, 060031, Bucharest, Romania

[2]University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, 313 Splaiul Independenei, 060042, Bucharest, Romania

*corresponding author e-mail address: ***ana6209@yahoo.com***

ABSTRACT

Small artificial lakes are discussed in this paper in terms of seven quality indicators: pH, total phosphorus (Ptot), biochemical oxygen demand (CBO_5), ammonia nitrogen ($N\text{-}NH_4^+$), nitrate nitrogen ($N\text{-}NO_3^-$), nitrite nitrogen ($N\text{-}NO_2^-$) and sulfates (SO_4^{2+}). In the 2013-2015 period, randomly were taken eleven samples from four small artificial lakes located in the Bucharest-Ilfov area. From the computed basic statistic on 77 values were obtained both perfect positive correlation and perfect negative correlation for the Pearson's correlation coefficient (*r*). Strong positive correlation was found between the pair pH - SO_4^{2+} and between SO_4^{2+} - $N\text{-}NO_2^-$ a low positive correlation. From the cluster analysis of six indicators, five clusters were achieved. The high level of similarity was obtained between CBO_5 and SO_4^{2+} with a percent of 87.7%. For the analyzed water samples, the obtained value of 3.05 indicates a low degree of contamination for the monitored small artificial lakes. The Ptot values ranged from 0.02 mg/L to 0.23 mg/L and led to the establishment of the eutrophication status of the lakes water, from eutrophic status to hypereutrophic status, according to Romanian Order no. 161 of 2006. According to the same legislative act, the water of the monitored lakes falls within second class of water quality.

Keywords: *physical indicators, chemical indicators, water quality, artificial lakes.*

1. INTRODUCTION

Water is an indispensable resource for life support on earth [1]. The lakes are water bodies globally important and need to be assessed in accordance with the requirements of Water Framework Directive 60/2000/CE [2]. It is well known that eutrophication is one of the great issues causing degradation of the worldwide freshwater ecosystems [3-5]. It is an issue (eutrophication) because it causes the increase of the cyanobacteria and aquatic macrophytes, decomposition of aquatic flora and fauna, and even their death. One of the consequences of this issues is the oxygen consumption in excess near the lowermost water body mass. So, in the last years many research paper approaches with this topic [6-9]. The water bodies quality may change from oligotrophic to mesotrophic, eutrophic and finally to hypertrophic by the excessive nutrient enrichment of waters, mostly when the waters are located near the large population centers [1]. The major sources that may change the quality of the water bodies are: sewage, household detergents, industrial discharges, runoff from agriculture, construction sites, and urban areas [1,10, 18-22]. Currently, at EU level, the nitrogen pressure on the environment has reached up to 18 millions tons from agricultural sources [23]. The most important role in minimizing or preventing eutrophication plays the public by regulating the resource utilization of nutrients, reducing the fertilizer use, proper use of soil management practices, phytoremediation etc [1]. In a water-body like the lake, the development of eutrophication status is maintained by several physical factors (physical nature of lake, thermal stratification which implying the temperature and light) [23].

2. EXPERIMENTAL SECTION

2.1. Study site. The southern region of Romania includes numerous natural and artificial lakes [11,12]. In this paper, the studied lakes are part of the water bodies of Bucharest-Ilfov metropolitan area, Romania (Figure 1). Many streams (deep wells and rivers) fed those lakes formed in an artificially excavated area. These small artificial lakes are a great place for fish habitats in order to fish and the monitoring of their waters quality is necessary.

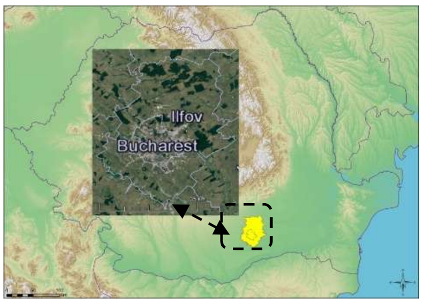

Figure 1. Bucharest-Ilfov metropolitan area, Romania.

2.2. Materials and methods. The sampling stage was performed according to SR EN ISO 5667.1-2007 [13] and SR EN ISO 5667.3-2013 [13], during the period 2013-2015. The water samples were collected randomly at depth between 0.50 ÷ 1.00 m from four small artificial lakes, here numbered from L1 to L4. These samples were stored during transportation in labelled metalfree 2L polypropylene bottles prior to be prepared and analyzed. Before sampling, the bottles with double-distilled water were cleaned and rinsed minimum two times with lake water at the sampling point.

The preparation and analyze stages of the water samples were performed according to the standardized methods specified in the Table 1. The analytical methods applied for the indicators determination use the ultraviolet (UV) - visible (VIS) absorption technique and the operating instrument was ATI Unicam UV2 spectrometer with wavelength range 190:900nm. The pH was measured by direct reading in the water sample using a multi-parameter (CONSORT C830) [13], able to measure also the temperature and conductivity.

Table 1. Standardized methods used.

Quality Indicator	**Analysis Method**	
	Index	***Title***
pH	SR ISO 10523:2012	Water quality - Determination of pH
Biochemical oxygen demand after 5 days (CBO_5)	SR EN 1899-2:2002	Water quality - Determination of biochemical oxygen demand after n days (BODn) - Part 2: Method for undiluted samples
Ammonia nitrogen (NH_4^+)	SR ISO 7150-1:2001	Water quality. Determination of ammonium. Part 1: Manual spectrometric method
Nitrate (NO_3^-)	SR ISO 7890-3:2000	Water quality. Determination of nitrate. Part 3: Spectrometric method using sulfosalicylic acid
Nitrite (NO_2^-)	SR EN 26777/C91:2006	Water quality - Determination of nitrite - Molecular absorption spectrometric method
Sulphates (SO_4^{2-})	STAS 3069:1987	Drinking water. Sulphates content determination
Total phosphorus (P_{tot})	SR ISO 6878/2005	Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method

The assessment of water quality of the four small artificial lakes was based on information provided in the Order No. 161/2006 [14]. Under this Order can be determined the ecological status of a water bodies by assessing chemical and physicochemical elements. Table 2 show the levels of the water quality classes and Table 3 show the standards for the lakes eutrophication indicator - total phosphorus.

Table 2. Standard level of indicators corresponding to water quality class of Order No. 161/2006.

Indicator	Quality Class				
	I	*II*	*III*	*IV*	*V*
pH	6.5-8.5				
CBO_5 (mgO_2/L)	3	5	7	20	>20
$N\text{-}NH_4^+$ (mgN/L)	0.4	0.8	1.2	3.2	>3.2
$N\text{-}NO_3^-$ (mgN/L)	1.0	3.0	5.6	11.2	>11.2
$N\text{-}NO_2^-$ (mgN/L)	0.01	0.03	0.06	0.3	>0.3
P_{tot} (mgP/L)	0.15	0.4	0.75	1.2	>1.2
SO_4^{2+} (mg/L)	60	120	250	300	>300

Table 3. Biological quality indicator for lakes according to the Order No. 161/2006.

Indicator	**Eutrophication Class**				
	Ultraoligotrophic (Utrof)	***Oligotrophic (Otrof)***	***Mezotrophic (Mtrof)***	***Eutrophic (Etrof)***	***Hypereutrophic (Htrof)***
Ptot (mgP/L)	0.005	0.01	0.03	0.1	>0.1

2.3. Determination of pollution indices. The degree of contamination - pollution index - (C_{dI}) suggested by Hakanson in 1980 [15] was used in this study to assess the overall lakes water from Bucharest-Ilfov area. First, was calculated the contamination factor (C_f) for each indicator, as can be seen from the Equation (1) and Equation (2) [15-17]. Where the C_{sample} represents the obtained concentration of the indicator in the sample and $C_{background}$ represents the background concentration (in this study: I water quality class). The C_{dI} represents the sum of all the contamination factors determined from the sample.

$$C_f = \frac{C_{sample}}{C_{background}} \quad (1)$$

$$C_{dI} = \sum_{i=1}^{n} C_f^i \quad (2)$$

In the Table 4, are defined the categories for the C_f and C_{dI} in order to interpret the results.

Table 4. Interpretation of the Cf and CdI by range [15,16].

Index acronym	**Range**	**Interpretation**
C_f	$C_f < 1$	low contamination - LC
	$1 \leq C_f < 3$	moderate contamination - MC
	$3 \leq C_f < 6$	considerable contamination - CC
	$C_f \geq 6$	high contamination - HC
C_{dI}	$C_{dI} < 8$	low contamination - LC
	$8 \leq C_{dI} < 16$	moderate contamination - MC
	$16 \leq C_{dI} < 32$	considerable contamination - CC
	$C_{dI} \geq 32$	high contamination - HC

3. RESULTS SECTION

3.1. Water quality. By determining the indicators in the water samples, 77 values were obtained. The obtained concentrations for indicators were measured in mg/L, except pH. Analysis of data revealed that Ptot in year 2014 at L1, $N\text{-}NO_3^-$ in year 2014 at L1/L3, and SO_4^{2+} in year 2015 at L2/L3/L4 exceeds the I water quality class of Order No. 161/2006. The biological quality indicator, Ptot, fall the lakes water in different classes during the monitoring period. Thereby, L1 falls into Htrof class, L2, L3 and L4 fall into Etrof class of trophic classifications.

3.2. Basic statistics. The sum, the mean, the median, the standard deviation, the coefficient of variation and the concentration's range for the analyzed indicators in water are summarized in Table 5. The standard deviation (StDev) measures the homogeneous of the data set and is based on the outliers (minimum and maximum values in the data set). Thus, at most of the indicators (pH, Ptot, CBO_5, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$) the StDev is small, which means that the concentration values are close to the mean of the data set. For SO_4^{2+}, because the standard error is large (StDev =14.040 mg/L), the data set is not homogeneous. Statistically, the obtained concentration values did not vary much between them during the monitoring period, except SO_4^{2+}. Increasing order of homogeneity of the data set is: SO_4^{2+}>CBO_5>$N\text{-}NO_3^-$>pH>Ptot>$N\text{-}NH_4^+$>$N\text{-}NO_2^-$.

Table 5. Summary statistics for concentration levels found in water lakes from Bucharest-Ilfov metropolitan area.

Variable	Total Count	Mean	StDev	CoefVar	Sum	Min→Max	Median
pH	11	7.296	0.294	4.030	80.250	6.880→7.740	7.290
Ptot	11	0.049	0.061	123.870	0.543	0.017→0.230	0.028
CBO_5	11	1.375	0.848	61.680	15.120	0.000→2.520	1.020
$N\text{-}NH_4^+$	11	0.014	0.007	46.110	0.158	0.010→0.030	0.010
$N\text{-}NO_3^-$	11	0.228	0.469	205.970	2.506	0.010→1.240	0.020
$N\text{-}NO_2^-$	11	0.004	0.001	23.790	0.041	0.003→0.006	0.003
SO_4^{2+}	11	46.480	14.040	30.210	511.330	31.390→70.260	43.270

3.3. Contour plot of indicators. In order to explore the potential relationship that occur between pH (X axis) - CBO_5 (Y axis) and nutrients contour plots were drawn. Thus, in Figure 2 are shown the 3D surface graphs, where the response variable (Z-axis: $N\text{-}NO_2^-$, $N\text{-}NO_3^-$, $N\text{-}NH_4^+$ and Ptot) is based on the predictor variables (X,Y - axes) and can be viewed the contours of the predicted response variable.

The $N\text{-}NO_2^-$ vs CBO_5, pH 3D graph shows that at 7.05-7.08 pH and 0.50-0.57 mgO_2/L CBO_5 the $N\text{-}NO_2^-$ has the maximum values. The $N\text{-}NO_3^-$ vs CBO_5, pH 3D graph shows that at 6.94-7.00 pH and 0.72-0.89 mgO_2/L CBO_5 the $N\text{-}NO_3^-$ has the maximum values. The $N\text{-}NH_4^+$ vs CBO_5, pH 3D graph shows that at 7.01-7.10 pH and 0.31-0.63 mgO_2/L CBO_5 the $N\text{-}NH_4^+$ has the maximum values. The Ptot - vs CBO_5, pH 3D graph shows that at 6.89-7.02 pH and 0.65-0.99 mgO_2/L CBO_5 the Ptot has the maximum values. The darker regions on the graphs indicate the maximum values.

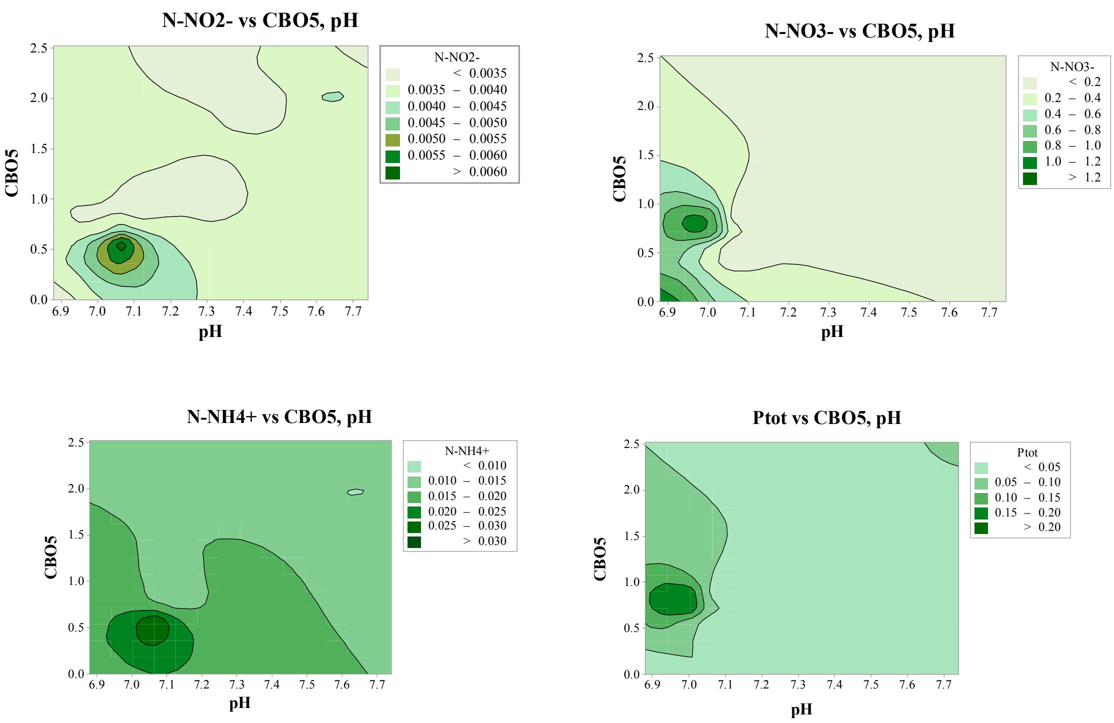

Figure 2. Contour plot of nutrients vs CBO_5 and Ph.

3.4. Correlation coefficient test. Correlation coefficients (*p*-value and *r*) between the water-quality indicators are given in Table 6. These coefficients are based on the concentration levels found in lakes water. The *r* represents the Pearson's correlation coefficient and *p* represents the value that indicates a significant correlation between the involved indicators in matrix. The correlation coefficient was calculated using a formula in which were involved the standard deviation and the covariance of two parameters once involved, indicating how the two parameters move together.

According to the matrix, both positive and negative correlations were obtained. Thus, the stronger correlation was obtained for the pair pH-SO_4^{2+} with $r = 0.931$ and the lower correlation for the pair SO_4^{2+} - $N\text{-}NO_2^-$ with $r = 0.070$.

The *p*-values range from a very high significance correlation (where the confidence level is 99%) namely p = (0.001-0.000) to an insignificant correlation namely $p > 0.05$, as presented in this study. From the data observation in the Table 6 was revealed that almost 70% of the p-values are over the 0.05 level, meaning there is no significant correlation between those pairs.

Table 6. Pearson correlation matrix for the analyzed indicators.

Indicator	Coef.	pH	Ptot	CBO_5	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	$N\text{-}NO_2^-$
Ptot	*r*	-0.202					
	p	0.550					
CBO_5	*r*	0.867	-0.110				
	p	0.001	0.748				
$N\text{-}NH_4^+$	*r*	-0.564	0.179	-0.657			
	p	0.071	0.599	0.028			
$N\text{-}NO_3^-$	*r*	-0.612	0.687	-0.557	0.320		
	p	0.045	0.019	0.075	0.337		
$N\text{-}NO_2^-$	*r*	-0.075	-0,178	-0.218	0.677	-0.212	
	p	0.827	0.601	0.519	0.022	0.531	
SO_4^{2+}	*r*	0.931	-0.116	0.755	-0.405	-0.410	0.070
	p	0.000	0.734	0.007	0.217	0.210	0.837

3.5. Hierarchical clustering method. To determine the differences and similarities between indicators a multivariate correlation was used (Figure 3). The vertical axis of the following dendrogram represents the distance between the formed clusters. The horizontal axis represents the variables (here the determined indicators) and clusters. The pH was not included in cluster analysis, only the indicators that have the same measuring unit. Thereby, 5 clusters were formed (in decreasing order of similarity level): CBO_5 - SO_4^{2+} (87.7%) > Ptot - $N\text{-}NO_3^-$ (84.4%) > $N\text{-}NO_2^-$ - $N\text{-}NH_4^+$ (83.9%) > { Ptot - $N\text{-}NO_3^-$} - { $N\text{-}NO_2^-$ - $N\text{-}NH_4^+$} (39.39%) > [{ Ptot - $N\text{-}NO_3^-$} - { $N\text{-}NO_2^-$ - $N\text{-}NH_4^+$}] – [CBO_5 - SO_4^{2+}] (17.15%).

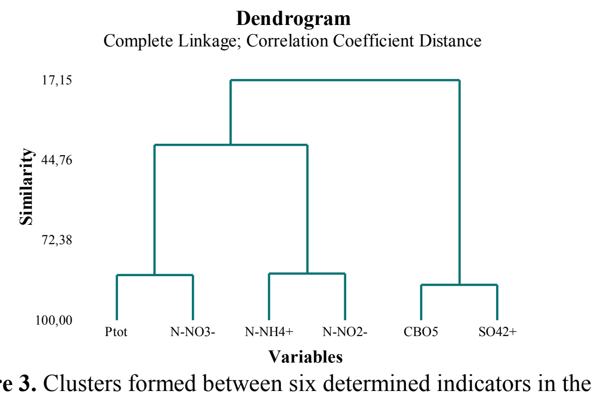

Figure 3. Clusters formed between six determined indicators in the lake water samples.

Also, by clustering the concentration values of the nutrients (here: Ptot, $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$), for the four lakes, two clusters were obtained: L1-L3 (99% similarity) and L2-L4 (95.1% similarity) and can be seen in Figure 4. Probably, this similarities between lakes are due to the spatial location of them, the sampling points location, the pollution sources around the lakes and the water quality of the streams that feed this lakes.

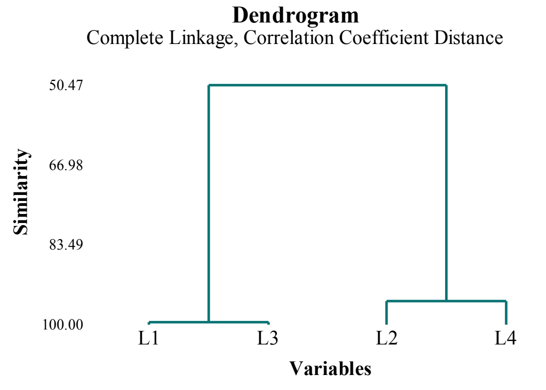

Figure 4. Similarities between the studied lakes (L1, L2, L3, L4) based on nutrient content.

3.6. Contamination level by C_{dI}. The contamination factor and the degree of contamination computed for determined indicators together with the interpretations are presented in Table 7. The obtained values for C_f and C_{dI} indicated a low contamination level of the determined indicators in the lacks water.

4. CONCLUSIONS

By comparing experimental data with the Order No. 161/2006 standards indicates that some indicators (Ptot, SO42+, N-NO3-) exceeded the I quality class standards in less than 10% of values. The results of multivariate analysis indicate the classification of the six indicators in three clusters with over 80% similarity levels. The correlation coefficient test concludes that the 67% of p-values are significantly different from 5% level (p>0.05), in this case there is not a significant linear relationship between determined concentrations of the indicators. The contamination level in the lakes water from the Bucharest-Ilfov metropolitan area remains low during the entire monitoring period, 2013-2015 respectively. Thereby, the lakes water studied is proper as habitat for fish.

The relationships established in this paper can contribute to a better understanding of the selected indicators in the evaluation of water quality of small artificial lakes. It's not enough to assess these lakes only by measuring the nutrient concentration levels, so, further investigations in this area should focus on benthic macroinvertebrates as bioindicators of environmental pollution and continue the water monitoring for maintain proper conditions to fish.

5. REFERENCES

[1] Khan F.A., Naushin F., Rehman F., Masoodi A., Irfan M., Hashmi F., Ansari A.A., Eutrophication: global scenario and local threat to dynamics of aquatic ecosystems, *Eutrophication: causes, consequences and control*, vol.2, Springer Netherlands, **2014**.

[2] Radu V. M., Diacu E., Ionescu P., Deák Gy., Spatio-Temporal Characterization of Nutrient Pollution in Lower Danube Area, *Revista de chimie*, 66, 5, 601-606, **2015**.

[3] Ilie M., Marinescu F., Ghiță G., Anghel A.-M., Deák Gy., Raischi M., Assessment of Nutrients-Chlorophyll-a Relationship in the Lower Danube River, *International Journal of Advances in Chemical Engineering and Biological Sciences*, 4, 1, 15-20, **2017.**

[4] Radu V.M., Diacu E., Ionescu P., Characterization of the eutrophication potential for the lower part of the Danube River, *UPB Sci Bull, Series B*, 76, 4, 137-146, **2014**.

[5] Ilie M., Ghiță G., Deák Gy., Anghel A.-M., Raischi M., Spatial distribution of water quality and eutrophication levels of Divici-Pojejena wetlands, *SGEM2016 Conference Proceedings*, Book 3, 3, 267-274, **2016**.

[6] Bacu A., Babani F., Evaluation of phytoplankton biomass and composition based on Chlorophyll pigments at waters of Shkodra lake, Albania, *Journal of Environmental Protection and Ecology*, 17, 1, 222-227, **2016**.

[7] Tudor I., Ibram O., Teodorof L., Burada A., Tudor M., Present status of zooplankton and benthic invertebrate community structure in Danube Delta shallow lakes, *Journal of Environmental Protection and Ecology*, 17, 1, 228-236, **2016**.

[8] Shtereva G., Velikova V., Doncheva V., Human Impact on Marine Water Nutrients Enrichment, *Journal of Environmental Protection and Ecology*, 16, 1, 40-48, **2015**.

[9] Rakaj M., Biological conditions of the lake Shkodra and the Buna river, *Journal of Environmental Protection and Ecology*, 13, 3, 1397-1404, **2012**.

[10] Tociu C., Marcu E., Ciobotaru I.E., Maria C., Risk assessment of population exposure to nitrates/nitrites in groundwater, A case study approach, *ECOTERRA - Journal of Environmental Research and Protection*, 13, 3, 39-45, **2016**.

[11] Marinescu F., Lazar, V., Origins, transfer and accumulation of antibiotic resistance genes in the aquatic environment, *Biointerface Research in Applied Chemistry*, 3, 3, 588-598, **2013**.

[12] Pănuș E., Bleotu C., Roșoiu N., Lazăr V., Mitache M., Phenotypic and genetic investigation of virulence and antibioresistance hallmarks in Escherichia coli strains isolated from Black Sea water on Romanian coast, *Biointerface Research in Applied Chemistry*, 2, 2, 306-312, **2012**.

[13] Iancu A.V., Chifiriuc M.C., Tutunaru D., Arbune M., Gurau G., Coman G., Lazar V., Etiological investigation and antibiotic resistance profiles encountered in systemic bacterial infections, *Biointerface Research in Applied Chemistry*, 3, 4, 599-605, **2013**.

[14] Gheorghe I., Chifiriuc M. C., Anastasiu P., Marutescu L., Oprea E., Lazar V., Study of the antagonist interactions between invasive plants from Danube Delta and the associated microbiota. *Biointerface Research in Applied Chemistry*, 3, 1, 520-522, **2013**.

[15] Marinescu F., Tociu C., Ilie M., Anghel A.-M., The influence of toxic pollutants on the absolute value and on the kinetics of the degradation of organic substances quantified as BOD, *Bionterface Research in Applied Chemistry*, 7, 1, 1955-1958, **2017**.

[16] World Health Organization, Eutrophication and health, Luxembourg: Office for Official Publications of the European Communities. Geneva: *WHO*, **2002**.

[17] Popescu D.-C., The disparities analysis of the Bucharest-Ilfov region, *Proceedings CAFEE2013*, 306, **2013**.

[18] Ionescu P., Deák Gy., Diacu E., Radu V.-M., Assessment of heavy metal levels in water, sediment and fish from Plumbuita Lake, Romania, *Revista de chimie*, 67, 11, 2148-2150, **2016**.

[19] Reșetar-Deac A.-M., Diacu E., Influence of climate change on aquatic ecosystem contaminated with toxic substances originating from historical mining activities, *UPB Sci Bull, Series B*, 77, 3, 59-72, **2015**.

[20] ***Order of the Ministry of Environmental and Water No 161/2006 for the Approval of the Norm Concerning the Reference Objectives for the Surface Water Quality Classification (including Quality Standards for Sediments). Official Monitor of Romania, Part 1, No 511 bis.

[21] Singh P.K., Verma P., Tiwari A.K., Sharma S., Purty P., Review of various contamination index approaches to evaluate groundwater quality with geographic information system (GIS), *International Journal of ChemTech Research*, 7, 4, 1920-1929, **2014**.

[22] Anghel A.-M., Ilie M., Ghiță G., Marinescu F., Deák Gy., Assessing the Aquatic Environment Quality Contaminated with Heavy Metals as a Result of Polymetallic Mining in the North-West Region of Romania Using Pollution Indices, *International Journal of Environmental Science and Development*, 8, 2, 111-115, **2017**.

[23] Ilie M., Marinescu F., Szep R., Ghiță G., Deák Gy., Anghel A.-M., Petrescu A., Urițescu B., Ecological risk assessment of heavy metals in surface sediments from the Danube River, *Carpathian Journal of Earth and Environmental Sciences*, 12, 2, 437-445, **2017**.

6. ACKNOWLEDGEMENTS

This study was supported by the *National Institute for Research and Development in Environmental Protection Bucharest - INCDPM* and the set of experimental values is part of the Laboratory Department database.