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PhD THESIS

Trends in main Danube water quality physiscal-chemical parameters on Romanian territory during the period 1996-2017

SUMMARY

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Table of contents

INTRODUCTION

Danube is the second longest river in Europe, flowing 2858 km from its springs, in the Black Forest Mountains, in Germany, to its mouths at the Black Sea. The Danube passes through 10 countries but drains a much larger area, its river basin having an area of over 800.000 km^2 and a population of 81 million inhabitants, including territories from 19 countries (Albania, Austria, Bosnia and Hezegovina, Bulgaria, Croatia, Switzerland, Gemany, Italy, Macedonia, Moldova, Montenegro, Poland, Czech Republic, Romania, Serbia, Slovakia, Slovenia, Ucraine and Hungary) [1]. Among these, Romanian territories represent the highest share of the Danube river basin, namely 29%.

The river plays an important role in the life of the people living nearby, and human activities have a significant impact upon water quality and the aquatic ecosystem. Pollutant discharges into the Danube originate mainly from domestic and industrial wastewater, mining, agriculture and animal farming. Danube pollution control requires close cooperation at international level among countries located in the river basin, particularly because it is a drinking water source for many communities [2].

During the last decades, particularly after intensification of cooperation between riparian countries, some of them members of the European Union, measures were taken to reduce pollution, as part of international agreements and European Union regulations. Starting from 1996, Danube Water Quality is monitored within the TransNational Monitoring Network (TMNM) of the International Commission for the Protection of the Danube River (ICPDR) [3].

Danube water quality is important both for authorities and for the scientific community, so there are lots of publications regarding the results of the monitoring programmes and research carried out on the hydrological regime [5], physical-chemical properties [6], pollutants concentrations [7] and their effect upon ecosystems in the Danube and on the Black Sea coast affected by it [8], to mention some recent examples.

Although a lot of progress has been made in monitoring water quality and increased data collection, there are still a lot of aspects to be studied regarding data exploration, making connections between causes and their effects upon water quality parameters, between causes, the ecological state of water bodies and ecosystems functioning [9,10]. This limits the capacity of knowing and understanding ecosystems response to various stress factors, and consequently the possibility that decision makers adopt the most appropriate strategy in response.

Moreover, most studies do not carry out an advanced statistical analysis of data, comparisons between different monitoring stations and trend analysis.

There is still a lot of research potential in this field, to obtain new monitoring data, to analyse statistically existing data, and to apply new, wider analysis methods, particularly for longer periods of time, to highlight the impact of Romanian tributaries upon the Danube and how it evolved in time.

The topic of the present work fits within this context: trends in Danube water quality from the first monitoring station on Romanian territory to the Black Sea (1071 km) over a long period of time, the influence of the main Romanian tributaries upon the Danube, and a case study for Dâmbovița river, receiving effluents from the Bucharest wastewater treatment plant.

The main physical-chemical water quality parameters were analysed on the Romanian section of the Danube (14 parameters, 15 monitoring stations), a distance of 1071 km, for a period of 22 years (1996-2017). Water quality data were determined and analysed (6 nutrients parameters) at 8 monitoring stations on Dâmbovița river (Arges tributary, draining into the Danube), before and after Bucharest, for the period 2010-2015.

Data were analysed using advanced statistical methods (descriptive, inferential and multivariate), as well as the Water Quality Index method (WQI). A comparison is made between Danube water quality and its main Romanian tributaries (Jiu, Olt, Argeș, Ialomița, Siret, Prut), as well as between values at entry on Romanian territory, at Baziaș, and those at discharge into the Black Sea, for the analysed period.

The research has the following objectives:

- literature review on Danube water quality, with focus on Romania and the topic of the thesis;
- presentation of statistical methods that are frequently used in processing monitoring data of surface waters quality;
- analysis of monitoring data from Romanian territory at 15 locations (9 on the Danube and 6 on tributaries) from the entrance into the country to discharge into the Black Sea (1071 km) during the period 1996-2017;
- presentation and analysis of experimental monitoring data (6 nutrients parameters) of Dâmbovița river at 8 monitoring stations, upstream and downstream Bucharest, for the period 2010-2015;
- applying statistical methods for data analysis (descriptive, inferential and multivariate);
- analysis of compliance of determined values with quality classes defined by Romanian norms at each monitoring station;
- identification of correlations between analysed physical-chemical parameters and of long-term trends that are statistically significant (increase or decrease) for the analysed parameters at each station during the analysed period;
- analysis of Danube pollution loads on Romanian territory by comparing water quality at entry into the country to that at discharge into the Black Sea;
- a global assessment of Danube pollution using the Water Quality Index (WQI) method.

The work is structured in two parts: ***Theoretical Aspects and Literature Review*** (around 44 pages) and ***Experimental Methodology and Own Contributions*** (around 100 pages), followed by general conclusions and bibliography.

The ***Theoretical Aspects and Literature Review*** part includes 3 chapters.

CHAPTER 1 presents general information regarding the Danube River Basin, the main water quality parameters (hydromorphological, physical, chemical, biological, hazardous and priority substances), main sources of pollution and pollution prevention and control measures.

CHAPTER 2 presents statistical methods for data processing that are applied, namely descriptive statistics, ANOVA analysis, t test, Spearman rank correlation test, principal component analysis, multiple factor analysis and Water Quality Index calculation method.

CHAPTER 3 is a presentation of the main scientific works regarding the Danube that were identified, grouped in six sub-chapters, namely (1) hydromorphological studies, (2) physical-chemical parameters studies, (3) biological and microbiological parameters studies, (4) hazardous and priority substances studies, (5) complex studies, pollution indices and accidental pollution, (6) international cooperation, monitoring and common policies. Studies on the Danube in Romania are emphasised.

The second part of the work, *Experimental Methodology and Own Contributions*, includes 4 chapters and the general conclusions.

CHAPTER 4 presents the experimental methodology that was applied in the work, the study areas, the analysed data and data processing methods. 9 monitoring stations on the Danube were selected and 6 on the tributaries Jiu, Olt, Argeș, Ialomița, Siret and Prut, monitoring data from the period 1996-2017 were analysed. Monitoring data from 8 monitoring stations on the Dâmbovița river were also analysed, and they were compared to those from the Argeș river, downstream from their confluence.

The way in which statistical methods were applied in the work is described, as well as the Water Quality Index (WQI) calculation method. The applied methods are descriptive statistics, inferential statistics and multivariate data analysis. Descriptive statistics include numerical and graphical methods, allowing primary analysis and visualisation of data, providing a first set of information about values distribution and their evolution in time. Inferential analysis includes formulation and testing of statistical hypotheses, to assess if differences between groups and long-term trends are significant or not. Multivariate analysis takes into account several types of variables at the same time and highlights correlations between parameters and their influence on the dataset.

CHAPTER 5 includes wide data analyses of monitoring data from selected stations during the period 1996-2017. The analysed parameters are: flow, water temperature, pH, dissolved oxygen, oxygen saturation, biochemical oxygen demand, chemical oxygen demand, ammonium, nitrites, nitrates, total nitrogen, orthophosphates and total phosphorus. For each parameter, data are represented graphically in scatterplots and boxplots, the main descriptive statistical values are calculated (minimum, maximum, mean, median, 1^{st} and 3^{rd} quartiles), values distributions in datasets are analysed, as well as their compliance with Romanian quality classes. The analysis of variance ANOVA indicates if there are significant differences between values determined at different monitoring stations. A comparison is made between values at Danube's entry into the country, at Baziaș, and those at other stations along the Danube and tributaries, in order to assess if pollution increases or decreases on the segment between Baziaș and the Black Sea. In order to identify how the values of parameters evolved during the analysed period, Spearmen rank correlation coefficient is calculated between values and their respective sampling dates at each station, and long-term trends are analysed. In this chapter, each parameter is analysed individually.

CHAPTER 6 includes a complex, simultaneous analysis of several types of variables, aiming at finding out which parameters have a stronger influence on the dataset, eventual correlations between parameters, as well as the influence of the sampling point on the obtained values. Principal Component Analysis (PCA) is applied on annual means from the period 1996-2017 and multiple factor analysis is carried out to highlight, at the same time, both the differences between values of parameters and those between monitoring stations. The Water Quality Index (WQI) was calculated, one of the 25 indicators used to assess environmental quality, called Environmental Quality Indices (EQI) [21]. The weighted arithmetic method was applied for calculating WQI, and long-term trends were analysed for the study period at each station. Also, multivariate analysis methods were applied on WQI sub-indices in order to highlight the contribution of each parameter to the global index, as well as the differences between analysed stations. The index may be an indicator of water quality needed by decision makers to prioritise pollution abatement measures.

CHAPTER 7 focuses on the contribution of insufficiently treated municipal wastewater from Bucharest city to the pollution with nutrients of Dâmbovița river, Argeș tributary that, in its turn, flows into the Danube. Mean annual values from 8 monitoring stations on Dâmbovița river are presented, and one on Argeș river, from the period 2010-2015, for ammonium, nitrites, nitrates, total nitrogen, orthophosphates and total phosphorus, and their compliance with Romanian water quality classes is analysed. During the studied period, the biological treatment step of the Bucharest wastewater treatment plant was commissioned, in the end of 2011, with advanced treatment capacity for only half of the wastewater flow. Principal component analysis and factor analysis were applied to highlight differences between analysed stations.

The GENERAL CONCLUSIONS summarise the main results that were obtained.

Danube monitoring data that were analysed were provided by the ICPDR database to be used in scientific purposes. Monitoring Data for Dâmbovița river were obtained by the author as member of the implementation team of the Ministry of Environment Project P093775 *Romania Integrated Nutrient Pollution Control Project* (2008-2017) / *World Bank.*

The work includes over 160 pages and over 200 citations.

Research results were partly published or communicated in journals and national and international scientific events: ISI journals, 1 paper in Revista de Chimie (Bucharest) and 2, in press, in UPB Scientific Bulletin and in Ecohydrology & Hydrobiology with IF=2.820, 3 communications at international scientific events: 20th Romanian International Conference on Chemistry and Chemical Engineering RICCCE 2017, International Conference CHIMIA 2018 "New Trends In Applied Chemistry" and International Symposium Chemistry Priorities for a Sustainable Development PRIOCHEM 2016.

CHAPTER 4. EXPERIMENTAL METHODOLOGY

The current work aims at analysing the long-term trends in water quality on the Romanian section of the Danube during the period 1996-2017, by assessment and statistical analysis of certain parameters.

The purpose of this analysis is to find out if pollution sources and tributaries from Romanian territory have a significant negative impact on Danube water quality, as well as the way in which the parameters have evolved in the analysed period.

Dâmbovița river water quality is also analysed, as it is an Argeș tributary, carrying insufficiently treated sewerage wastewater from Bucharest, Romania's Capital City, to the Danube. Mean annual values of nutrients were analysed for the period 2010-2015.

4.1. STUDY AREA

Several structured data series were analysed in a way that would lead to the identification of the main sources of pollution (in particular human agglomerations), namely:

- Data from 9 monitoring stations on the Danube selected from the entry into the country, at km 1071, to the discharge into the Black Sea (km 0), from the period 1996-2017;
- Data from 6 monitoring stations located on main Romanian tributaries, close to the point where they drain into the Danube, from the period 1996-2017;
- Data from 8 stations along the Dâmbovița river, from the period 2010-2015, during which period insufficiently treated municipal wastewater was discharged from Bucharest's sewerage system, serving a population of over 2 mil. inhabitants. Dâmbovița flows into the Argeș river which, in its turn, is a Danube tributary.

The first two types of data, used for long-term trend analysis of water quality parameters in the Danube and tributaries were retrieved from the database of the International Commission for the Protection of the Danube River – ICPDR [185]. Data were used in this work with permission of the authorities, for scientific purposes. This database includes both monitoring data provided by riparian countries (TransNational Monitoring Network – TNMN), as well as data from Joint Danube Surveys, carried out every 6 years. In Romania, surface waters monitoring is carried out by the National Administration "Romanian Waters" (*Administrația Națională Apele Române – ANAR*), who reports to the ICPDR office in Vienna [11, 185].

For Dâmbovița, data were obtained by the author as member of the project team of Ministry of Environment Project P093775 *Romania Integrated Nutrient Pollution Control Project* (2008-2017) / *World Bank* [187].

In Figure 4.1. the monitoring stations located on the Danube and its tributaries that are analysed in Chapters 5 and 6 are represented on the physical map of Romania, and in fig. 4.2. the monitoring stations on Dâmbovița river.

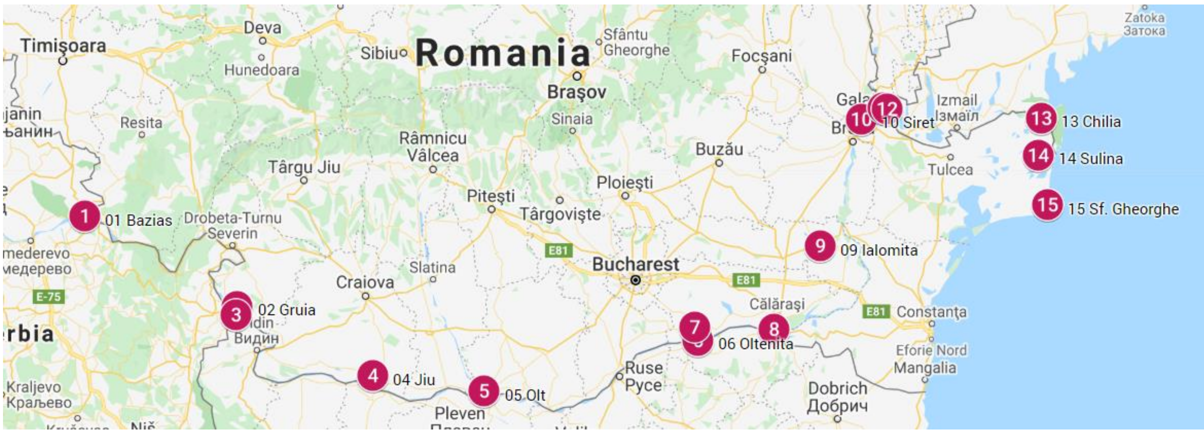

Fig. 4.1. Locations of surface water monitoring stations on the Danube and Romanian tributaries, analysed for the period 1996-2017: 1 Baziaş, 2 Gruia, 3 Pristol, 4 Jiu, 5 Olt, 6 Oltenița, 7 Argeş, 8 Chiciu, 9 Ialomița, 10 Siret, 11 Prut, 12 Reni, 13 Chilia, 14 Sulina, 15 Sf. Gheorghe [186]

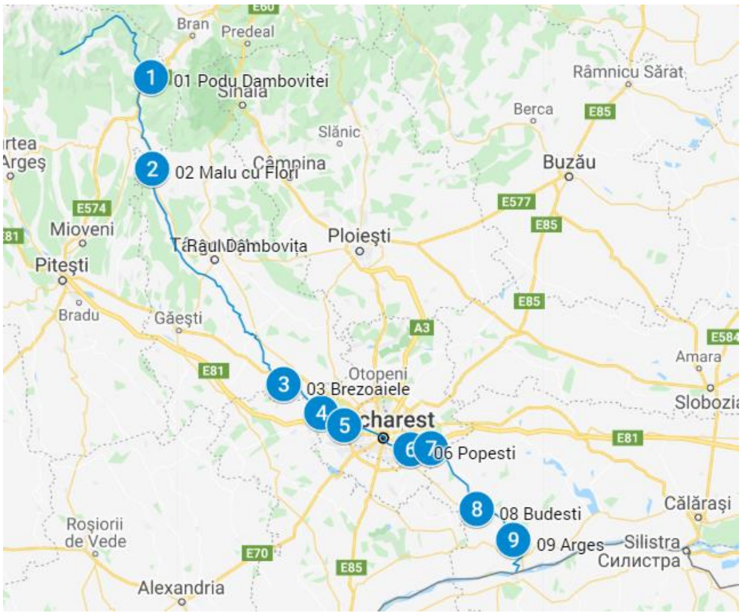

Fig. 4.2. Location of monitoring stations analysed in Chapter 7 for the period 2010-2015: Dâmbovița (1-8), Argeş (9). Locations:1 Podu Dambovitei, 2 Malu cu Flori, 3 Brezoaiele, 4 Arcuda, 5 Dragomiresti, 6 Popesti, 7 Balaceanca, 8 Budesti, 9 Arges [186]

4.2. MONITORING DATA

Water samples were taken and analysed according to corresponding standards.

4.3. STATISTICAL DATA PROCESSING AND ANALYSIS

The following statistical methods were used:

- descriptive statistics, including calculation of statistical values and graphical representationof data in scatterplots and boxplots;
- analysis of variance ANOVA;
- statistic t test (two tailed);
- Spearman rank correlation analysis;
- Principal Component Analysis;
- Multiple Factor Analysis.

In addition, the Water Quality Index (WQI) was calculated using the arithmetic weighted method. WQI is one of the indicators that can be used for assessing environmental quality, called Environmental Quality Indices (EQI) [21].

The research went through several steps in which the above statistical methods were applied.

In the first step, the primary analysis of data was carried out using **descriptive statistics**. Data were graphically represented in **scatterplots and boxplots** so they can be easily visualised.

This step allows the identification of differences in water quality between the different monitoring stations that are analysed, for example by comparing mean, median or maximum values.

In order to find out if dfferences between stations are statistically significant, the **analysis of variance ANOVA** was carried out. ANOVA indicates if there are significant differences between groups of data, but cannot identify which groups are different than the others.

Statistic t test is used to identify these differences and, in particular, to see if there are significant changes in water quality along the last segment of the Danube. Values from each station are compared to those from Baziaș and results are analysed, particularly for the stations located on the Danube, in order to find out if, between Baziaș and the Black Sea, Danube water quality improves or declines.

Spearman rank correlation, as a nonparametric method, is used to assess long-term trends in water quality parameters. It was applied because this method is not sensitive to normal distribution of data (existence of outliers) and can identify monotonic correlations, linear or not.

In order to see if the increasing or decreasing trends are statistically significant, t test statistic was applied for a level of confidence of 0.95.

Multivariate analysis was applied as a method that has the purpose of extracting information from large datasets, including both numerical (values of analysed parameters) and qualitative data (the sampling location). The multivariate analysis methods applied in the work are principal component analysis (PCA) and multiple factor analysis.

Principal Component Analysis has identified the parameters with the highest influence on the variance of the dataset and to highlight eventual correlations between parameters. Also, in the case of a large number of variables, the dataset may be reduced to a smaller number of principal components, without losing essential information.

Multiple factor analysis additionally highlights the differences between sampling locations regarding pollutants loads. This is carried out in two phases. In the first phase, PCA is applied to each group (location), then data are normalised so that they can be compared. In the second phase, normalised datasets are merged and PCA is applied to the resulting dataset. Individual datasets are then compared to the global analysis to identify similarities and differences.

Water Quality Index WQI was used to assess pollution levels at each analysed station, based on annual means of 10 relevant parameters. The weighted arithmetic method was applied, in which the weight of each parameter is calculated based on limit values of each parameter, according to water quality standards applicable to the study area. WQI trends were estimated and values were compared for stations along the Danube and on tributaries.

Statistical analyses of data and their graphical representations were carried out using the RStudio 1.1.463 software, based one R 3.6.2. [188].

CHAPTER 5. TRENDS IN WATER QUALITY PARAMETERS DURING THE PERIOD 1996-2017

Passing along Romanian territory, the Danube flows 1071 km and receives important tributaries, namely the rivers Jiu, Olt, Argeș, Ialomița, Siret and Prut.

In this chapter, the evolution of the main water quality indicators on the Romanian section of the Danube is analysed, for the period 1996-2017, by statistical processing of monitoring data reported by Romania to the ICPDR through the transnational network TNMN. Data were retreived from ICPDR database, with permission to be used for scientific purposes.

15 monitoring stations located on the Danube and its main Romanian tributaries were selected. The analysis was carried out for those parameters that were consistently monitored for long periods of time, so that data analysis could lead to relevant results. The monitoring stations located on the Danube are: 01 Bazias, 02 Gruia, 03 Pristol, 06 Oltenita, 08 Chiciu, 12 Reni, 13 Chilia, 14 Sulina, 15 Sf Gheorghe, and those on tributaries are: 04 Jiu, 05 Olt, 07 Arges, 09 Ialomita, 10 Siret, 11 Prut, presented in Chapter 4 (fig. 4.1.). The numbering was done in the order of spatial succession in the longitudinal profile of the Danube, from upstream to downstream.

The parameters analysed in this chapter are: flow, water temperature, pH, dissolved oxygen (DO), dissolved oxygen saturation (SOD), biochemical oxygen demand (BOD5), chemical oxygen demand (COD-Mn, COD-Cr), ammonium ($N\text{-}NH_4^+$), nitrites ($N\text{-}NO_2^-$), nitrates ($N\text{-}NO_3^-$), total nitrogen (TN), soluble orthophosphates ($P - PO_4^{3-}$) and total phosphorus (TP).

Monitoring data were analysed in order to assess:

- the compliance of determined values with quality classes defined by Romanian norms at each analysed station;
- the existence of statistically significant differences between the 15 analysed monitoring stations according to the values recorded for different parameters;
- the pollution load of Romanian tributaries and if they have a significant impact on Danube water quality, by comparing water quality at entrance into the country, in tributaries and at discharge into the Black Sea;
- the existence of significant trends in time (increasing or decreasing) in the analysed parameters at each station for the period 1996-2017.

The methods used for this purpose were: descriptive statistics, Spearman rank correlation analysis, ANOVA analysis and t test statistic.

Descriptive statistic analysis provides primary information regarding datasets like: minimum and maximum values, median, mean 1st (Q1) and 3rd (Q3) quartiles, statistical values that allow the assessment of data distribution in their domain of variation. While the arithmetic mean is sensitive to outliers, the median is placed in the middle of the row of values, arranged in increasing order, so that it is not influenced by outliers [190]. In perfectly symetrical datasets (with normal distribution), the mean and the median are equal. In this chapter, the main focus is on how these statistical values comply with Romanian quality classes. For instance, if a parameter has to have a low value for water to have a good quality, the fact that the third quartile, Q3, is in class I, means that 75% of determined values are in class I and that, for this parameter, the water had an excellent quality during most of the analysed period of time.

However, statistical values do not give indications regarding the periods when class limit values were exceeded, which is why scatterplots are useful, because they represent values according to the sampling date.

Example of parameter analysis:

5.2.5. Chemical Oxygen Demand (COD-Cr)

Chemical oxygen demand determined by potassium dichromate method, a strong oxidising agent, is an indicator of pollution with organic compounds, both biodegradable and not biodegradable. Thus, COD-Cr values are usually higher than those for BOD5 and COD-Mn.

According to Romanian norms (*Normativul privind clasificarea calităţii apelor de suprafaţă în vederea stabilirii stării ecologice a corpurilor de apă* [28]), the limit values for Chemical oxygen demand COD-Cr for the five quality classes are presented in table 5.2.13.

Table 5.2.13. Limit values of quality classes for COD-Cr in Romania [28]

No.	Quality indicator	Unit of measure	Quality class				
			I	II	III	IV	V
5	COD-Cr	mg O_2/L	10	25	50	125	>125

The COD-Cr values determined at the analysed monitoring stations during the period 1996-2017 are represented in figure 5.2.9. The number of observations at each location varies between 131 and 332.

In figure 5.2.9 it can be noticed that the values are similar at most stations, but there are some outliers on Ialomița and Siret rivers, which could have been caused by accidental pollution.

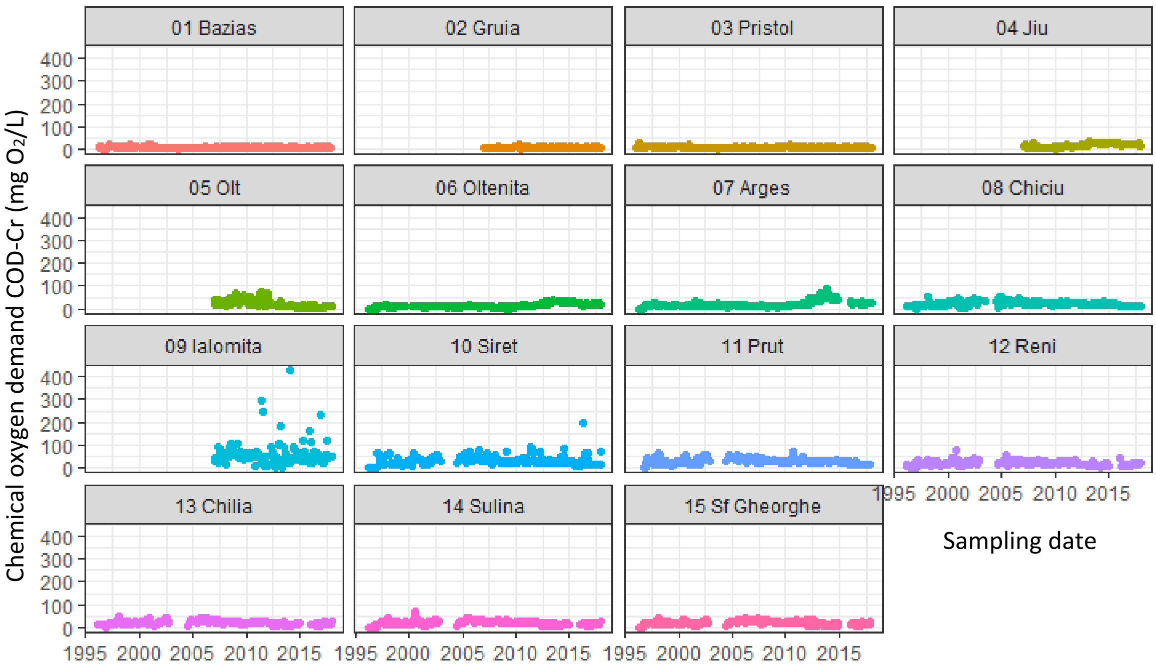

Fig. 5.2.9. Chemical oxygen demand COD-Cr at analysed monitoring stations during the period 1996-2017

The descriptive statistical values for chemical oxygen demand COD-Cr are presented in table 5.2.14. and represented graphically in boxplot charts in figure 5.2.10. Medians are usually between 9.34 and 22.58 mg O_2/L, and arithmetical means between 9.46 and 22.58 mg O_2/L, which indicates large differences between the analysed stations with respect to organic matter content. In most cases, the median is close to the mean, which means that datasets are symmetrical, except for the rivers Olt, Argeș, Ialomița and Siret, where the mean is higher that the median, because of some high values.

Table 5.2.14. Main descriptive statistical values for chemical oxygen demand COD-Cr at the analysed stations during the period 1996-2017 (mgO_2/L)

Location	Minimum value	1st quartile (Q1)	Median	Arithmetic mean	3rd quartile (Q3)	Maximum value
01 Bazias	0.00	8.06	9.58	9.46	10.60	22.00
02 Gruia*	0.00	9.05	9.90	9.99	10.75	21.53
03 Pristol	0.00	8.18	9.34	9.60	10.59	25.40
04 Jiu*	0.00	11.20	16.86	17.87	24.33	32.17
05 Olt*	6.24	9.80	16.08	22.33	33.44	71.40
06 Oltenita	0.00	9.00	10.90	14.32	19.53	37.96
07 Arges	0.00	13.20	16.40	20.44	23.04	87.80
08 Chiciu	0.00	17.20	22.58	22.58	25.39	57.00
09 Ialomita*	5.00	31.93	50.00	59.17	68.03	431.09
10 Siret	0.00	21.62	29.05	32.62	39.61	194.88
11 Prut	0.00	23.40	28.12	29.46	34.44	74.88
12 Reni	0.00	15.22	22.35	21.56	25.00	78.00
13 Chilia	0.00	14.00	19.69	20.38	24.70	45.00
14 Sulina	0.00	15.30	21.00	20.99	26.53	67.00
15 Sf Gheorghe	0.00	15.00	20.00	20.74	25.08	42.00

*Monitoring started in year 2007

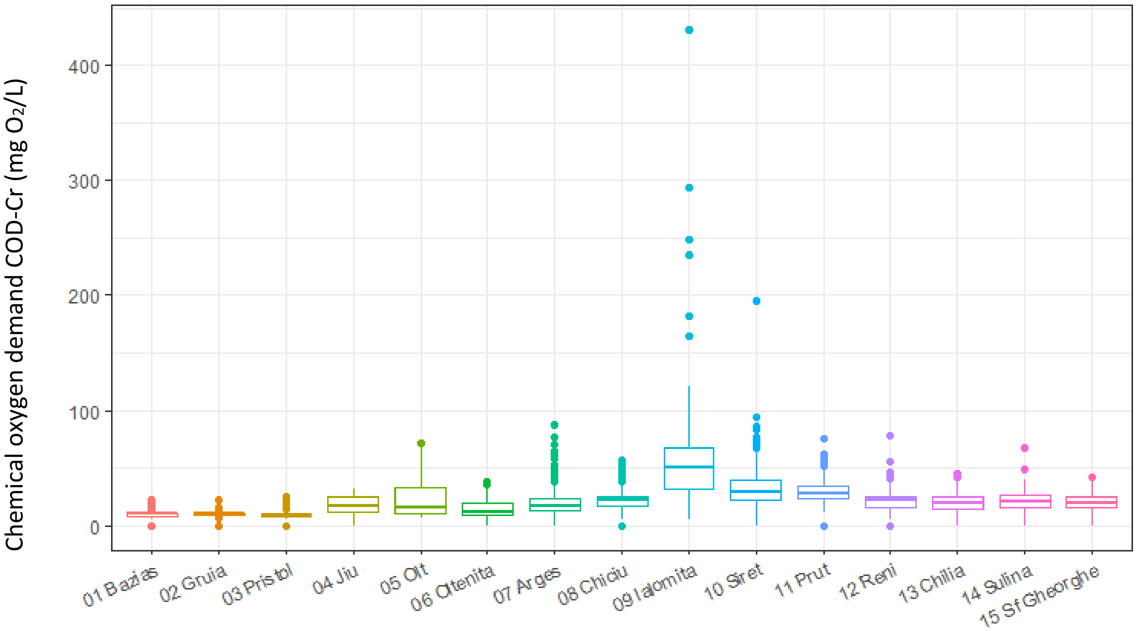

Fig. 5.2.10. Boxplot chart representing the main statistical values for COD-Cr at the analysed stations during the period 1996-2017 (mg O_2/L)

In the case of organic pollution determined by COD-Cr, it can be noticed that, until the Jiu river flows into the Danube, most of the determined values, almost up to the 3rd quartile, are in the first quality class, and downstream the values increase and go to class II. In the case of Prut and Siret rivers, mean and median values are in quality class III. In the case of Ialomița river, the mean value is in quality class IV, which indicates severe organic pollution.

The graphical representation of COD-Cr statistical values (figure 5.2.10) highlights a very serious situation on Ialomița river, where pollution level is much higher than at the other analysed locations (the mean is five times higher than at Baziaș). This pollution with organic compounds may be related to the fact that Ialomița collects the water of Prahova river, which, in its turn, has Teleajen river as tributary, collecting wastewaters from Ploiești industrial area, an important oil processing centre.

The ANOVA analysis highlights significant differences between the analysed locations ($p<2e^{-16}$). In order to compare COD-Cr values along the Danube, the t test was applied between Baziaș and the other locations. In the case of this parameter, values increase significantly from Baziaș to the Black Sea, except for Pristol station, which is not significantly different from Baziaș. The highest differences are between Baziaș and Chiciu, Ialomița, Siret, Prut and Reni, and the difference persists until the sea, with a slight decrease in the Danube Delta.

The results of the Spearman rank correlation analysis between chemical oxygen demand COD-Cr and the sampling date are presented in table 5.2.15.

Table 5.2.15. Results of Spearman rank correlation test between chemical oxygen demand COD-Cr and the sampling date for the period 1996-2017

Location	No. of observations	ρ correlation coefficient	p	Significant (p<0.05)	Trend
01 Bazias	298	0.1773	0.0021	YES	↑ increase
02 Gruia*	137	0.3051	0.0003	YES	↑ increase
03 Pristol	332	0.1465	0.0075	YES	↑ increase
04 Jiu*	131	0.7049	5.64E-21	YES	↑ increase
05 Olt*	122	-0.7671	6.96E-25	YES	↓ decrease
06 Oltenita	237	0.6353	3.41E-28	YES	↑ increase
07 Arges	235	0.4831	3.80E-15	YES	↑ increase
08 Chiciu	303	-0.0205	0.7218	NO	
09 Ialomita*	132	-0.0733	0.4033	NO	
10 Siret	232	-0.1802	0.0059	YES	↓ decrease
11 Prut	229	-0.2645	0.0001	YES	↓ decrease
12 Reni	314	-0.1174	0.0376	YES	↓ decrease
13 Chilia	226	-0.1606	0.0157	YES	↓ decrease
14 Sulina	223	-0.2355	0.0004	YES	↓ decrease
15 Sf Gheorghe	220	-0.1955	0.0036	YES	↓ decrease

*Monitoring started in year 2007

In the case of COD-Cr, the situation is different from BOD5 and COD-Mn, because potassium dichromate can oxidise complex organic compounds, which are not biodegradable. The statistical analysis highlights the fact that this type of pollution increases between Baziaș and Chiciu, including Jiu and Argeș rivers, except for Olt river. A possible explanation could be the fact that such compounds cannot be removed by wastewater treatment plants, so that increasing domestic wastewater treatment cannot address this type of pollution. At stations Chiciu and Ialomița the test results are not statistically significant. On the last portion of the Danube, from Reni until the Black Sea, including rivers Siret and Prut, organic pollution has a decreasing trend in time. The increase of COD-Cr on Argeș river during the period 1996-2014 was highlighted in the work [194].

The study carried out by Jaruskova and Liska for the period 1996-2005 has identified decreasing trends at Pristol, increase at Chiciu and Reni, while at Oltenița the result was not statistically significant [11].

The main results obtained in Chapter 5 are synthesised in tables 5.a and 5.b.

Table 5.a. Results of two tailed t test to compare values recorded during the period 1996-2017 at Baziaș to those from the other monitoring stations [189]

Comparison between 01 Bazias and station	Parameter												
	Temp.	pH	DO	Sat O2	BOD5	COD-Mn	COD-Cr	N-NH4	N-NO2	N-NO3	TN	P-PO4	TP
02 Gruia*	ns	ns	ns	ns	<	<	>	<	<	ns	ns	ns	>
03 Pristol	ns	ns	ns	ns	ns	ns	ns	<	ns	ns	ns	ns	ns
04 Jiu*	ns	ns	>	>	>	>	>	<	<	>	>	<	<
05 Olt*	ns	<	ns	ns	<	<	>	ns	<	<	ns	<	<
06 Oltenita	ns	ns	>	>	>	>	>	<	ns	>	ns	<	ns
07 Arges	ns	<	<	<	>	>	>	>	>	>	>	>	>
08 Chiciu	ns	>	>	ns	<	>	>	>	ns	>	>	<	ns
09 Ialomita*	ns	<	ns	ns	>	>	>	>	>	>	>	>	>
10 Siret	ns	>	ns	<	>	>	>	>	>	>	>	<	ns
11 Prut	ns	>	ns	<	>	>	>	>	ns	>	>	<	<
12 Reni	ns	>	>	>	<	>	>	ns	ns	>	>	<	ns
13 Chilia	ns	ns	ns	ns	<	>	>	>	ns	>	>	<	<
14 Sulina	ns	ns	ns	ns	ns	>	>	>	ns	>	>	<	<
15 Sf Gheorghe	ns	ns	ns	ns	<	>	>	ns	ns	>	>	<	<

*monitoring started in year 2007; ns=not significant; > values higher than at Baziaș; < values smaller that at Baziaș; green- better water quality than at Baziaș; red- worse water quality than at Baziaș.

Table 5.b. Long-term trends in main water quality parameters at the analysed stations during the period 1996-2017 [189]

Location	Parameter													
	Flow	Temp.	pH	DO	Sat O2	BOD5	COD-Mn	COD-Cr	N-NH4	N-NO2	N-NO3	TN	P-PO4	TP
01 Bazias	↓	ns	↑	ns	↑	↓	↓	↑	↓	↓	↓	ns	↓	↓
02 Gruia*	-	ns	↑	ns	↑	ns	↓	↑	↓	ns	↓	ns	↓	↓
03 Pristol	↓	ns	↑	↑	↑	↓	↓	↑	↓	↓	↓	ns	↓	↓
04 Jiu*	-	ns	↑	ns	↓	↑	↑	↑	↓	↓	↓	ns	ns	ns
05 Olt*	-	ns	↑	ns	ns	ns	ns	↓	↓	↓	↑	↓	ns	↓
06 Oltenita	↓	ns	↑	ns	↓	↑	↑	↑	↓	↓	↓	↓	↓	↓
07 Arges	↑	ns	↓	ns	↓	↓	↓	↑	ns	↑	↓	↓	↑	ns

08 Chiciu	↓	↑	↑	↑	↑	↓	↓	ns	↓	↓	↓	↓	↑	ns
09 Ialomita*	-	ns	ns	ns	ns	ns	ns	ns	ns	↓	ns	↓	↑	ns
10 Siret	↓	ns	ns	↑	↑	↓	↓	↓	↓	↓	↓	↓	↓	↓
11 Prut	↓	↑	ns	↑	↑	↓	↓	↓	↓	↓	↓	↓	ns	ns
12 Reni	↓	ns	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓	↑	ns
13 Chilia	↓	ns	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓	ns	ns
14 Sulina	↓	ns	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓	ns	ns
15 Sf Gheorghe	ns	ns	↑	↑	↑	↓	↓	↓	↓	↓	↓	↓	ns	ns

*monitoring started in 2007; ↑- values have increased during the analysed period; ↓ - values have decreased during the analysed period; ns=test not significant; green- water quality has improved during the analysed period; red- water quality has declined during the analysed period.

CHAPTER 6. MULTIVARIATE ANALYSIS OF WATER QUALITY PARAMETERS FOR THE PERIOD 1996-2017 AND WATER QUALITY INDEX

In Chapter 5, some of the most important water quality parameters were analysed for the Danube and its main Romanian tributaries, and the long-term trends were assessed at each location. While some parameters had a positive evolution, some have deteriorated, so it was not possible to estimate how the overall pollution in the Danube has evolved during the studied period, and if water quality has improved. Also, it should be mentioned that not all the analysed parameters have the same impact upon the aquatic environment.

Thus, the descriptive analysis study is completed in Chapter 6 by applying multivariate analysis methods: Principal Component Analysis (PCA) and Multiple Factor Analysis, in order to identify which parameters' variation has the strongest influence on the dataset, the correlations between them, as well as the differences between locations. In this way, it can be found which locations are most affected by pollution and which parameters differ most between them.

At the same time, the Water Quality Index in calculated, as a study instrument that is used more and more for water bodies, because it can provide information regarding the overall water quality. The Weighted Arithmetic Water Quality Index Method was used for calculation [77], for which a stepwise methodology is applied, where scaling and weighting the values of monitored parameters according limit values allowed by national standards are important.

The results obtained by applying the Water Quality Index method are presented.

The values obtained for the water quality index are presented in table 6.4. and figure 6.5.

Table 6.4. WQI indices calculated using mean annual values of parameters at the analysed stations during the period 1996-2017 [197]

Location	WQI										
	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006
01 Bazias	30	38	40	29	49	41	32	30	35	41	29
02 Gruia	-	-	-	-	-	-	-	-	-	-	-
03 Pristol	34	37	38	32	45	34	31	29	30	53	31
04 Jiu	-	-	-	-	-	-	-	-	-	-	-
05 Olt	-	-	-	-	-	-	-	-	-	-	-
06 Oltenita	38	34	39	38	44	42	51	37	30	31	33
07 Arges	202	99	115	113	167	132	129	176	117	87	172
08 Chiciu	42	41	45	36	34	38	44	35	64	50	40
09 Ialomita	-	-	-	-	-	-	-	-	-	-	-
10 Siret	95	84	70	43	40	55	45	-	74	91	57
11 Prut	51	59	70	40	47	49	51	-	74	65	50
12 Reni	32	40	44	37	32	35	34	-	41	65	46
13 Chilia	34	40	47	37	26	37	33	-	43	39	40
14 Sulina	36	38	43	36	30	37	35	-	43	40	41
15 Sf Gheorghe	38	38	48	36	28	34	31	-	27	39	41

Locația	WQI										
	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
01 Bazias	34	58	54	28	27	32	26	24	26	-	22
02 Gruia	26	56	53	32	28	31	26	23	26	24	21
03 Pristol	28	60	57	33	30	32	25	22	25	-	21
04 Jiu	46	30	25	28	36	32	27	27	23	27	31
05 Olt	36	-	37	32	27	15	19	26	19	15	16
06 Oltenita	33	27	26	29	29	25	25	26	26	-	33
07 Arges	196	152	124	110	169	217	140	95	-	-	157
08 Chiciu	40	31	35	36	28	26	23	25	27	-	26
09 Ialomita	68	-	-	-	87	247	81	84	51	68	70
10 Siret	39	36	33	36	33	36	35	30	25	-	32
11 Prut	44	30	36	33	29	34	29	31	25	-	27
12 Reni	33	29	28	-	29	33	32	31	-	30	28
13 Chilia	33	31	29	28	26	31	31	31	-	-	29
14 Sulina	33	32	29	28	24	31	30	30	-	-	26
15 Sf Gheorghe	38	32	28	27	28	28	31	30	-	-	27

Based on the WQI values obtained using the weighted arithmetic method, water quality can be assessed according to the ranking presented in table 6.5. [80]. This instrument for assessing water quality was applied in order to compare different analysed stations and to assess the evolution of water quality in time.

Table 6.5. Assessment of water quality according to WQI values calculated using the weighted arithmetic method [80]

WQI	Water Quality
0-25	Excellent
26-50	Good
51-75	Poor
76-100	Very poor
Peste 100	Unsuitable

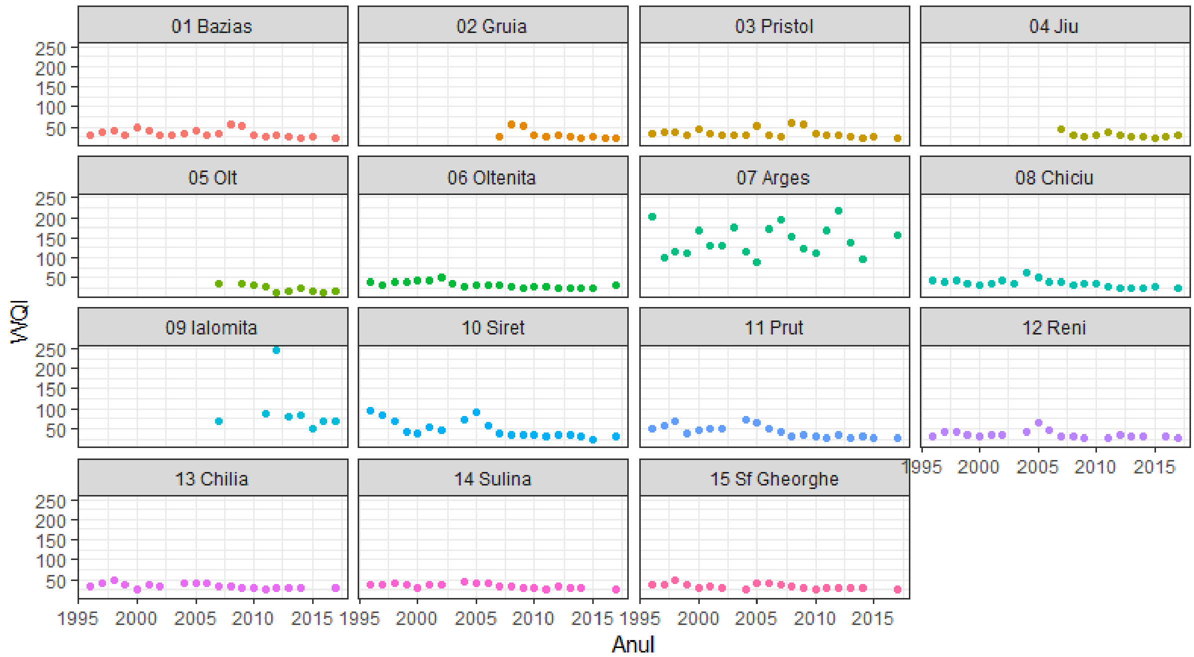

Fig. 6.5. WQI values calculated by the weighted arithmetic method, using mean annual values of selected parameters at the analysed monitoring stations during the period 1996-2017

From figure 6.5., as well as by comparing calculated WQI values from Table 6.4. with the limit values from Table 6.5., it can be noticed that, during the analysed period, the water quality was good, and in most cases the figure suggests an improvement in time, as it resulted in a first analysis of individual parameters, in Chapter 5. Exceptions are the rivers Argeș and Ialomița, which were identified by the multiple factor analysis as extremely polluted.

From figure 6.5 and table 6.4 it can be noticed that at most stations the index tends to decrease in time. At this stage in the research it results that, in the Argeș river, WQI values remain high, indicating a high degree of pollution, for this case a separate analysis being dedicated in Chapter 7, in order to identify eventual sources of pollution. In the year 1996 WQI values range between 30 (Baziaș) and 51 (Prut), while in 2017 they are between 21 (Gruia and Pristol) and 33 (Oltenița) except for Argeș and Ialomița rivers, so overall WQI values have decreased during the analysed period.

The information obtained by calculating the WQI are very useful for assessing how the global water quality has evolved in time.

6.2.2. Evolution in time at analysed stations during the period 1996-2017

The Spearman rank correlation test was applied in order to assess if the evolution trends in WQI values and, consequently, in water quality at the analysed stations during the period 1996-2017, are statistically significant. The results of the Spearman rank correlation analysis between WQI values and the year for which they were calculated are presented in Table 6.7. The table includes, for each analysed station, the number of values from the dataset, the Spearman rank correlation coefficient (ρ), the probability (p) values that the null hypothesis is true (there in no increasing or decreasing trend), the test significance and the WQI trend in time. When correlation coefficients are negative, WQI values decrease in time, so water quality has improved (marked with an arrow pointing downwards ↓), and when they are positive the trend is increasing (marked with an arrow pointing upwards ↑), so water quality has declined.

Table 6.7. Results of Spearman correlation test between WQI and the corresponding year for the period 1996-2017

Location	No. of values	Coefficient of correlation ρ	p	Significant ($p<0.05$)	Trend
01 Bazias	21	-0.5403	0.0126	YES	↓ decrease
02 Gruia*	11	-0.8273	0.0031	YES	↓ decrease
03 Pristol	21	-0.5623	0.0090	YES	↓ decrease
04 Jiu*	11	-0.3818	0.2484	NO	
05 Olt*	10	-0.8061	0.0082	YES	↓ decrease
06 Oltenita	20	-0.7987	0.0000	YES	↓ decrease
07 Arges	20	0.0842	0.7239	NO	
08 Chiciu	21	-0.7429	0.0002	YES	↓ decrease
09 Ialomita*	7	-0.4524	0.2675	NO	
10 Siret	19	-0.8752	0.0000	YES	↓ decrease
11 Prut	20	-0.8195	0.0000	YES	↓ decrease
12 Reni	19	-0.6123	0.0063	YES	↓ decrease
13 Chilia	19	-0.6105	0.0065	YES	↓ decrease
14 Sulina	19	-0.6667	0.0024	YES	↓ decrease
15 Sf Gheorghe	19	-0.5246	0.0228	YES	↓ decrease

*Monitoring started in year 2007

From the p values, it can be seen that they are lower than the significance threshold 0.05, so the tests are significant for 12 out of the 15 analysed stations. At stations Jiu, Argeș and Ialomița p values are higher than 0.05, so the WQI trends in time are not significant.

The values of the Spearman rank correlation coefficients are negative at all locations, except for the Argeș river, which confirms the general trend of water quality improvement.

On Jiu, Argeș and Ialomița rivers water quality trends are not statistically significant ($p>0.05$). At all the other stations, the analysis shows a significant improvement of water quality during the analysed period.

6.2.3. Principal Component Analysis (PCA) and multiple factor analysis for sub-indices

As previously mentioned, PCA has the aim to reduce the number of variables and to identify those parameters whose variation has the highest impact on the dataset. In order to identify which of the 10 parameters included in the WQI have the strongest influence on the Water Quality Index, PCA was applied on the sub-indices $Q_i, \cdot W_i / \sum W_i$ that were used in calculating the WQI.

The results of the PCA analysis on sub-indices in the first and second principal components, after scaling and centring, are presented in figure 6.7.

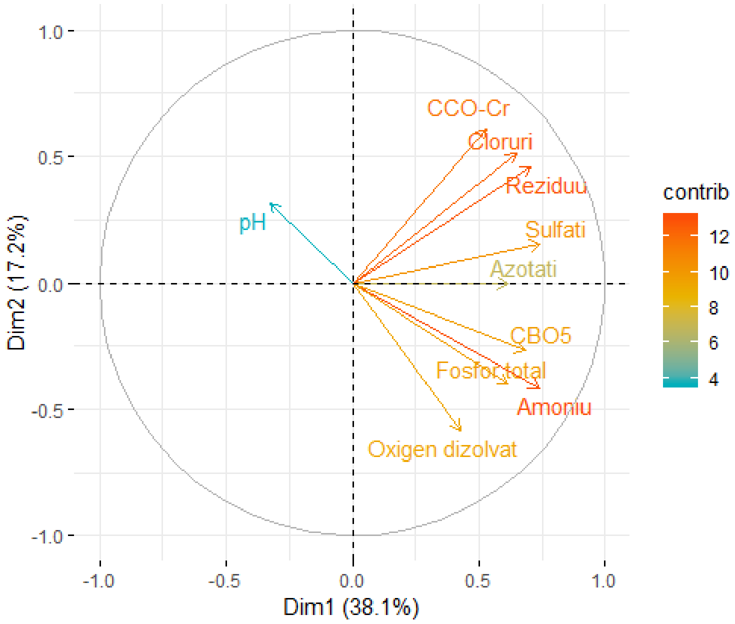

Fig. 6.7. Graphical representation of the first two principal components PC1 (Dim1) and PC2 (Dim2), obtained by applying PCA on water quality sub-indices $Q_i, \cdot W_i / \sum W_i$ after scaling and centring

In Figure 6.7. it can be seen that, in this case, ammonium, chlorides and total suspended solids have the highest variances (the longest arrows), and pH has the smallest (the shortest arrow). Also, strong positive correlations can be noticed between total suspended solids and chlorides, and between total phosphorus and ammonium, as well as negative correlations between pH and total phosphorus and between pH and dissolved oxygen (diametrically opposed arrows). Further positive correlations can be noticed between chlorides and, between sulphates and nitrates, BOD5 and ammonium.

The strong positive correlations between phosphorus and ammonium, as well as their domination on the WQI, suggest as main pollution factor insufficiently treated municipal wastewater discharged into the Danube and its tributaries.

The parameters from the upper-right quadrant of figure 6.7. are positively correlated both with the first principal component PC1 (Dim1), which explains 38.1% of sub-indices variation, and with PC2 (Dim2), which explains 17.2% of the variation. Those from the lower-right quadrant are positively correlated with PC1 and negatively with PC2.

Further on, factor analysis was carried out in order to identify differences in WQI sub-indices according to locations, and the result is presented in figure 6.8.

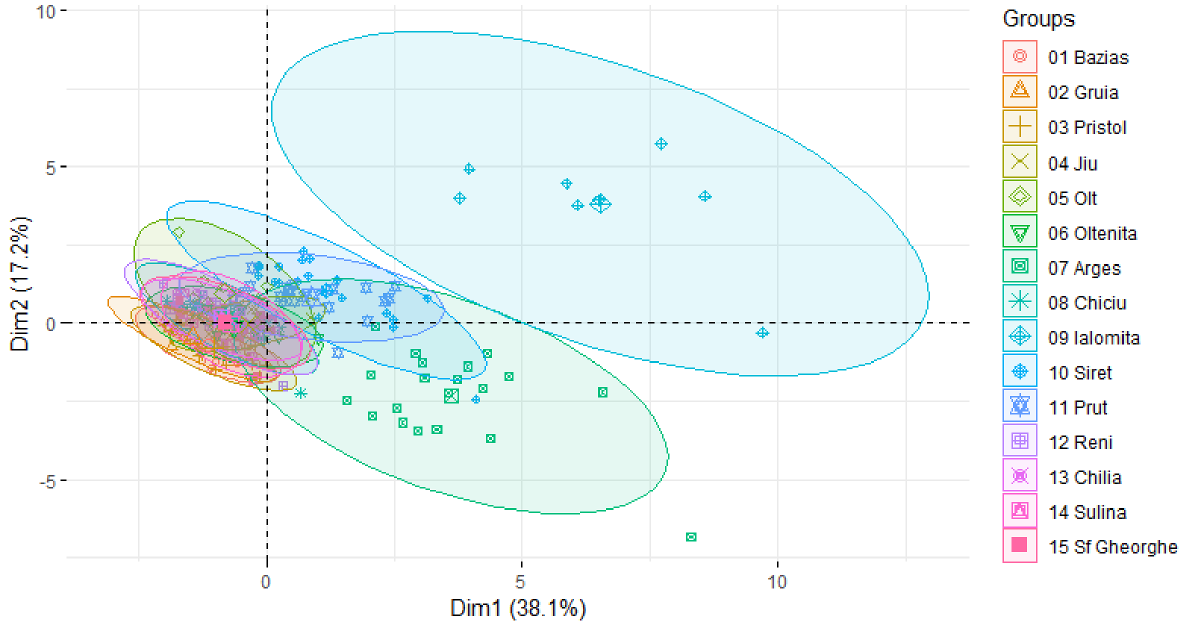

Fig. 6.8. Multiple factor analysis of water quality sub-indices (represented by points) depending on analysed monitoring stations (represented by ellipses) for the period 1996-2017

Also, in the case of WQI, in the rivers Ialomița (light blue ellipse in the upper-right part of figure 6.8.) and Argeș (green ellipse in the lower-right quadrant), water quality is much worse than in the Danube, followed by Siret and Prut, where the values are closer to the ones in the Danube.

Similar results were obtained in the study carried out by Iticescu et al. 2013 in Reni area, using the same calculation method, for the period 2011-2013, on a different set of parameters [152]. In that study WQI values were influenced particularly by Cadmium concentration. Also, these studies have highlighted a seasonal variation in parameters' domination on the dataset.

CHAPTER 7. NUTRIENTS CONCENTRATION ANALYSIS IN THE DÂMBOVIȚA RIVER DURING THE PERIOD 2010-2015

In Romania, nutrients pollution control has already become a concern in the year 2002, when the implementation of the pilot project ”Agriculture Pollution Control” started. The project was carried out during the period 2002-2007 and was funded by GEF (*Global Environmental Facility*), USAID (*United States Agency for International Development*), Romanian Government and co-funded by beneficiaries. Later, during the period 2008-2017, the project ”Integrated Nutrients Pollution Control”, was implemented, where the author of the present work was involved.

The project included the extension of the water quality monitoring network by making new drills, increasing the monitoring capacity, as well as data analysis to assess the efficiency of the implemented pollution abatement measures.

As it was shown in the previous chapters, some of Danube’s tributaries have a high pollution load, originating mainly from sewerage systems of human agglomerations, but also from agricultural sources and groundwater. These are the Argeș river, receiving waters from Dâmbovița river, which crosses Romania’s capital city, Bucharest, and Ialomița river, receiving Prahova and Teleajen rivers.

Bucharest City has a population of over 2 million inhabitants, and, during most of the analysed period, it had no secondary wastewater treatment to reduce nitrogen discharges. As Romania joined the European Union (EU) in 2007, EU wastewater regulations became mandatory, but, at the same time, the EU made available a large part of the funding needed to make investments in this field. Thus, the Bucharest wastewater treatment plant, located in Glina, was upgraded using EU funds, and the first phase of the works was completed in the end of 2011. In this phase, mechanical treatment was ensured for the entire wastewater flow without rain (~10 m^3/s), and advanced treatment (biological nitrogen removal) for half of this flow. The second upgrading phase has started in September 2017, and its completion is expected to ensure advanced treatment for the entire wastewater flow of the city, which is discharged, after treatment, into Dâmbovița river.

The evolution of Dâmbovița water quality during the period 2010-2015 was analysed, based on annual mean values for the nutrients nitrogen (ammonium, nitrites, nitrates, total nitrogen) and phosphorus (orthophosphates and total phosphorus), which are the most important parameters for urban pollution.

The samples were taken from Dâmbovița river, from 8 monitoring stations, which were compared to data from the Argeș river, after confluence with Dâmbovița. The geographical location of the analysed stations and their positioning on the map are presented in Fig. 4.2.

The purpose of this analysis is to highlight the impact that wastewater from Bucharest has on nutrients concentrations in Dâmbovița and Argeș rivers, as well as the way in which pollution levels have evolved during the analysed period.

In a first phase, each parameter was analysed: data were represented in scatterplots and their compliance with quality classes was analysed. Then principal component analysis (PCA) was carried out in order to identify which parameters have the highest influence on the dataset, as well as the correlations between them. Multiple factor analysis was used to highlight differences between the analysed stations and to identify the most polluted ones.

Multivariate data analysis is presented as example.

7.3. MULTIVARIATE DATA ANALYSIS

7.3.1. Principal component analysis (PCA)

In order to assess the influence of all the analysed parameters on the variance of the dataset, the principal component analysis method was applied, highlighting at the same time the influence of the parameters, as well as the correlations between them.

The first two components (PC1 and PC2) explain 88.09% of the variation of the dataset, and the first three components explain 98.66%, so the dataset could be reduced from 6 parameters to 3 principal components without losing essential information.

In PC1 the highest influence is given by ammonium (0.4734), followed by orthophosphates (0.4669), total phosphorus (0.4629) and total nitrogen (0.4519). It is very clear that this component reflects wastewater discharge from Bucharest, from Glina wastewater treatment plant, having a major impact on the dataset (73.39%).

The second component is dominated by nitrates (-0.8955), nitrites having also an influence, but smaller (-0.4049). PC2 reflects the pollution between Arcuda and Dragomirești, which is of a different nature than the one from domestic wastewater, the impact being much smaller than the one from Glina (14.71%).

The first two components (PC1 and PC2) are represented graphically in figure 7.8., in which arrow lengths are proportional with the coefficients of the respective parameters, and angles between arrows reflect correlations between parameters. Narrow angles reflect positive correlations, diametrically opposed arrows reflect negative correlations, and right angles indicate the absence of any correlation.

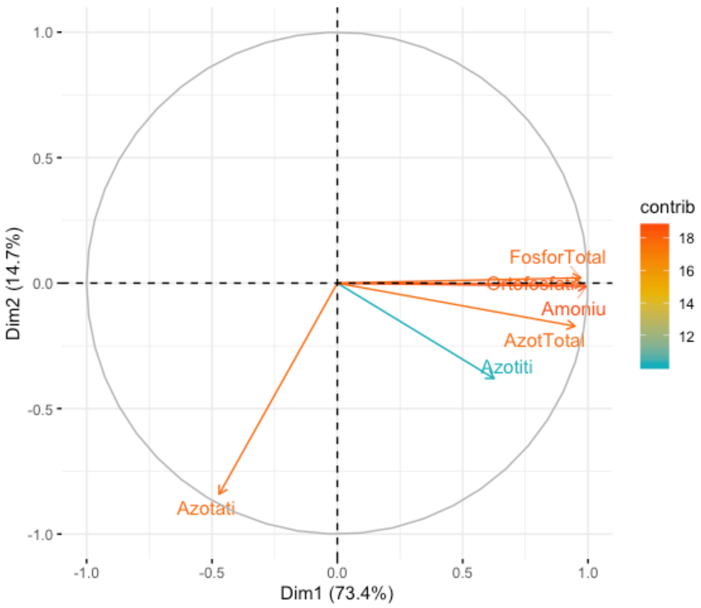

Fig. 7.8. Graphical representation of PC1(Dim1) and PC2 (Dim2) for annual means at analysed stations during the period 2010-2015

In figure 7.8. the major influence of the group ammonium, orthophosphates, total phosphorus can be noticed, which are in a close correlation, the arrows being almost overlapped. Total nitrogen is also positively correlated with ammonium, but the angle between the arrows is larger, because it is also influenced by nitrates.

Nitrates influence is quite high, but it is independent from the other parameters, and nitrites have the smallest influence on the variation of the dataset.

7.3.2 Factor analysis

In order to differentiate at the same time both the influence of the parameters and of the sampling point, the multiple factor analysis method was applied. The results of this analysis are represented graphically in figure 7.9., where ellipses correspond to locations and points represent parameters.

In figure 7.9. in the upper-left area the group of stations 1-4 can be noticed, characterised by reduced pollution, where water quality is mostly in class I. Stations 7-8 (Bălăceanca and Budești) dominate the right side of the figure, being strongly affected by domestic wastewater discharge from Bucharest wastewater treatment plant. The figure also highlights the case of Dragomirești (5) station, located before Dâmbovița river enters Bucharest, which is affected by nitrates pollution.

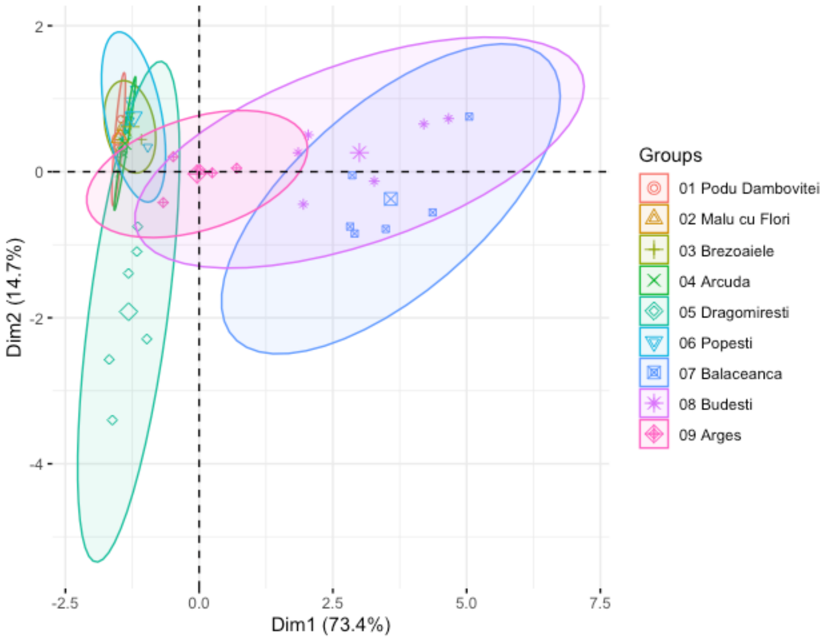

Fig. 7.9. Multiple factor analysis of the dataset of annual means at the analysed stations during the period 2010-2015

The station on the Argeș river (9), located after the confluence with Dâmbovița, is located in the middle, here the pollution level being lower than at stations 7-8, at the same time the water quality being worse than at stations 1-4. The figure suggests that, apart from the fact that the Argeș river has a higher flow than Dâmbovița, it is also less polluted, so that pollutants are diluted at confluence, reducing the impact of Bucharest wastewater upon the aquatic environment.

In the end, a last factor analysis was carried out, to differentiate locations, the results being presented in figure 7.10.

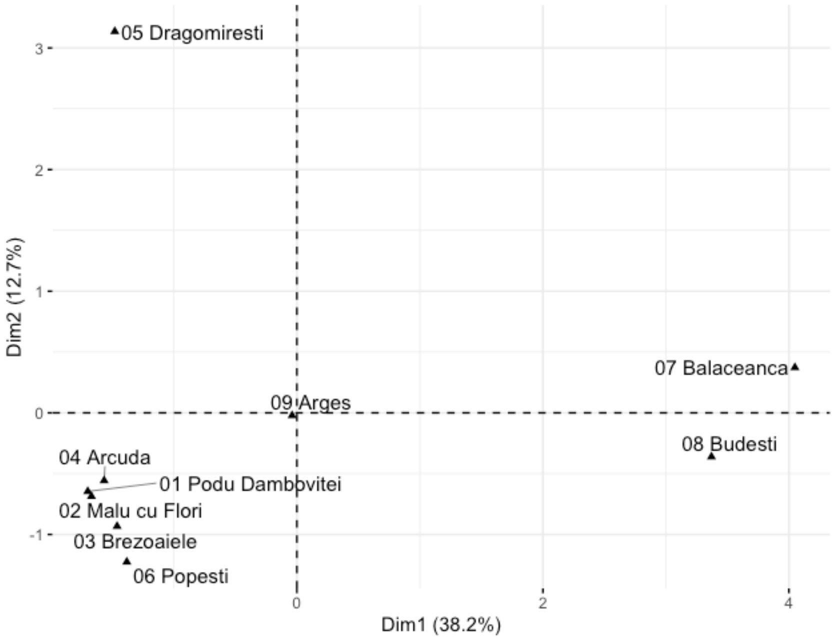

Fig. 7.10. Data analysis according to location, for annual means at Dâmbovița and Argeș stations during the period 2010-2015

The conclusions drawn from the analysis of figure 7.10 are similar to those from figure 7.9. In addition, it can be observed more clearly that the effects of nitrates pollution between Arcuda and Dragomirești are removed by self-purification, so that downstream, at Popești, before Glina, water quality is close to the one upstream, from stations 1-4.

The discharge of domestic wastewater from Bucharest Municipality has a major impact upon Dâmbovița water quality, highlighted by severe pollution with ammonium and phosphorus, as it results from the analyses carried out in this chapter.

A study carried out by Ionescu et al. in June 2018 in the area of confluence between Dâmbovița and Argeș also highlighted the fact the ammonium was in class V in Dâmbovița river before confluence, in class I in the Argeș river before confluence, and in class IV in Argeș after confluence [20], which shows that the problem persisted in the years after the period analysed in this work.

GENERAL CONCLUSIONS

Trend analysis of water quality parameters is of high interest for researchers and authorities because it provides information regarding the long-term changes taking place in the river basin and allows the assessment of the efficiency of the measures taken for pollution abatement, in the context of national and international commitments.

The present work is in line with national and international scientific interest in integrated management of water resources in general, and the interest of Romanian scientists regarding the trends in Danube water quality. The study is focused on the Lower Danube and on the main Romanian tributaries at 15 monitoring stations by analysing 14 parameters. Also, for the Argeș river, which is highly polluted, a case study is focused on Dâmbovița river, which receives wastewater from the Bucharest treatment plant, at 8 monitoring stations, for 6 parameters that are important for urban pollution. Thus, a first step is done towards water resources management, monitoring and data analysis, required for the next steps of forecast and intervention.

The analysis of Danube water quality parameters for the period 1996-2017

Water quality parameters' trends in time for the period 1996-2017

- Results of the Spearmen rank correlation statistical analysis between parameter values and sampling date, highlighting evolutive trends in time (increasing or decreasing), significant or not, for the analysed parameters at each station during the period 1996-2017, are presented.
- From the analysis of existing data regarding the daily average flow at 11 stations, at 9 stations flows have decreased significantly during the analysed period, on the Argeș river they increased, and at Sf. Gheorghe the result is not statistically significant.
- Water temperature only had significant changes from the statistical point of view at 2 of the 15 analysed stations, Chiciu and Prut, where there is an increasing trend. The data from the period 1996-2017 reflects a normal thermal regime, with no anomalies, typical for a temperate climate, with a mean water temperature around 14ºC.
- pH has increased at 11 out of the 15 analysed stations, decreased in Argeș river, and at Ialomița, Siret and Prut the result of the analysis was not significant. The wide majority of data are in the 6.5-8.5 range specified in Romanian norms.
- Dissolved oxygen increased at 8 stations (located towards the Danube mouths), reflecting an improvement in water quality, and at 7 stations the result of the analysis was not significant. Over 75% of the values are in the quality classes I and II (>7 mg O_2/L). On the Argeș river, the values are lower than at the other stations, but over 50% of the values are in the classes I and II.

- Oxygen saturation has increased at 10 stations, has decreased at 3 (in the rivers Jiu, Oltenița and Argeș) and had no significant change at 2 locations (Olt and Ialomița). Over 75% of the values are in quality class I, so oxygen saturation was very good in the analysed period.
- BOD5 and COD-Mn trends were similar, with a significant increase on Jiu river and at Oltenița, while at most of the other stations water quality has improved.
- Biochemical oxygen demand BOD5 has decreased at 10 stations, has increased at 2 stations (Jiu and Oltenița), and had no significant trend at 3 stations (Gruia, Olt and Ialomița). Over 75% of the values are in quality classes I and II (<5 mg O_2/L), with higher values in rivers Jiu, Argeș and Ialomița, as well as at Oltenita.
- Chemical oxygen demand COD-Mn has decreased at 11 stations, has increased in Jiu river and at Oltenița, and there was no significant trend at 2 stations (Olt and Ialomița). Over 75% of the values are in quality class I (<5 mg O_2/L), except for the rivers Argeș, Ialomița and Siret, where the values are higher.
- COD-Cr has increased significantly in time on the first segment of the Danube, from its entry into the country to Chiciu, but on the last segment, from Reni to the Black Sea, pollution with organic compounds has decreased during the analysed period. Around 75% of the values are in quality class I (<10 mg O_2/L) at the entrance into the country and in class II (<25 mg O_2/L), at the Danube mouths, at the Black Sea, but there are also much higher values, particularly in the Ialomița river.
- The long-term trends in nitrogen parameters (N-NH4, N-NO2, N-NO3, TN) show a significant improvement of water quality during the analysed period at most of the selected stations, and particularly on the last segment of the Danube, from Reni to the Danube mouths, as well as on the rivers Siret and Prut. The decrease of ammonium concentrations may be an indication of improved wastewater treatment capacity in the localities that are discharging into the Lower Danube basin.
- Ammonium has decreased at 13 stations, and at 2 stations (Argeș and Ialomița) there were no statistically significant trends. Over 75% of ammonium values are in quality class I (<0.4 mg N/L), except for the tributaries Argeș and Ialomița, ammonium pollution being an indication of discharges of insufficiently treated municipal wastewater.
- Nitrites have decreased at 13 stations, at Gruia there were no significant changes, and in the Argeș river values have increased during the analysed period. Over 50% of the values are in quality classes I and II (<0.03 mg N/L), except for the rivers Argeș and Ialomița.
- Nitrates have decreased at 13 stations, have increased in Olt river had no significant change in Ialomița river. Over 75% of the values are in quality classes I and II (<3 mg N/L) at all analysed stations.
- Total nitrogen has decreased at 9 stations, and at 4 stations there were no significant trends. All values are in quality classes I and II (<7 mg N/L) at all stations, except for the rivers Argeș and Ialomița, where over 75% of the values are in the first two classes.
- Phosphorus parameters (P-PO4 and TP) have decreased on the segment from Baziaș to Oltenița, then they decreased or had no significant trends on the last segment of the Danube.

- Orthophosphates have decreased at 5 stations, from Bazias to Oltenita, have increased at 4 stations (Arges - Reni), and had no significant trends at 6 stations. Over 75% of the values were in quality class I (<0.1 mg P/L), except for the rivers Argeș and Ialomița, where the values were higher.
- Total phosphorus has decreased from Bazias to Oltenița and had no significant trends at 9 stations, from Chiciu to the mouths. Over 75% of the values were in quality class I (<0.15 mg P/L), except for the rivers Argeș and Ialomița, where most of the values were in class II.

Comparison between the values at Baziaș and those at the Danube mouths, at the Black Sea (Chilia, Sulina, Sf. Gheorghe)

- The results of applying ANOVA analysis of variance and the t test to compare the values at Baziaș to those from each of the other stations, to assess the spatial evolution of water quality, in the sense of improvement of decline, from the entrance in Romania to the mouths, at the Black Sea, are presented.
- For water temperature, pH, dissolved oxygen, oxygen saturation and nitrites there are no significant differences between the values at entrance and exit from the country.
- 5 days biochemical demand (BOD5), orthophosphates and total phosphorus had lower values at exit than at entrance into the country during the studied period (except for BOD5 at Sulina, where the difference is not significant), which indicate a lower level of pollution on the Romanian segment than upstream.
- Chemical oxygen demand (COD-Mn for oxidising biodegradable organic substances and COD-Cr for oxidising both biodegradable and not biodegradable organic matter), ammonium, nitrates and total nitrogen had higher values at exit from the country than at the entrance (except for ammonium at Sf. Gheorghe), indicating an increased pollution on Romanian territory compared to upstream values. However, the biodegradable compound load is low, COD-Mn values at stations on the Danube being in quality class I up to the 3rd quartile, even at the Black Sea mouths. Regarding COD-Cr, mean values are in quality class I at entrance into the country and in class II at exit.

Multivariate data analysis

- Principal Component Analysis, PCA, was carried out using annual mean values for 12 parameters at the 15 selected stations. It provides information regarding the parameters that have the highest influence on the dataset, as well as correlations between parameters.
- In PC1, the parameters with the most important contribution are ammonium, sulphates, total phosphorus and BOD5, and this component explains 36.77% of the variance of the dataset.
- In PC2 the parameters with the highest contribution are COD-Cr and chlorides, and this component explains 17.10% of the variance of the dataset.
- The first 6 components explain together over 80% of the variance of the dataset, so the number of variables could be reduced from 12 to 6 without losing essential information.
- Strong positive correlations we noticed between dissolved oxygen (DO) and pH, between chlorides and total suspended solids, between sulphates and nitrates, and

negative correlations between DO and orthophosphates and between pH and total phosphorus.

- Multiple factor analysis (which considers at the same time both the water quality parameters and the sampling location) highlights the pollution in the tributaries Argeș and Ialomița, wich are clearly differentiated from the other analysed stations. The Argeș river is more affected by the total phosphorus – ammonium group, and the Ialomița river by the group COD-Cr, chlorides, total suspended solids. COD-Cr indicates pollution with organic compounds. These aspects were highlighted for each parameter by descriptive statistics and t test.

Water Quality Index (WQI)

- The water quality index (WQI) method was applied as an instrument for global evaluation of Danube water quality, which is useful for assessing if water is suitable for different uses, quality evolution in time and identification of eventual sources of pollution.
- The weighted arithmetic method was used for WQI calculation, using 10 water quality parameters that were carefully selected and their annual means from the period 1996-2017, for the 15 analysed stations. The weighting was done using limit values for quality class II, according to national standards for the respective parameters.
- Out of the 260 calculated WQI values for the 15 analysed stations, 23 values ranged between 0-25 (*excellent* quality), 186 ranged between 26-50 (*good* quality), 23 between 51-75 (*poor* quality), 9 between 76-100 (*very poor*), 17 over 100 (*unsuitable*).
- Over 80% of the calculated values indicate *excellent* or *good* water quality (values between 0-50).
- The analysis in time of WQI values highlighted significant improvement of water quality at 12 (Baziaș, Gruia, Pristol, Olt, Oltenița, Chiciu, Siret, Prut, Reni, Chilia, Sulina, Sf. Gheorghe) out of the 15 analysed stations. For the other 3 stations (Jiu, Argeș and Ialomița) the results were not statistically significant.
- In the Argeș river, water quality was *very poor* or *unsuitable* during the entire analysed period.
- The WQI method is useful for assessing overall water quality and, in particular, for analysing long-term water quality trends. It also highlights the differences between the analysed monitoring stations, which are in agreement with those obtained through the other analyses and complete them.

Analysis of nutrients concentrations in the Dâmbovița river during the period 2010-2015

- Mean annual values from 8 monitoring stations located on Dâmbovița river were analysed, and they were compared to those from the Argeș river, after confluence with Dâmbovița. 6 stations are located upstream from Bucharest wastewater treatment plant in Glina, and 2 stations are located after Bucharest wastewater discharge into Dâmbovița river.
- Water quality was, in general, in class I upstream from Glina, and in classes IV and V downstream, after receiving municipal wastewater.

- Domestic wastewater pollution is characterised by high values for ammonium, nitrites, total nitrogen, orthophosphates and total phosphorus. Nitrates values remain in class I downstream from Glina.
- Between Arcuda and Dragomirești, there is a nitrates pollution source (possibly from agricultural activities), which does not affect downstream stations, values going back to class I at Popești.
- The level of pollution produced by Bucharest wastewater discharge is diminished after the confluence between Dâmbovița and Argeș by dilution.
- It is necessary to improve the treatment capacity of Glina wastewater treatment plant in order to reduce pollution of Dâmbovița river and, consequently, of the Argeș and Danube rivers, with nitrogen and phosphorus compounds.

The statistical analysis and data processing methods applied in this work are useful in analysing complex datasets, in order to extract important information, to assess evolutive trends and to identify eventual correlations between different parameters, to support authorities in making decisions and developing action plans for achieving environmental objectives.

Even if pollution levels in some tributaries are much higher than in the Danube, this does not affect significantly Danube water quality, because its flow is much higher than those of the tributaries.

Overall, during the analysed period Danube water quality was good (the analysed parameters were mostly in quality classes I and II), and values have improved in time for most of the analysed parameters.

Original contributions

This work represents a basis for further studies regarding the Danube, and the results may be used in various practical and theoretical application areas.

For the first time, a wide study in time and on a large area was carried out concerning Danube water quality and Dâmbovița river, around Bucharest city, which drains insufficiently treated sewerage water into Dâmbovița, further reaching Argeș and Danube rivers.

Available data were analysed for 14 important water quality parameters for a period of 22 years (1996-2017) for the Danube on Romanian territory, and data were obtained and analysed for Dâmbovița water regarding 6 parameters related to nutrients nitrogen and phosphorus, which represent the most important urban pollution parameters, for a period of 6 years (2010-2015).

Complementary descriptive and multivariate, complex statistical methods were applied, in order to assess the values determined at different monitoring stations against limit values set by Romanian water quality norms and to evaluate the way values have evolved during this period.

New types of analysis, that were not applied by other researchers, were carried out for the proposed locations. Thus, parameters' values at entrance into the country were compared with downstream values, as well as with those from the main Romanian tributaries (t test).

PCA analysis was applied for mean annual values, and the parameters with the highest variations (in time and between analysed stations) were identified and correlations between parameters were highlighted.

By factor analysis, the differences between Danube and tributaries water quality were identified, particularly for Argeș and Ialomița rivers.

Water quality was assessed using the Water Quality Index method (WQI) and its evolution in time was analysed at the selected stations.

Nutrients pollution of Dâmbovița river and the role played by Bucharest Municipality wastewater treatment plant during the period 2010-2015 were analysed.

FURTHER DEVELOPMENT PERSPECTIVES

Study and selection of a water quality modelling and forecast software. Use of research results to make predictions regarding future water quality trends.

Identification of organic pollution sources on the Ialomița river, which lead to increased chemical oxygen demand COD-Cr.

Use of data for a complex study including water, suspended matter and sediments for the same period of time.

Follow-up on Dâmbovița river water quality after the year 2015 to assess the performance of the Glina wastewater treatment plant after completion of the second extension and upgrading phase of construction works.

PUBLICATIONS

PUBLICATIONS IN THE FIELD OF THE THESIS

ISI articles in the field of the thesis

- ***R.M. Frincu****, O. Iulian*, Long-term Trends in Water Quality Indices in The Lower Danube (1996-2017), Ecohydrology & Hydrobiology (in press), FI=1.877.
- ***R.M. Frincu****, O. Iulian*, Long-term Water Quality Trends in The Lower Danube (1996-2017), UPB Scientific Bulletin, (in press).
- ***R.M. Frincu****, C. Omocea, C. Eni, M.E. Ungureanu, O. Iulian,* ”Seasonality and Correlations between Water Quality Parameters in the Lower Danube at Chiciu for the Period 2010-2012”, Rev. Chim., **vol. 71(2)**, 2020, pp. 449-455, FI-1.755.

National and international conferences participation

- ***R.M. Frîncu****, O. Iulian*, ”Long Term Trends of Oxygen Parameters in the Lower Danube (1996-2014)”, poster, International Conference CHIMIA 2018 "New trends in applied chemistry", 24-26 May 2018, Constanta, Romania, Book of Abstracts, pp. 53, ISSN 2360-3941.
- ***R.M. Frîncu****, O. Iulian*, ”Organic pollution in the Lower Danube and Romanian Tributaries (1996-2014)”, poster, 20th Romanian International Conference on Chemistry and Chemical Engineering, RICCCE, 2017, 6-9 Sept. 2017, Poiana Brasov, Romania.
- ***R.M. Frîncu****, O. Iulian*, ”Trends in Nutrients Concentrations in the Lower Danube (1996-2012)”, comm., International Symposium: Priorities of Chemistry for a Sustainable Development - PRIOCHEM, ed. XII, 27-28 Oct. 2016, Bucharest, Book of Abstracts, pp. 71, ISSN 2285 8334.

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