



# Overall assessment of surface water quality in the Lower Danube River

Violeta-Monica Radu · Petra Ionescu · Gyorgy Deak · Elena Diacu · Alexandru Anton Ivanov · Stefan Zamfir · Maria-Iuliana Marcus

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**Abstract** Water is an important receptor of environmental problems generated by anthropogenic activities, the water quality being affected by their magnitude and impact as well as by climate change. Given the international and cross-border nature of the Danube River and being aware that the pollution risk assessment is one of the key elements of the ecology and health of the people in its region, this paper assessed the state of water quality in the Lower Danube River in accordance with Water Framework Directive (Directive 2000/60/EC). The intensive monitoring program applied by the National Institute for Research and Development in Environmental Protection (INCDPM) took place during the period 2011–2017, in which approximately 1500 samples were taken and processed from 10 monitoring sites and the quality indicators stipulated in M.O. 161/2006 were analysed according to the standards in force. In this monitoring area (km 375–km 175), hydrotechnical works have been done in order to improve navigation conditions. Therefore, on the basis of the data obtained from the monitoring campaigns, multivariate statistical methods of water quality

assessment were applied on the complex set of data, and at the same time, the multiparametric quality index (ICPM) was applied, an index of global comparative assessment of water quality over historical trends, developed by INCDPM. Following the evaluation of the results, the water quality in the Lower Danube River was characterized as moderately polluted and corresponds to Class III of surface water quality. The ecosystem approach indicates that the values of the monitored indicators did not correspond to the target values according to the Water Framework Directive.

**Keywords** Danube River · WFD · Water quality · ICPDR

## Introduction

One of the indispensable necessities of humanity is to find solutions to environmental problems, especially those related to water pollution, which require urgent action for a sustainable development of society (Hodisan et al. 2018; Ren et al. 2018). Among the key elements of sustainable development, one of the leading roles is the management and protection of water resources (Grizzetti et al. 2016a).

As a result of the increasing impact of anthropogenic activities on water resources in Europe, the European Union has decided that water protection should become a major priority of water management policies. The Water Framework Directive (Directive 2000/60/EC) (WFD) was created as a long-term policy of the European Union with the aim of ensuring good surface water

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V.-M. Radu · P. Ionescu (✉) · G. Deak (✉) ·  
A. A. Ivanov · S. Zamfir · M.-I. Marcus  
National Institute for Research and Development in  
Environmental Protection, 294 Spl. Independentei, 6th District,  
06003 Bucharest, Romania  
e-mail: petraionescu2012@yahoo.ro  
e-mail: dkrcontrol@yahoo.com

V.-M. Radu · P. Ionescu · E. Diacu  
Faculty of Applied Chemistry and Materials Science, University  
“Politehnica” of Bucharest, 1-7 Polizu Str., 011061 Bucharest,  
Romania

quality (Cretescu et al. 2016; Kotamäki et al. 2019; Sousa et al. 2018). In accordance with the requirements of the WFD, the protection and improvement of river basin waters are essential for the sustainable development of the region, population health and the natural environment in the long term, while also pointing out that monitoring is an essential tool for the development of specific management policies and assessing their performance both at regional and at national levels (ICPDR 2015a; Grizzetti et al. 2016b). Monitoring water quality is an important issue, especially since Romania is a member of the European Union (EU) and must comply with the specific legislation in the field (Directive 2000/60/EC). Water quality monitoring is a difficult process due to the continuous variation in concentration and nature of chemical substances present in the environment, on the one hand, due to anthropogenic emissions of pollutants resulting from industrial discharges and, on the other hand, due to climate change that can influence the bioavailability and toxicity of pollutants (Ami and Tadi 2018; Raateoja and Kauppila 2019; Stojkovic Zlatanovic et al. 2018).

The status of water quality is influenced by changes in river hydromorphology, caused both by natural phenomena and by anthropogenic activities, as well as by climate change (Danalache et al. 2017; Dunca 2018; Kubiak-Wójcicka and Bąk 2018).

“Water and its availability and quality will be the main pressures on, and issues for, societies and the environment under climate change” according to the International Commission for the Protection of the Danube River (ICPDR)’s report (ICPDR 2018).

The Danube River, with a length of 2857 km (of which 1076 km in Romania) and a multiannual average flow rate of 6460 m<sup>3</sup>/s at the entrance in the Danube Delta, is the second largest river in Europe (after the Volga) (ICPDR 2019; Paun et al. 2017). The Danube River Basin, with a total area of approximately 800,000 km<sup>2</sup>, is an emissary to the Black Sea and a collector of all discharges from upstream riparian countries where water is collected from the territories of 10 countries, being considered to be the most international river basin in the world (Chapman et al. 2016). More than 80 million people live in this basin, many of them depending on the Danube for potable water, energy production, agriculture and transport. Its ecological diversity, ranging from plant and animal species to critical habitats, is also highly valued (Malago et al. 2017).

Approximately one-third of the hydrographic area and one-third of the length of the Danube River are located on Romanian territory, a territory which according to the provisions of the WFD was included in the Danube River Basin District (EC 2000). The European Commission recognizes the Danube as the “single most important non-oceanic body of water in Europe” and “a future central axis for the European Union” (Simonovic 2009). It also represents a habitat for many species of fish, some species such as sturgeons, being true indicators of the ecosystem health (Deak et al. 2014; Simonovic 2009).

Management of water quantity and quality in the Danube Basin has been a top priority for decades (Malago et al. 2017). By applying and complying with water quality directives, the Danube countries now maximise win-win synergies and work towards a truly integrated water management (ICPDR 2015a).

The Danube River Basin Management is coordinated by the ICPDR, which has recently developed an updated Danube River Basin Management Plan, following the approach to the requirements of the WFD (EC 2000; ICPDR 2015b).

The studied area, the Danube sector between Calarasi and Braila (km 375–km 175), represents an important commercial navigation route which ensures the connection between the Danube River, the maritime Danube and the Danube–Black Sea Canal. Also, it represents an important migration route for sturgeon species.

Due to the fact that during dry seasons, the minimum navigation depths are not respected in accordance with the Danube Commission’s recommendations, in the studied area have been implemented hydrotechnical works that included activities such as dredging, embankments and sills that may have a potential impact on water quality and biodiversity. In order to improve the navigation conditions, during the period 2011–2017, hydrotechnical constructions on the abovementioned sector of the Danube River were performed, respectively a bottom sill on the Bala branch and a guiding wall on the Old Danube (POS-T 2018). The aim of these hydrotechnical constructions was to increase the water flow on the Old Danube for facilitating commercial navigation during drought periods and to shorten their route to the Black Sea, by more than 100 km. For environmental protection purposes, during the entire construction period, as well as before and after it, the National Institute for Research and Development in Environmental Protection (INCDPM) analysed the

evolution of the environmental factors through an intensive monitoring program. The present study has been designed to continue and to integrate past research on the region of the Lower Danube (Ionescu et al. 2014; Ionescu et al. 2015; Radu et al. 2014, 2016a, b, 2017).

The importance of the study stems both from the sensitivity of aquatic ecosystems and from the fact that the quality of surface waters having a direct impact on human health and protecting and improving the water quality and the environment of the Danube River Basin is being essential for achieving sustainable development and is vital for the long-term health, well-being and prosperity of the Danube population.

The quality of the surface water has been assessed by monitoring a series of physicochemical parameters and by performing a complex multivariate statistical analysis of the results obtained during the monitoring program. Multivariate statistical analyses were used in order to simplify the complex datasets obtained and to identify the most relevant set of parameters (Babić et al. 2019; Ojok et al. 2017). Water quality index is used to assess the overall quality of a water body, and it may be seen as an instrument of communication between quality monitoring and operational control for different water uses, being an accessible tool for both population and decision-makers (Iticescu et al. 2016). The multivariate statistical analysis identifies the interdependencies established between two or more parameters which characterize the state of the system.

It is important to establish a possible interdependence between physical-chemical parameters analysed, because some existing problems may be solved and additional risk situations may be prevented in case the water flows are exposed to long periods of flood and/or drought.

This study was made by using a set of multivariate statistical methods of water quality assessment, and at the same time, as novelty, the multiparametric quality index (ICPM) was developed and applied as an index of global comparative assessment of water quality over historical trends, algorithm developed by INCDPM. The interpretation of the variation of the monitored physical-chemical parameters was made by using principal component analysis (PCA), cluster analysis (CA) and ICPM.

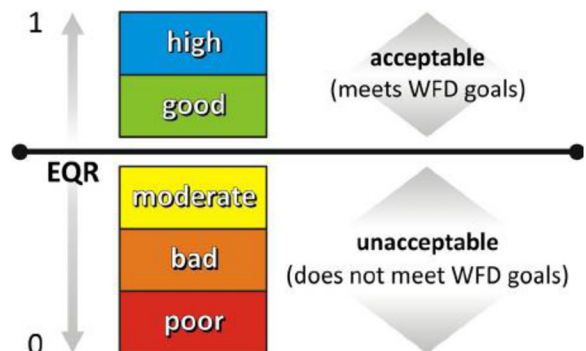
In this study, the general mathematical algorithm for determining the ICPM was used. This method was selected because it allows the use of national standards which in turn, allows using the results and

interpretations in surface water management in compliance with the national and EU legislation.

A water quality index is a mathematical tool that integrates complex data into a numerical score to describe an overview of the general water quality (Iticescu et al. 2019). Application of a quality index is of great importance, and this is evident by the development of a significant number of different types of quality indexes in different countries around the world, applied from general to specific purposes (Ionescu et al. 2019).

The five quality classes defined by the Water Framework Directive (WFD) on the basis of the ecological quality ratio (EQR), for Europe’s aquatic ecosystems, and transposed in Romania by Ministerial Order 161, provide descriptive definitions for five quality classes that characterize the ecological status of water (high, Class I (blue); good, Class II (green); moderate, Class III (yellow); poor, Class IV (orange); and bad, Class V (red)) classes established on the basis of biological quality elements, hydromorphological, chemical and physicochemical parameters with specific limits for each EU country (Fig. 1).

EQRs are defined for each area and ecosystem type on the basis of the least impacted localities in the area. High-quality sites are those for which  $EQR \approx 1$ , i.e. for which the observed conditions depart only little from reference conditions. According to the WFD, ecological status is acceptable for sites classified in “high” or “good” ecological status (Class I and Class II, respectively), while sites in “poor” to “moderate” status (Classes III–V) need to be brought up to acceptable ecological status through the implementation of ad hoc restoration plans. Terminology and colour coding is according to the European Commission (EC 2000).



**Fig. 1** The five quality classes (QCs) defined by the Water Framework Directive (WFD) (Miccoli et al. 2013)

The WFD includes categories which take into account each parameter separately and not the global quality index. Assessed by the EU legislation, the surface waters in Romania fall mainly in Class II (good water quality), and the Danube River water is included in categories good (Class II) and moderate (Class III).

The objective of this paper was to assess the overall water quality in the Lower Danube River during 2011–2017, in accordance with the WFD (Directive 2000/60/EC) and the Danube River Basin Management Plan, given the links between multiple pressures, ecological status and chemical status of the water body, as well as the hydrotechnical works that have been carried out in this study area.

The means to achieve this objective include the following: continuing studies on the quality of large aquatic ecosystems such as the Danube River; the most relevant set for the main pollutants by statistical method processing (PCA, CA); applying and evaluating general quality evolution with the developed multiparametric quality index (ICPM); and processing results over a significant period of time (7 years) for a system where seasonal and multiannual variations (such as water flow) are very important.

## Materials and methods

### Study areas

The Danube River represents the main waterway in Romania (Fairway Danube 2018). The Danube sector between Calarasi and Braila (km 375–km 175) represents both an important commercial navigation route and the migration routes for sturgeon species, which ensures the connection between the Danube River, the maritime Danube and the Danube–Black Sea Canal. In order to improve the navigation conditions, during the period 2011–2017, hydrotechnical constructions on the abovementioned sector of the Danube River were performed, respectively a bottom sill on the Bala branch and a guiding wall on the Old Danube (POS-T 2018). The aim of these hydrotechnical constructions was to increase the water flow on the Old Danube for facilitating commercial navigation during drought periods and to shorten their route to the Black Sea, by more than 100 km. For environmental protection purposes, during the entire construction period, as well as before and after it, INCDPM analysed the evolution of the

environmental factors through an intensive monitoring program. Innovative monitoring systems were designed and used to monitor both water quality and sturgeon migration routes for identifying the possible impact of the constructions and to develop timely alternative solutions to intervene for reducing and controlling the foreseen risks.

Between 2011 and 2017, approximately 1500 water samples were collected from 10 monitoring sites located in the lower part of the Danube River (Fig. 2), between Calarasi (km 375) and Braila (km 175).

During sampling campaigns, each water sample was collected directly from the river into a 5-L polyethylene container, which was transported directly to the analytical laboratory and stored at 4 °C. The water samples were taken monthly during the preconstruction and construction periods (September 2011–September 2015) and half-yearly during the post-construction period (December 2015–December 2017), on the left bank, the right bank and the centre of the river at three different depths (0.5 m, 1.5 m and 3 m). After transport and conservation, the water samples were processed and analysed according to the standards in force, and the quality indicators provided in M.O. 161/2006 (Table 1) were determined.

All reagents used in this study were of analytical quality, and all glassware used has been previously washed according to each analysis method specification and rinsed in double distilled water and deionized water before use. The quality of the results was ensured by periodical testing with reference materials for water. All indicators were analysed in accordance with European standards.

### Chemical analysis

### Statistical analysis

Statistical evaluation methods were applied to the complex database from the intense monitoring campaigns using the principal component analysis (PCA) and cluster analysis (CA), methods that facilitate the problem of interpreting the large number of data, generating useful and reliable information on the state of water quality fluctuations. The multiparametric quality index (ICPM), an overall water quality assessment index developed by INCDPM, has been applied, which highlighted the evolution and status of water quality during the monitored period (Radu et al. 2016a, b). Also, the obtained data

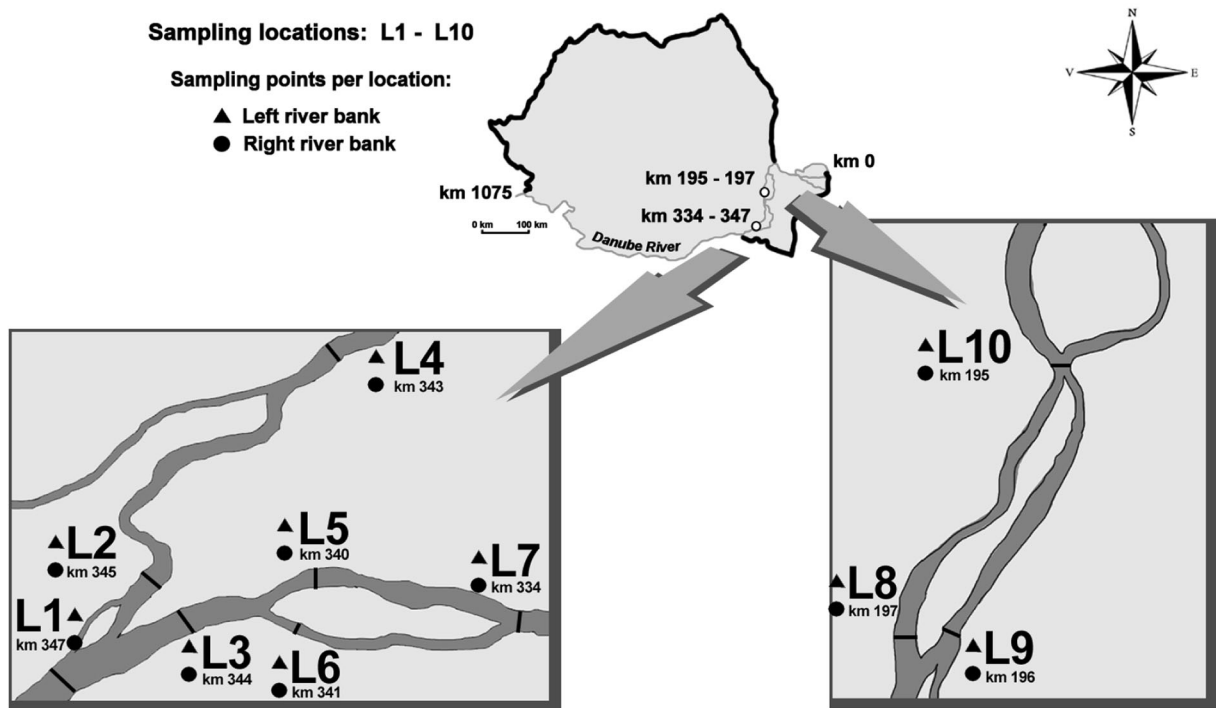


Fig. 2 Sampling locations on the Lower Danube River

was used to classify the water body status in quality classes according to WFD and M.O. 161/2006 (EC 2000; MO 2006).

To obtain information regarding the central tendency and distribution of each element in the studied area, multivariate statistical analysis methods were applied using the statistical software package JMP 10.

### Results and discussion

Multivariate statistical methods prove to be a powerful tool to identify the main factors that determine the variability of physical-chemical quality data and to provide a new insight in interpreting environmental quality based on measurement results.

PCA is an analytical technique for multivariate data analysis that reduces the number of variables, without modifying too much of the original dataset variability (Calazans et al. 2018). PCA provides information on the most significant parameters based on spatial and temporal variations that describe the whole dataset by excluding the less significant parameters with minimum loss of original variability (Diamantini et al. 2018; Uncumusaoğlu and Mutlu 2019). Tables 2 and 3 present

the correlation coefficient matrix (Pearson) between the determined physicochemical properties (Pearson absolute values greater than 0.5 are presented in italics).

From the correlation matrix, it can be observed that good correlations arise between some pairs of indicators either due to their common phenomenological source such as phenols and ammonium or by their physicochemical nature such as the inverse correlation between dissolved oxygen and temperature derived from physical properties relating to gas solubility in liquids and the correlation of total form of nutrients and their predominant chemical form in their makeup such as the direct correlations between total phosphorus and orthophosphates, between total nitrogen and nitrates and so on (Table 2). More indirect connections such as the indirect link between ammonium and pH or the direct correlation between phenol index and biochemical oxygen demand still yield correlation coefficients with absolute values greater than 0.5.

Table 2 shows the correlation of PO<sub>4</sub>-P with TP (0.612) and TN (0.531) and NO<sub>3</sub>-N with TN (0.767), probably due to leaching of nutrients from adjacent soil or tributaries (PO<sub>4</sub>-P and NO<sub>3</sub>-N are main constituents of fertilizers).



**Table 1** Parameters measured for water, their units, abbreviations used and analytical methods

Parameter	Units	Abbreviation	Analytical method
Temperature	°C	T	Thermocouple
pH	pH units	pH	Potentiometric measurements
Water flow	m <sup>3</sup> /s	Q	RiverSurveyor M9, ultrasonic measurements
Dissolved oxygen	mgO <sub>2</sub> /L	DO	Titrimetric measurements
Oxygen saturation	%	OS	
5-day biochemical oxygen demand	mgO <sub>2</sub> /L	BOD	
Chemical oxygen demand	mgO <sub>2</sub> /L	COD	
Total nitrogen	mgN/L	TN	
Ammonium-nitrogen	mgN/L	NH <sub>4</sub> -N	Molecular absorption spectrometric measurements
Nitrite-nitrogen	mgN/L	NO <sub>2</sub> -N	
Nitrate-nitrogen	mgN/L	NO <sub>3</sub> -N	
Orthophosphates	mgP/L	PO <sub>4</sub> -P	
Total phosphorus	mgP/L	TP	
Phenol	µg/L	Phenol	
Methylene blue active substances	µg/L	MBAS	
Chlorophyll “a”	µg/L	Chl. “a”	
Heavy metals (nickel, chromium, copper, zinc, cobalt, lead, cadmium)	µg/L	Ni, Cr, Cu, Zn, Co, Pb, and Cd	Atomic absorption spectrometric measurements
Heavy metals (iron and manganese)	mg/L	Fe and Mn	

Phenol index has a good direct correlation with NH<sub>4</sub>-N (0.863) probably due to the anaerobic processes generated by the pollutants present in wastewater discharged into the emissary and a reversed correlation with pH (−0.574) probably due to the acidic environment created by their presence.

As it can be seen in Table 3, the group of metals is strongly interrelated with Pearson factors predominantly greater than 0.5.

Tables 4 and 5 contain significant load values selected for the first major components from the PCA analysis. Usually, even if the main contributors to a principal component (PC) are few, the rest of the parameters play a minor role that can be eliminated in order to facilitate interpretation of the main component's significance.

The results showed that the first component comprised pH, TN, PO<sub>4</sub>-P, NO<sub>3</sub>-N and TP (Table 4). The second component was mainly associated with DO, NO<sub>2</sub>-N, phenol and NH<sub>4</sub>-N. The third component includes COD, BOD, Q, T, OS and Chl. “a”, and PC4 only has MBAS as a major constituent where we can deduce that this parameter comes from other sources (anthropic) than the natural cycle of the river, given its uncorrelated tendency.

As it can be seen in Table 5, results revealed that the first component comprised Pb, Cu, Ni, Cr, Mn, Cd, Fe and Zn. The second component was mainly associated with only Co, and the third component has only As as a major constituent.

Figures 3 and 4 show the eigenvalues associated with the principal components and the percentage of variability covered by each PC.

Figure 3 shows that the first component represents a variability of 27.94% of the entire dataset, the second major component supplemented it by 17.82% variance and the third major component covered 11.37% more from the dataset variance. All three main components accounted for 57.13% of the entire variability of the dataset, highlighting the major trends of the monitored ecosystem.

The data from Fig. 4 shows that the first component represents a variability of 46.58% of the entire dataset, the second main component supplemented by 24.95% of variance and the third main component covered 9.94%. This indicated that the first component collected much of the information in the samples, which contained heavy metals from the common source of alluvium supplied by the river. All three main components accounted for

**Table 2** Correlation matrix for the analysed physicochemical parameters

T	pH	Q	BOD	COD	DO	OS	NH <sub>4</sub> -N	NO <sub>2</sub> -N	NO <sub>3</sub> -N	TN	PO <sub>4</sub> -P	TP	Chl. “a”	MBAS	Phenol index	
T	1.000															
pH	0.005	1.000														
Q	-0.079	-0.063	1.000													
BOD	-0.066	-0.662	-0.060	1.000												
COD	-0.044	-0.202	0.142	0.575	1.000											
DO	-0.775	0.099	0.073	-0.022	0.017	1.000										
OS	0.514	-0.017	0.014	0.045	0.077	-0.134	1.000									
NH <sub>4</sub> -N	-0.088	-0.597	-0.123	0.576	0.132	-0.087	-0.118	1.000								
NO <sub>2</sub> -N	-0.285	-0.316	-0.016	0.372	0.121	0.190	-0.035	0.396	1.000							
NO <sub>3</sub> -N	-0.452	0.309	0.294	-0.265	0.114	0.306	-0.363	-0.362	-0.081	1.000						
TN	-0.311	0.402	0.298	-0.350	0.090	0.228	-0.338	-0.408	-0.105	0.767	1.000					
PO <sub>4</sub> -P	-0.136	0.477	0.193	-0.456	0.007	0.124	-0.055	-0.445	-0.202	0.427	0.531	1.000				
TP	0.001	0.206	0.198	-0.112	0.412	0.005	0.100	-0.287	-0.146	0.293	0.406	0.612	1.000			
Chl. “a”	0.463	0.154	0.063	-0.106	-0.012	-0.277	0.171	-0.181	-0.257	-0.110	-0.004	-0.087	0.001	1.000		
MBAS	0.004	0.018	-0.080	0.062	0.145	0.057	-0.043	-0.102	-0.139	0.022	0.030	-0.108	-0.024	0.172	1.000	
Phenol index	-0.139	-0.574	-0.100	0.597	0.203	-0.008	-0.007	0.863	0.412	-0.401	-0.457	-0.393	-0.232	-0.230	-0.074	1.000

**Table 3** Correlation matrix for heavy metals

	Cr	Cu	Zn	As	Co	Pb	Cd	Fe	Mn	Ni
Cr	1.000									
Cu	0.800	1.000								
Zn	0.063	0.197	1.000							
As	0.044	0.117	0.181	1.000						
Co	-0.034	0.049	0.952	0.165	1.000					
Pb	0.851	0.853	0.181	0.097	0.035	1.000				
Cd	0.303	0.362	0.809	0.111	0.786	0.361	1.000			
Fe	0.387	0.359	0.074	0.054	-0.029	0.376	0.112	1.000		
Mn	0.600	0.737	0.182	0.167	0.066	0.641	0.286	0.615	1.000	
Ni	0.832	0.836	0.211	0.111	0.074	0.889	0.372	0.335	0.619	1.000

81.48% of the entire variability of the dataset, highlighting the major trends of the monitored ecosystem.

Figure 5 represents the score plot of the first two principal components and shows the data coagulation patterns and the loading plot for physicochemical parameters.

After analysing the coagulated groups, we observed the following tendencies: samples from the score group blue are sampled in an autumn period, samples from the score group yellow are sampled in a winter period, samples from the score group green are sampled in a

spring period and samples from the score group red are sampled in a summer period. Samples with the scores black do not belong to any of the identified groups and are anomalies that occur in a monitoring program.

Cluster analysis is another type of multivariate analysis providing details of similarities between groups of parameters (Dołęgowska and Michalik 2019; Hora Alves et al. 2018; Salah et al. 2012), and 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. 6).

In order to identify sources of contamination, natural or anthropogenic, an exploratory hierarchical cluster analysis was performed based on heavy metal concentrations and monitored physical and chemical indicators. The results are illustrated by hierarchical dendrograms as can be seen in Fig. 6. It is known that the lower the value on the group of distances, the more important the association is.

**Table 4** Loading matrix for physicochemical parameters

Parameters	PC1	PC2	PC3	PC4
pH	0.74508			
TN	0.74009			
PO <sub>4</sub> -P	0.71573			
NO <sub>3</sub> -N	0.65882			
TP	0.46527			
DO		0.66674		
NO <sub>2</sub> -N		0.46245		
Phenol		0.28783		
NH <sub>4</sub> -N		0.26326		
COD			0.81311	
BOD			0.43236	
Q			0.32465	
T			0.27196	
OS			0.34313	
Chl. "a"			0.17930	
MBAS				0.83526

**Table 5** Loading matrix for heavy metals

Parameters	PC1	PC2	PC3
Pb	0.90174		
Cu	0.89986		
Ni	0.89342		
Cr	0.84902		
Mn	0.79507		
Cd	0.57594		
Fe	0.51288		
Zn	0.41904		
Co		0.93616	
As			0.83399



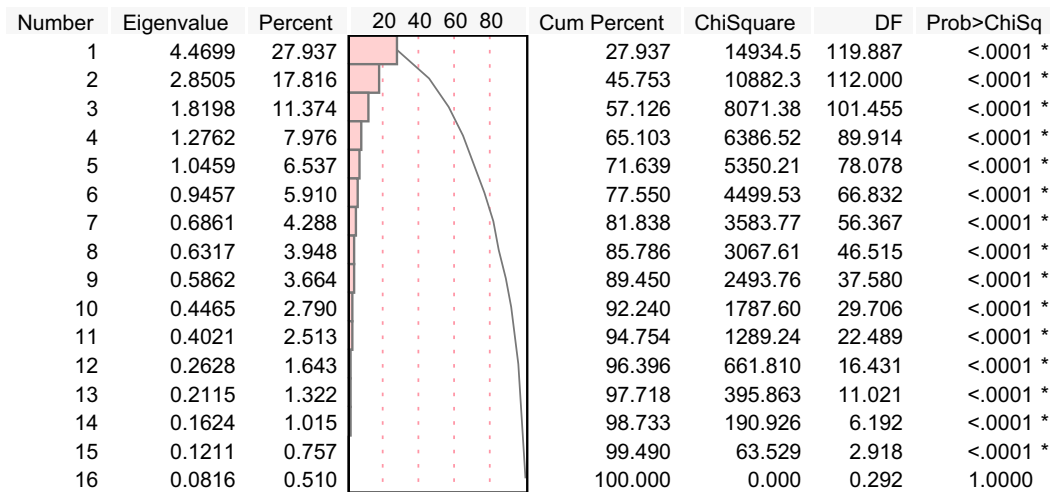


Fig. 3 Eigenvalues and percentage of data variability accounted by each PC for physicochemical parameters

Generally we can observe an association of nutrients both in reduced and in higher oxidation forms, and behaviour was also observed for the parameters describing the organic matter content (Fig. 6a). The final group shows the overall association of the monitored indicators and the oxygen saturation with the flow rate.

Depending on the degree of association between metals, two distinct clusters could be identified (Fig. 6b): the first group includes Cr, Pb, Cd, Mn and Fe supporting a common origin and the second group Cu, Ni, Co and Zn, which probably derives from other anthropogenic activities. Overall, the clusters seemed to indicate the presence of both natural and anthropogenic sources of heavy metal origin.

An overall assessment of water quality was also achieved through the multiparametric quality index (ICPM), developed by INCDPM. The multiparametric quality index (ICPM) is a non-dimensional number used to assess the overall quality of water, which characterizes the water quality status during the monitored period

compared with a reference period, being a useful tool in quality management, policymakers and the public.

In Table 6 are presented the variability of multiparametric quality index (ICPM) which shows that the intermediary results for the evaluated months show moderate to slightly elevated values, exceeding the reference set, mainly caused by heavy rainfalls in June 2014 (86%) and March 2016 (88%). The ICPM levels for the evaluated periods had values ranged from 34 to 88%. Based on interpolation/extrapolation functions, the final ICPM value may vary from negative to zero if the majority of quality indicators are lower than historical values between 0 and 100% if the majority quality indicators have values that were found in the range of historical data and values above unit (> 100%) when sufficient quality indicators have values that exceed historical maximum values.

Given the development of the ICPM algorithm so far, further improvements could be made to the automatic subroutine that favours certain types of weights as

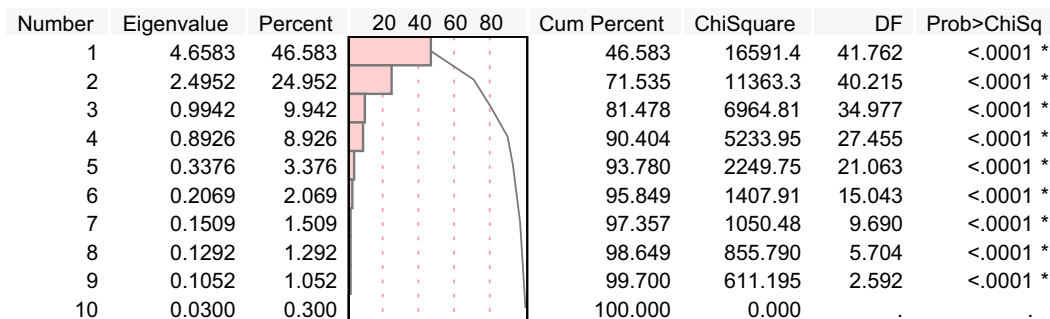
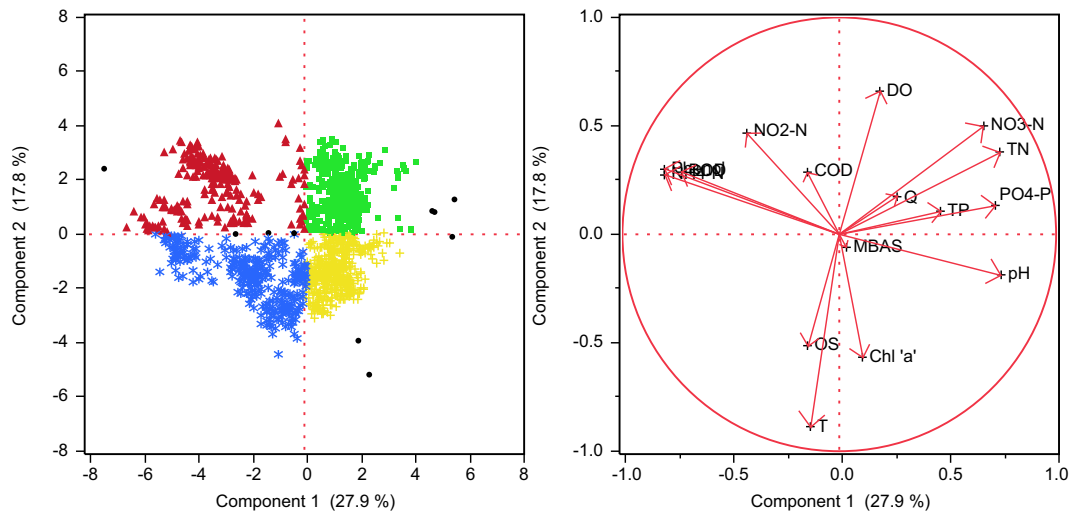


Fig. 4 Eigenvalues and percentage of data variability accounted by each PC for heavy metals



**Fig. 5** Summary plots for physicochemical parameters

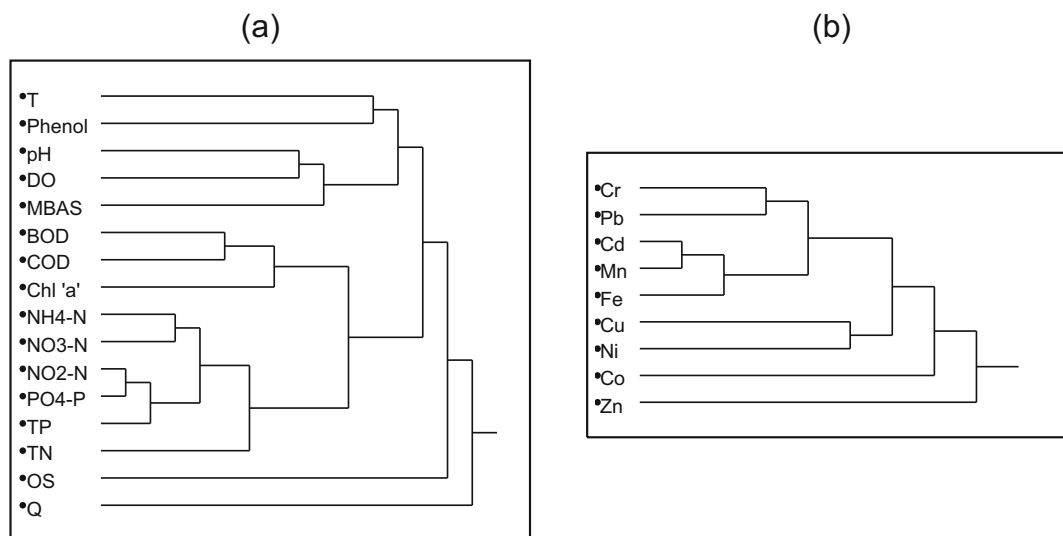
opposed to others. Further efforts are also needed to adequately correlate the final ICPM values and factual effects at ecosystem level. Further information regarding this developed algorithm may be found in our previous publications (Radu et al. 2016a, b).

According to M.O. 161/2006 and WFD, on the basis of the results from the monitoring campaigns, a classification of the determined indicators by their value quality class was made, which shows a rating of the indicators in the quality Classes I–III (Tables 7 and 8), indicating a “moderate ecological state”, which is also

confirmed by other available specialized studies (Fairway Danube 2018; Misikova Elexova et al. 2018).

To establish the homogeneity of the data, Table 8 presents a descriptive analysis of the quality parameter concentrations using several statistical descriptors: maximum, quartile 90%, median, quartile 10%, minimum, mean, standard deviation, standard error of the mean, upper 95% mean, lower 95% mean and reference values according to the applicable legislation.

From Table 8, it can be observed that the dataset is homogeneous for most of the evaluated indicators, with



**Fig. 6** Dendrogram of the physicochemical parameters (a) and of heavy metals (b)

**Table 6** Variability of ICPM

Year	Month	ICPM (A)	ICPM (B)	ICPM
2014	January	47	43	43
	February	55	68	57
	March	52	123	61
	April	57	111	64
2014	May	46	61	59
	June	88	71	86
	July	41	83	46
	August	47	85	52
2015	May	35	57	55
	June	54	36	52
	July	31	55	34
	August	30	65	34
2016	March	89	72	88
	June	43	83	48
	September	47	62	56
	December	48	15	44
2017	March	56	94	63
	June	53	49	50
	September	49	70	58
	December	44	39	42

relative small differences between the minimum and the quartile 10%. There are few situations where more pronounced differences appear between the maximum value and quartiles 90%, but these extremes are met sporadically, at least 90% of the values being within normal limits. Values exceeding the normal values for the measured indicators are being relatively isolated.

For the majority of the indicators, at least 90.0% of the values were found within the normal limits.

Higher occurrences of exceeding values were recorded in the case of nutrients: NO<sub>2</sub>-N (maximum 0.06 mg N/L), NO<sub>3</sub>-N (maximum 1.88 mg N/L), TN (maximum 3.42 mg N/L) and Chl. “a”(maximum 49.75 µg/L), where we conclude that the quality of water falls in Class III in accordance with M.O. 161/2006. The problem of nutrient background assessment is not an easy task, particularly for N where the air deposition of NO<sub>x</sub> and NH<sub>3</sub> should also be considered.

Probably, the “nutrient problem” is caused mainly by the diffuse pollution with nitrogen (N) and phosphorous (P), which may be mitigated by proper wastewater treatment plant development. In the case of agriculture target group, the potential solutions are much more

complex. The increase of the nutrients leads to a cumulative effect of the share of diffuse pollution; the increase of Chl. “a” with the nutrients can be attributed to the gap between increased nutrient concentrations and algal growth. Also, the annual evolution of Chl. “a” concentration is strongly influenced by seasonal changes and local hydrological conditions, while nutrient levels are largely dependent on rainfall.

The loading with nutrients of the Danube River is influenced mainly in spring and early summer due to high variations in flow, which are influenced by snow melt and high precipitation fall, respectively.

The phenol index recorded values over the normal limits (value specific for the quality Class III) are mainly caused by the presence in surface water of effluents resulting from chemical industry, oil refineries or municipal wastewater discharge.

After evaluation of the values obtained for heavy metals, the following aspects may be observed: higher occurrences of exceeding values were recorded in the case of Cu (maximum 49.84 µg/L), As (maximum 0.96 µg/L), Co (maximum 20.56 µg/L), Pb (maximum 22.8 µg/L), Fe (maximum 1.97 mg/L), Mn (maximum 0.25 mg/L) and Ni (maximum 32 µg/L). Heavy metals are pollutants both of natural and of man-made origin, and their elevated presence in the environment is mainly due to industrial and agricultural activities, and also to wastewater discharge. Probably, Ni has above normal values due to its current use in the modern consumer market, from various stainless steels or electroplating of day-to-day materials to nickel-cadmium batteries.

It is known that the contamination with heavy metals of the surface waters is a major problem as they accumulate in the trophic chains, but a high bioaccumulation potential does not always involve a high toxicity potential, the situation being different for each metal. Cu, Fe, Mn and Ni are essential for proper functioning of vital biological processes, but may become harmful at high concentrations.

Metals like As, Co and Pb are highly toxic to living organisms even at very low concentrations and can cause disorders of the nervous system, cardiovascular problems and cancer.

The water flow (*Q*) has recorded values between a minimum of 5 m<sup>3</sup>/s and a maximum of 11,200 m<sup>3</sup>/s, with a median value of 2613 m<sup>3</sup>/s. Lower water flow rates have been recorded where navigation conditions have been improved, more exactly between L3 and L7 sampling locations.

**Table 7** Ranking of monitored indicators in quality classes

Quality Indicator	Number of Values According to MO 161 Quality Class				
	I	II	III	IV	V
BOD	1553	0	0	0	0
COD	1547	26	0	0	0
DO	631	942	0	0	0
NH <sub>4</sub> -N	1550	23	0	0	0
NO <sub>2</sub> -N	234	1077	262	0	0
NO <sub>3</sub> -N	1295	278	0	0	0
TN	664	909	0	0	0
PO <sub>4</sub> -P	1565	8	0	0	0
TP	1522	47	4	0	0
Chl 'a'	1545	28	0	0	0
Cr	1573	0	0	0	0
Cu	1552	17	4	0	0
Zn	1573	0	0	0	0
Co	1343	229	1	0	0
Pb	1558	4	11	0	0
Cd	1573	0	0	0	0
Fe	768	334	450	21	0
Mn	1311	231	31	0	0
Ni	1559	11	3	0	0
MBAS	1573	0	0	0	0
Phenol	891	432	241	9	0

The integrated results indicated that the Lower Danube River has a state of moderate quality, the hydrotechnical works for improvement of the navigation conditions that took place in the monitored area, having no long-lasting negative influence on the water quality, the River's quality state being mainly characterized by anthropic influences such as the agriculture, industry and climate change, this state being established in previous studies under the same conditions (POS-T 2018; Radu et al. 2014, 2016, 2017). This is also underlined by EU auditors who specified in the Special Report of 2015 that "Danube water quality: little improvement due to 'lack of ambition' in management plans" (EC 2016).

A part of the load may come from the carry-over from the large hydrographic catchment area, the Danube River with an approximate length of 2800 km representing the general collector of wastewater discharges and soil runoff from the crossed countries on its course (Ionescu et al. 2014).

The information obtained in this study can be useful in exploring further possible cases of accidental pollution and in the effort to assess the overall quality of ecosystems that depend on local environmental factors.

## Conclusion

In order to assess the water quality of the Lower Danube River, the quality indicators stipulated in M.O. 161/2006 were taken into account for the entire time period. The integrated assessment of the data obtained from the intensive monitoring campaigns has highlighted a classification of the indicators in quality Classes I–III, indicating a "moderate ecological status", which is also confirmed by the ICPDR of the Danube River Basin.

From the correlation matrix, it can be observed that good correlations arise between some pairs of indicators either due to their common phenomenological source or by their physicochemical nature. More indirect

**Table 8** Statistical analysis of parameters in water

Parameter	Unit of measurement	Variables										
		Max	Quartile 90%	Median	Quartile 10%	Min	Mean	St dev	St err mean	Upper 95% mean	Lower 95% mean	Normal values*
T	°C	27.2	22.5	16.1	4.2	1.1	13.78	7.26	0.19	14.13	13.43	-
pH	Unit,pH	8.64	8.35	8.19	7.69	7.16	8.09	0.25	0.006	8.10	8.07	6.5–8.5
Q	m <sup>3</sup> /s	11,200	5734	2613	482	5	2901	2004	49	2997	2804	-
BOD	mg O <sub>2</sub> /L	4.65	2.34	1.38	0.73	0.42	1.48	0.65	0.02	1.51	1.45	3
COD		7.61	3.4	2.5	1.63	0.93	2.56	0.78	0.02	2.59	2.52	10
DO		11.48	10.73	8.61	7.62	7.12	8.96	1.19	0.03	9.02	8.90	9
OS		99.14	92.69	83.41	78.01	67.7	84.07	5.53	0.14	84.33	83.80	90–110
NH <sub>4</sub> -N	mg N/L	0.68	0.29	0.05	0.02	0.01	0.09	0.10	0.002	0.09	0.08	0.4
NO <sub>2</sub> -N		0.06	0.03	0.02	0.01	0.001	0.02	0.01	0.0002	0.02	0.01	0.01
NO <sub>3</sub> -N		1.88	1.18	0.78	0.35	0.02	0.77	0.32	0.007	0.79	0.76	1
TN		3.42	2.16	1.63	0.87	0.13	1.58	0.51	0.01	1.61	1.56	1.5
PO <sub>4</sub> -P	mg P/L	0.21	0.07	0.05	0.03	0.006	0.05	0.02	0.0004	0.05	0.04	0.1
TP		0.68	0.13	0.10	0.07	0.02	0.10	0.04	0.001	0.10	0.10	0.15
Chl. “a”	µg/L	49.75	11.85	3.27	1.18	0	5.09	5.07	0.12	5.34	4.85	25
MBAS		55.59	16.78	7.38	2.46	0.5	8.69	6.09	0.14	8.99	8.39	100
Phenol index		20.90	14.45	0.95	0.50	0.50	3.35	5.42	0.13	3.61	3.09	1
Fe	mg/L	1.97	0.76	0.29	0.12	0.004	0.37	0.26	0.006	0.38	0.36	0.3
Mn		0.25	0.06	0.03	0.01	0.002	0.04	0.03	0.001	0.04	0.03	0.05
Cr	µg/L	13.63	1.89	0.70	0.33	0.08	1.02	1.13	0.03	1.07	0.96	25
Cu		49.84	5.83	3.44	1.94	0.37	4.02	3.86	0.09	4.21	3.84	20
Zn		93.5	60	7.4	2.80	0.20	17.84	22.84	0.56	18.94	16.74	100
As		0.96	0.74	0.52	0.32	0.15	0.52	0.16	0.004	0.53	0.52	0.05
Co		20.56	15.64	0.34	0.09	0.01	3.09	5.64	0.14	3.36	2.82	10
Pb		22.08	1.94	0.72	0.24	0.02	1.05	1.73	0.04	1.13	0.97	5
Cd		0.35	0.12	0.03	0.02	0.01	0.05	0.04	0.001	0.06	0.05	0.5
Ni		32.00	3.61	1.90	1.00	0.23	2.37	2.45	0.06	2.48	2.25	10

\*Normal values for Class I according to M.O. 161/2006 (MO 2006)

connections still yield correlation coefficients with absolute values greater than 0.5.

From data variability, the first 3 principal components of physicochemical parameters accounted for 57.13% of the entire variability of the dataset, and the first 3 principal components of heavy metals accounted for 81.48% of the entire variability of the dataset, highlighting the major trends of the monitored ecosystem. Overall, the cluster analysis seems to indicate the presence of both natural and anthropogenic sources of origin.

The final ICPM value for June 2014 is 86% and for March 2016 is 88%, representing an increased

ecosystem pressure compared with the other assessed periods, mainly due to heavy rainfalls from those periods.

The results can be used as a database for specialists and environmental authorities to identify and reduce environmental pollution, and the application of multivariate statistical techniques can provide logistical support for accidental contamination detection.

This study is a useful support for protecting water resources and water quality monitoring in the context of providing information for a basin management plan that can help improve ecosystem services of water resources and improve the quality of life and the environment.

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