U.P.B. Sci. Bull., Series B, Vol. 79, Iss. 3, 2017 ISSN 1454-2331

APPLICATION OF MULTIVARIATE STATISTICAL TECHNIQUES TO ASSESS WATER QUALITY OF THE LOWER DANUBE

Violeta-Monica RADU[1], Elena DIACU[2], Petra IONESCU[3], Alexandru Anton IVANOV[4]

The water quality of Danube River is constantly monitored by developing water management, the aquatic ecosystem being affected permanently from the differentially distributed pollutants.

The objective of this study was to assess the water quality of the Danube River on the Calarasi-Braila section, where works to improve navigation conditions took place, for a period of two years (September 2013 - August 2015) applying multivariate statistical techniques. Samples were collected monthly from 10 monitoring locations, and total chromium (Cr), zinc (Zn), copper (Cu), cobalt (Co), lead (Pb), cadmium (Cd), iron (Fe), manganese (Mn), nickel (Ni), temperature (T), pH and average water flow (Q) were determined.

Results obtained by applying Principal Component Analysis (PCA) and cluster analysis (CA) showed the relationship between the chemical and physical parameters, indicating the differences and similarities between sample locations and sampling period, also highlighting the human impact on water quality parameters.

Keywords: water quality, PCA, CA, Danube River

1. Introduction

Globally, water quality is the most stringent environmental issue, water being an important part of all living organisms. Human activities cause pollution, increased toxicity, eutrophication, all resulting in decreased water quality [1-3]. Also, unsustainable use of water, along with population growth has led, in some regions to the emergence of a social and environmental collapse, with serious repercussions on the health of the environment [4, 5].

[1] PhD. Chem., National Institute for Research and Development in Environmental Protection - INCDPM, Romania, e-mail: radumonica33@yahoo.com

[2] Prof., Dept. of Analytical Chemistry and Environmental Engineering, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: elena_diacu@yahoo.co.uk

[3] PhD. Chem., National Institute for Research and Development in Environmental Protection - INCDPM, Romania, e-mail: petraionescu2012@yahoo.ro

[4] PhD student, Eng., National Institute for R&D in Environmental Protection - INCDPM, Romania; Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: aa_ivanov.incdpm@yahoo.com

Of particular interest for water quality and its intended use is the contamination of aquatic ecosystems with heavy metals, which also pose a major threat on the environment [6]. Some metals are essential for the proper functioning of vital processes [7] and become dangerous only at high concentrations, other metals are extremely toxic even at very low concentrations [8].

At European level, the Water Framework Directive 2000/60/EC aims at maintaining and improving the aquatic environment by establishing a common framework for the protection of surface waters [9].

Water is essential for agriculture, industry, transport and domestic use, so it is our obligation to prevent and control the pollution of the aquatic environment and to effectively process and manage the information on water quality [10, 11].

Rivers as dynamic ecosystems require a complex monitoring scheme, the natural hydrological cycle being a very important part of a healthy environment on earth [12, 13]. Because of that, numerous water quality monitoring programs were implemented leading to the accumulation of large informational volumes, from which information such as the distinction between natural and anthropic influences is difficult to be achieved.

The multivariate statistical techniques addressed the question of the interpretation of high volumes of data, generating useful and reliable information on the state of water quality. Water quality analysis is an essential tool for the management of water bodies as resources. It also creates a feed-back for the monitoring activity, allowing the optimisation of spatial and temporal density parameters and the need for follow-up or secondary quality indicators.

For rivers, after the monitoring programs informational volumes are processed with statistical techniques, it is possible to estimate the capacity to tolerate anthropogenic pressures [14, 15].

The aim of this study was to assess the state of Danube's water quality, Calarasi-Braila section (km 375 - km 175), applying multivariate statistical techniques.

2. Materials and methods

Within the monitoring program water samples were collected monthly from 10 locations (Table 1, Fig. 1), for a period of 24 months (September 2013 - August 2015) the parameters: total chromium, zinc, copper, cobalt, lead, cadmium, iron, manganese, nickel, temperature, pH and average water flow being investigated.

Table 1

Water sampling locations [16]

Watercourse	Location	Length (km)	Geographical coordinates	
			longitude	latitude
Bala Area	L1	347	27°34'9.549"	44°11'24.35"
	L2	345		
	L3	344		
	L4	343		
Epurasu Island	L5	340	27°37'2.349"	44°11'59.10"
	L6	341		
	L7	334		
Lupu Island	L8	197	27°54'27.93"	45°4'0.316"
	L9	196		
	L10	195		

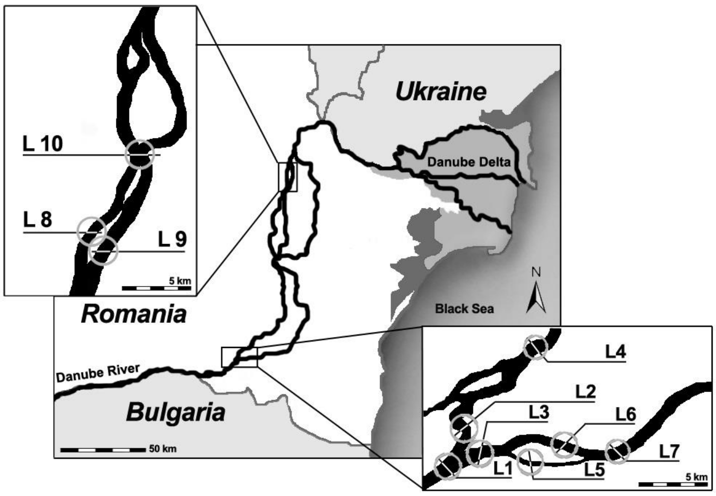

Fig. 1. Sampling locations (L1 to L10) on the Lower Danube km 375-175 section [4]

In this section of Danube (L1-L10), works to improve the conditions of navigation took place, trying to fulfil the Danube Commission recommendation to maintain minimum depths during dry periods, to ensure normal conditions of navigation [17].

During the sampling campaigns, each water sample was taken directly from the river into a polyethylene container of 5 litres, being transported directly to the laboratory for analysis.

Water samples were monthly collected from the left bank, right bank at 0.5 m depth and middle of the river from 3 different depths (0.5 m, 1.5 m and 3 m). After their transport and conservation, the samples were processed and the heavy metals (Cr, Zn, Cu, Co, Pb, Cd, Fe, Mn, Ni) were determined using Atomic

Absorption Spectrometry (Solaar M5, Thermo). For the determination of the heavy metals total concentration, the water samples were acidified to prevent hydrolysis of the metals by adding nitric acid (65 %) to lower the pH under 2.

The quality of the results was ensured by blind-testing a reference material for water (TM - 28.3).

All reagents used in this study were of analytical grade and all glassware used has been previously washed with nitric acid 1.5 mol/L and rinsed in double distilled water and deionized water.

3. Results and discussions

Multivariate analysis of the surface water quality data set was performed with principal component analysis (PCA) and cluster analysis (CA) statistical techniques [18].

For the multivariate statistical calculations, the statistical software package JMP 10 for windows was used.

Principal Component Analysis (PCA) provides information on the most significant parameters which describe the entire data set, being used for reducing data dimensionality with minimal loss of original information [18, 19] and for detecting underlying patterns hidden under data noise.

Table 2 shows the correlations matrix for the evaluated parameters.

Table 2

Correlation matrix for water quality parameters

	Cr	**Zn**	**Cu**	**Co**	**Pb**	**Cd**	**Fe**	**Mn**	**Ni**	**T**	**pH**	**Q**
Cr	1.0000											
Zn	**0.8141**	1.0000										
Cu	**0.7856**	**0.7195**	1.0000									
Co	**0.9046**	**0.8077**	**0.8699**	1.0000								
Pb	**0.9392**	**0.8231**	**0.7795**	**0.9219**	1.0000							
Cd	0.4547	**0.5014**	**0.5779**	**0.6776**	**0.5697**	1.0000						
Fe	0.4545	0.4211	0.3986	0.3408	0.3363	0.3838	1.0000					
Mn	**0.8330**	**0.7284**	**0.7547**	**0.7854**	**0.7877**	**0.5569**	**0.6428**	1.0000				
Ni	**0.9112**	**0.7494**	**0.7677**	**0.8853**	**0.9302**	0.4641	0.3715	**0.7590**	1.0000			
T	0.1295	-0.1767	0.0642	0.1498	0.1484	0.0040	-0.0348	0.0637	0.1755	1.0000		
pH	-0.1981	-0.1715	-0.0493	-0.1068	-0.1222	0.0926	0.0127	-0.1171	-0.0700	-0.0619	1.0000	
Q	0.2015	***0.2737***	0.1761	0.1248	0.1241	0.0993	***0.3441***	***0.2700***	0.1011	-0.0629	-0.1712	1.0000

As it can be seen, the group of metals is strongly interrelated with Pearson factors predominantly greater than 0.5. The temperature and pH for the monitored section, in their evolution limits, appear to be uncorrelated with the evolution of heavy metal concentrations. The highest influence of water flow in the monitored section is exerted on the metals group of iron, zinc and manganese, with correlation factors between 0.34 and 0.27, mostly due to the increased presence of re-suspended sediment particles and other materials suspensions (containing metals) in the water column under high water flow rate.

Table 3 contains selected significant loading values for the first 4 principal components.

Table 3

Loading matrix

Parameters	PC1	PC2	PC3	PC4
Cr	0.94643			
Zn	0.86900			
Cu	0.87685			
Co	0.95269			
Pb	0.94334			
Cd	0.65396			
Fe	0.53684			
Mn	0.89586			
Ni	0.90964			
T				0,68554
pH			0.85081	
Q		0.71752		

Results revealed that the first component comprised Cr, Zn, Cu, Co, Pb, Cd, Fe, Mn and Ni. The second component was mainly associated with Q. The third component has only pH as major constituent and the fourth component has only T as major constituent.

These distributions of loads on the main components in the matrix of correlations confirm the observed phenomena, namely the independent evolution of the metals group with temperature, water flow and pH on the monitored section.

Fig. 2 shows the eigenvalues associated with the principal components and the percentage of variability covered by each PC.

Number	Eigenvalue	Percent	20 40 60 80	Cum Percent	ChiSquare	DF	Prob>ChiSq
1	6,6515	55,429		55,429	8827,34	61,730	<,0001*
2	1,3116	10,930		66,360	4885,18	62,093	<,0001*
3	1,1642	9,701		76,061	4315,24	52,375	<,0001*
4	0,9531	7,942		84,003	3625,17	42,852	<,0001*
5	0,5999	4,999		89,002	2849,31	34,272	<,0001*
6	0,5916	4,930		93,933	2345,55	26,301	<,0001*
7	0,2700	2,250		96,183	1370,87	19,652	<,0001*
8	0,1748	1,457		97,640	977,514	13,832	<,0001*
9	0,1491	1,242		98,882	728,037	8,787	<,0001*
10	0,0700	0,583		99,465	317,652	4,881	<,0001*
11	0,0479	0,399		99,864	177,996	1,912	<,0001*
12	0,0163	0,136		100,000	0,000	.	.

Fig. 2. Eigenvalues and percentage of data variability accounted by each PC

The first 3 PC accounted for about 75 % of the entire data set variability, underlying the major tendencies of the monitored ecosystem.

Fig. 3 is the score plot of the first two principal components and shows the data coagulation patterns.

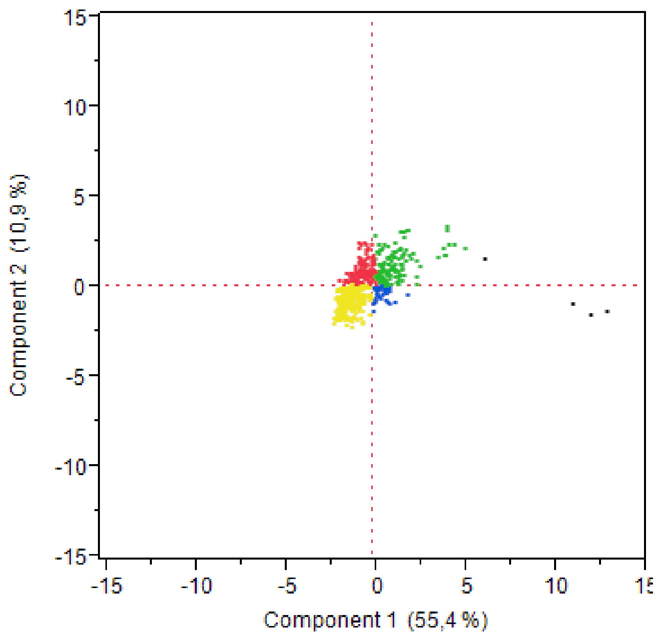

Fig. 3. Score plot of the first two principal components

After analysing the coagulated groups, we observed the following tendencies: samples from the score group yellow are sampled in a period of autumn, samples from the score group blue are sampled in a period of winter, samples from the score group green are sampled in a period of spring, samples from the score group red are sampled in a period of summer. Samples with the scores black do not belong to any of the identified groups and are anomalies that occur in a monitoring program. Depicting the seasonal influence on the overall water quality, the scores plots can serve as a comparison basis for the identification of accidental pollutions.

For a more detailed assessment of the relationship between metals and for identification of anthropogenic and natural sources, Cluster Analysis (CA) has been used (Fig. 4).

Cluster analysis is another type of multivariate analysis providing details of similarities between groups of parameters [19, 20].

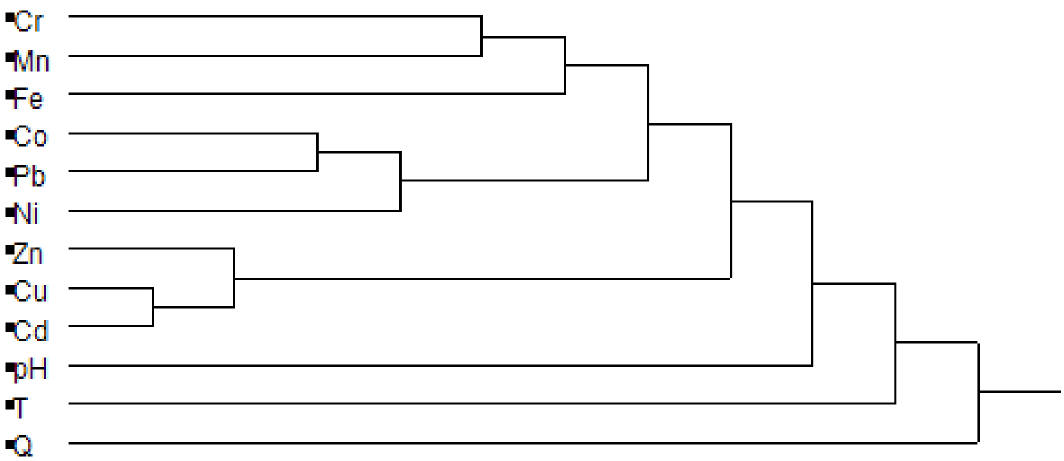

Fig. 4. Dendrogram of quality parameters

The first cluster is comprised of Cu and Cd with a link to Zn attesting to their probable common anthropic source. The next cluster of lower similarity is formed between Co and Pb with a link to Ni. Overall the clusters seemed to indicate the presence of both natural and anthropogenic heavy metal sources of origin.

4. Conclusions

In period from September 2013 to August 2015, the results show that the variation of indicators is due to the current environmental status of the Danube River as a result of environmental conditions and upstream anthropic influences, and not because of the works that took place during this period.

The method used for multi-parametric correlation of the evaluated indicators is accessible, easy to implement and provides a global picture of surface water quality.

The used techniques lead to insight on processes and interdependencies at the aquatic environment level in close correlation with other environmental spheres.

Based on the cluster analysis, both sources of pollution (anthropogenic and natural) may be involved, being revealed that the closest knit metal group is formed between Cu, Cd and Zn.

Also, applying multivariate statistical techniques provide logistical support for pollution detection in case of accidental contaminations.

Acknowledgments

The authors would like to thank the management and employees of the National Institute for Research & Development in Environmental Protection for their valuable assistance and suggestions and to the POS-T Project “Monitoring of Environmental Impact of the Works for Improvement of the Navigation Conditions on the Danube between Calarasi and Braila, km 375 - km 175”, (http://www.afdj.ro/en/content/romomed).

R E F E R E N C E S

[1]. *M.M. Panteli, D.M. Dolinaj, I.I. Lešešen, S.M. Savi, D.D. Miloševi*, “Water quality of the Pannonian Basin rivers Danube, Sava, and Tisa and its correlation with air temperature in Serbia”, Thermal Science, **vol. 19**, no. 2, 2015, pp. S477-S485.

[2]. *A. Policht-Latawiec, W. Kanownik*, “Hydrochemical conditions of the Łososina river water management in the area of Tymbark”, Journal of Ecological Engineering, **vol. 16**, no. 5, 2015, pp. 151–159.

[3]. *P. Ionescu, Gy. Deak, E. Diacu, V.M. Radu,* “Assessment of Heavy Metals Levels in Water, Sediments and Fish from Plumbuita Lake, Romania”, Rev. Chim. (Bucharest), **vol. 67**, no. 11, 2016, pp. 2148-2150.

[4]. *P. Ionescu, V. M. Radu, R. Szep, M. Raischi, M. Boboc,* “Characterization of metal flow dynamics along the lower section of Danube River using correlation algorithms”, Water resources, forest, marine and ocean ecosystems, SGEM, **vol. 1**, 2015, pp. 129-135.

[5]. *D.L.Childers, S.T.A. Pickett, J.M. Grove, L. Ogden, A. Whitmer*, "Advancing urban sustainability theory and action: Challenges and opportunities", Landscape and Urban Planning, Netherlands, **vol. 125**, 2014, pp. 320-328.

[6]. *P. Ionescu, V.M. Radu, Gy. Deak*, "Spatial and seasonal variations of heavy metals in water and sediment samples collected from the Lower Danube River", Scientific Annals of the Danube Delta, **vol. 21**, 2015, pp. 43-50.

[7]. *A.M. Wasim, M. Paramasivam, M. Ganguly, S. Purkait, D. Sengupta*, "Assessment and occurrence of various heavy metals in surface water of Ganga river around Kolkata: a study for toxicity and ecological impact", Environmental Monitoring and Assessment, Netherlands, **vol. 160**, no. 1-4, 2010, pp. 207-213.

[8]. *F.F. Xua, J.A. Imlay*, "Silver(I), Mercury(II), Cadmium(II), and Zinc(II) Target Exposed Enzymic Iron-Sulfur Clusters when They Toxify Escherichia coli", Applied and Environmental Microbiology, United States, **vol. 78**, no. 10, 2012, pp. 3614-3621.

[9]. Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy.

[10]. *D. Voza, M. Vukovic, L. Takic, D. Nikolic, I. Mladenovic-Ranisavljevic*, "Application of multivariate statistical techniques in the water quality assessment of Danube river, Serbia", Archives of Environmental Protection, **vol. 41**, no. 4, 2015, pp. 96–103.

[11]. *E. Durisch-Kaiser, A. Doberer, J. Reutimann, A. Pavel, S. Balan, S. Radan, B. Wehrli*, "Organic matter governs N and P balance in Danube Delta lakes", Aquat. Sci., **vol. 73**, 2011, pp. 21-33.

[12]. *M.K.N. Shamsuddin, S. Suratman, M.F. Ramli, W.N.A. Sulaiman, A. Sefie*, "Hydrochemical Assessment of Surfacewater and Groundwater Quality at Bank Infiltration Site", Materials Science and Engineering, **vol. 136**, 2016, pp. 1-13.

[13]. *D.V. Chapman, C. Bradley, G.M. Gettel, I.G. Hatvani, T. Hein, J. Kovács, I. Liska, D.M. Oliver, P. Tanos, B. Trásy, G. Várbíró*, "Developments in water quality monitoring and management in large river catchments using the Danube River as an example", Environmental Science and Policy, 2016, http://dx.doi.org/ 10.1016/j.envsci.2016.06.015 1462-9011/© 2016 Published by Elsevier Ltd.

[14]. *C. Iticescu, G. Murariu, L.P. Georgescu, A. Burada, C.M. Topa*, "Seasonal Variation of the Physico-chemical Parameters and Water Quality Index (WQI) of Danube Water in the Transborder Lower Danube Area", Rev.Chim.(Bucharest), **vol. 67**, no. 9, 2016, p. 1843-1849.

[15]. *M. Varol, B. Gökot, A. Bekleyen, B. Şen*, "Water quality assessment and apportionment of pollution sources of Tigris River (Turkey) using multivariate statistical techniques-a case study", River Research and Applications, **vol. 28**, no. 9, 2012, pp. 1428–1438.

[16]. *P. Ionescu, V.M. Radu, Gy. Deak, A.A. Ivanov, E. Diacu*, "Lower Danube Water Quality Assessment Using Heavy Metals Indexes", Rev. Chim. (Bucharest), **vol. 66**, no. 8, 2015, pp. 1088-1092.

[17]. *POS-T* Project Monitoring of Environmental Impact of the Works for Improvement of the Navigation Conditions on the Danube between Calarasi and Braila, km 375 - km 175 (http://www.afdj.ro/en/content/romomed).

[18]. *V.M. Radu, P. Ionescu, Gy. Deak, A.A. Ivanov, E. Diacu*, "Multivariate Statistical Analysis for Quality Assesment of Aquatic Ecosystem on the Lower Danube", Journal of Environmental Protection and Ecology, **vol. 15**, no. 2, 2014, pp. 412-424.

[19]. *H. Boyacioglu, H. Boyacioglu*, "Heavy Metal Fingerprinting in Surface Water Using Chemometrics", Kuwait J Sci Eng, **vol. 38**, no. 1A, 2011, pp. 125-139.

[20]. *F. Akbal, L. Gurel, T. Bahadir, I. Guler, G. Bakan, H. Buyukgungor:* "Water and Sediment Quality Assessment in the Mid-Black Sea Coast of Turkey Using Multivariate Statistical Techniques", Environ Earth Sci, **vol. 64**, no. 5, 2011, pp. 1387-1395.