

DANUBE – QUALITATIVE CHARACTERISTICS OF THE WATER IN THE PONTIC SECTOR

ELENA ȚUCHIU¹

Abstract. Danube - Qualitative characteristics of the water in the Pontic sector. The article analyses the spatial and temporal variation in the lower Danube sector of the physico-chemical quality indicators, selected to reflect the general characteristics and the effect / impact of the main pressures identified at basin level for the period 1996-2015, in 6 monitoring sections (from Baziaș to Reni). Based on the minimum, average and maximum multi-year values for all physico-chemical determinants that reflect the degree of variability of the values of the concentrations monitored for the analysed periods, they were interpreted in particular from the perspective of the interdependence between these parameters, their behaviour, the aquatic transformations / reactions, as well as from the point of view of correlation with the contribution of tributaries and sources of pollution. Longitudinal (upstream / downstream) variations have also been established over the 20-year period, concluding that most determinants / pollutants have an increasing spatial trend. From a temporal point of view, all determinants analysed from the point of view of the water quality improvement trends were determined, namely the temporal trends (especially in the Reni section) and the possible causes of variation were identified.

Key words: monitoring program, physico-chemical parameters, water quality, spatial and temporal analysis and trend

1. INTRODUCTORY ASPECTS

The Danube Transnational Monitoring Network (Danube Transnational Monitoring Network - TNMN) of the International Commission for the Protection of the Danube River (ICPDR) was implemented in 1996 and had the initial objective to develop the monitoring network and programs in view of ensuring trend analysis concentrations and loads of relevant pollutants, supporting water quality analysis and assessment, and identifying the contribution of major sources of pollution.

The criteria based on which the TNMN monitoring sections were established according to the ICPDR methodologies are the following: upstream and downstream crossing of the international borders (for the Danube and for the main tributaries), *localization at the confluence between the Danube and the main tributaries, or between the main tributaries and secondary ones, but with*

¹ Romanian National Water Administration

significant cross-border influence on water quality, downstream localization of important point sources of pollution; location upstream of main water uses, especially for drinking water; location in or near hydrometric stations to obtain flow data used to calculate the load transferred / transported across national boundaries of states and to the marine environment (Black Sea). In 2000, TNMN's main objective was developed to reflect the state of water (according to the Water Framework Directive) and on long-term the water quality and water constituents and pollutants loads for the Danube River and the main rivers in the Danube basin, in an international context. Thus, on the basis of the monitoring data, the nutrient loads transported by the Danube to the Black Sea are calculated by linking the Black Sea eutrophication process (the North-West area) and the effect of the measures implemented in the Danube basin to reduce nutrients discharges and emissions (forms of nitrogen and phosphorus). The implementation of the Water Framework Directive (2000/60 / EC) after 2000 required the review of the TNMN, a review process that was finalized in 2007, with the implementation of the Report on Monitoring Programs from the Danube River International Hydrographic District, in accordance with the requirements of Article 8 of the Directive. In 2015, TNMN monitoring was carried out by sampling and analysis of 156 monitoring points (profiles), located in 110 sections, of which 74 monitoring points, related to 39 sections located on Danube and 82 monitoring points corresponding to 71 sections located on the main tributaries of the Danube (Fig. 1).

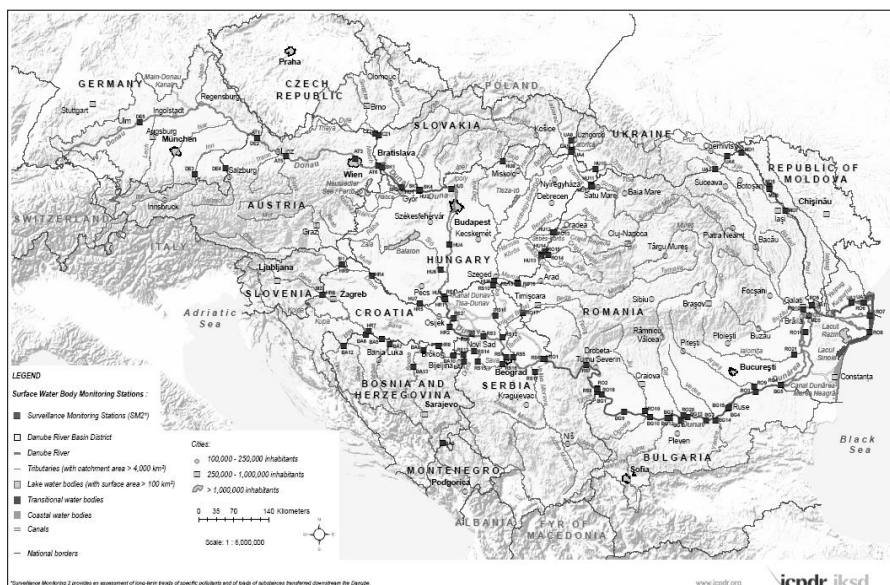


Fig.1. Danube Transnational Monitoring Network - TNMN (Source: ICPDR)

The TNMN monitors a basic (common) number of parameters, namely *1 hydrological* (water flow), *31 physico-chemical* (general indicators, parameters of the oxygen regime, nutrients, heavy metals and metalloids in dissolved form and organic micro-pollutants) and *2 biological elements* (phytoplankton - chlorophyll a and benthic invertebrate - macrozoobenthos) (TNMN Yearbook 2015). According to the procedures for producing primary data for the TNMN network, the main primary data producers are the laboratories of the water management authorities, the research institutes and the environmental protection agencies, as the case may be, from the Danube countries (eg "Apele Române" National Administration - through the two Reference Laboratories (Jiu Basin Water Administration and Dobrogea- Litoral Water Basin Administration in the case of Romania). The water quality analysis of the Lower Danube river sector (Bazias - Isaccea sector) was performed at the level of the 6 sections part of the TNMN (Table 1)

Table 1. TNMN sections from lower Danube and their localisation

Section	Section code	Profile*	Km of river	Section altitudine	Basin surface (kmp)
Bazias	RO1	L,M,R	1071	70	570.896
Gruia	RO18	L,M,R	851	32	577.085
Pristol	RO2	L,M,R	834	31	580.100
Amonte Argeş	RO3	L,M,R	432	16	676.150
Chiciu	RO4	L,M,R	375	13	698.600
Reni	RO5	L,M,R	132	4	805.700

*monitoring points: L-left bank, M-middle, R-right bank

2. DATA AND METHODS

In the present paper, the analysed period is 1996-2015 (20 years) for all sections except for the Gruia section, which is monitored since 2007. In general, the primary monitoring data for the physico-chemical parameters measured within the TNMN network are produced with monthly frequency except Pristol, Chiciu and Reni sections with bi-monthly frequency. The set of indicators selected for **physico-chemical** quality assessment included the **general indicators** (*thermal regime - water temperature, suspended matter, acidification status - pH and alkalinity; cations - sodium, potassium, calcium and magnesium, anions - chlorides and sulphates*), **oxygenation conditions** (*dissolved oxygen, organic substances measured by CBO₅*), **nutrients** (*nitrates and orthophosphates*).

3. RESULTS AND DISCUSSIONS

3.1. Analysis of the physico-chemical quality of the Danube's lower / Pontic sector

3.1.1. General indicators

Water temperature is a physical feature, its knowledge being useful in the use of water for various purposes (eg. cooling water), but also a factor influencing aquatic chemistry and ecosystem. From a natural point of view, the process of cooling and heating the aquatic environment is governed by the intensity of solar energy. Thus, the variation of the water temperature depends on the daily and annual variation of the solar radiation intensity, in the absence of hot water discharges (sources of thermal pollution). Its long-term measurement can show the impact of climate change and its analysis, in conjunction with other physico-chemical and biological data, shows that it is an important factor influencing chemistry (eg. oxygen levels in the water, the concentration of oxidized forms such as nitrates) and the state of the aquatic ecosystem. In the lower Danube sector, **the water temperature** varied between 0°C and 32°C (at Chiciu in 2001), depending on the air temperature and the moment of measuring this indicator, considering the daily and annual variation of the solar radiation intensity. Compared with the variation of the air temperature, the variation of Danube's water temperature is much reduced in the lower sector due to the high water volume.

The average multiannual temperature (1996-2015) varied from 14°C (at Baziaș), 14.6°C (in Oltenița) and 14.3°C (at Reni), so the multiannual average temperature has a increasing trend in spatial profile (from upstream to downstream), being a consequence of thermal inertia (Fig. 2).

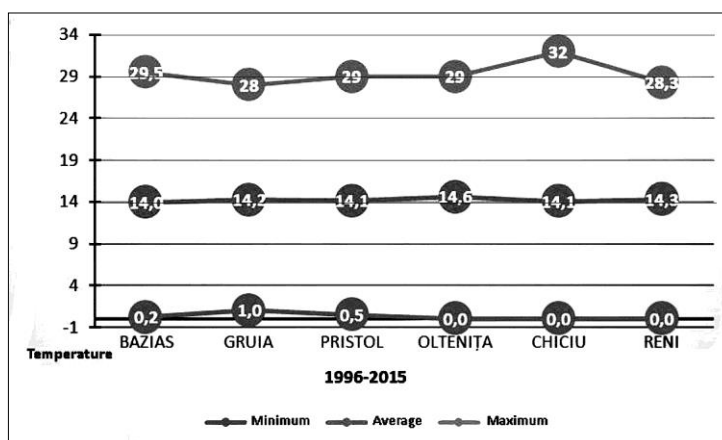


Fig. 2. Variation of multiannual minimum, average and maximum water temperature values

From the calculation of the minimum multi-annual values in the 6 sections analysed on the lower sector there is a small variation of water temperature between 0°C at most sections, and up to 1°C at Gruia. In terms of temporal variation (1996-2015), the annual average temperature at Reni has a slightly linear decreasing trend, as shown in Fig. 3. It is noted that the highest annual average temperatures were recorded in 2000, when in three sections (Oltenița, Pristol and Reni) they had high values of 16.7°C, 17.4°C and 18°C, respectively.

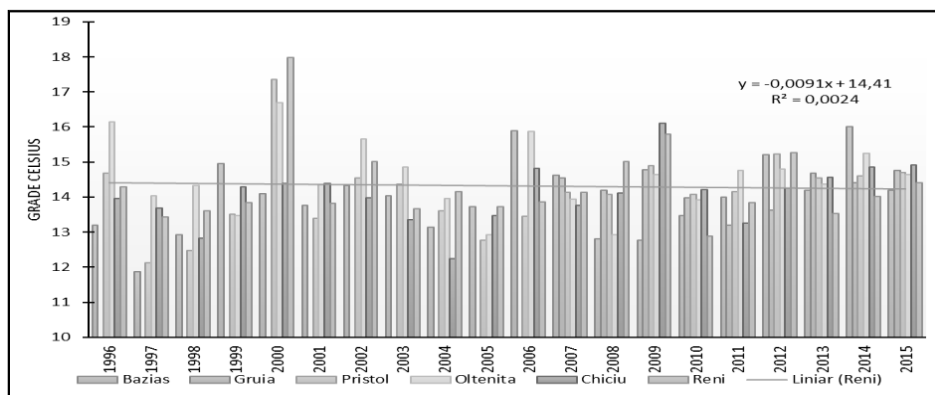


Fig. 3. Variation of annual average water temperature values

Suspended matter. Their concentration generally varies according to a number of factors such as the relief, the type of soils and their degree of coverage with vegetation, the nature and intensity of the precipitation, the loading of discharged waste water, as well as the existence of hydro-technical works and ballasts. The total suspended matter has mineral origins from erosion processes as well as anthropogenic ones; organic origin from the washing of vegetal and animal remains from the river basin, as well as from anthropogenic activities (discharges of waste water and products, including microplastics). In general, the maximum amounts of suspended matter are measured during the flood, due to washing, erosion and transport processes.

The data analysis shows that the mean annual concentrations of suspended matter decrease slightly from Baziaș to Pristol (from 37 to 35 mg / l), then increase significantly in the Oltenița section (57 mg / l), again decreasing to 36 mg / l at Reni. The highest recorded value was 898 mg/l at Chiciu in 2005 and the minimum in the analyzed period was 1 mg / l at Oltenița (2011), Chiciu (in 2002 and 2011) and Reni in 2004 (Fig. 4).

The higher annual average values of suspended matter recorded at Chiciu and Oltenița may be due to the contribution of Jiu, Olt, Vedea and especially Argeș rivers, with the anthropogenic influence of the lack of water treatment in Bucharest until the construction and operation of the Glina station. Lower values of

suspension concentrations recorded at Baziaș are explained by sedimentation processes due to the slowing of the water velocity in the Iron Gates reservoir, respectively the barrier and the loss of longitudinal continuity of the sediments.

As shown in Fig. 5, the tendency for temporal variation of suspended matter is increasing at Reni, and the highest annual average values (over 80 mg/l) were recorded at Oltenita in 1999, 2001-2003, 2005 and 2007, and Chiciu respectively in 2005. The lowest annual average values (below 15 mg/l) were recorded at Chiciu between 2002-2003 and Reni in 2003.

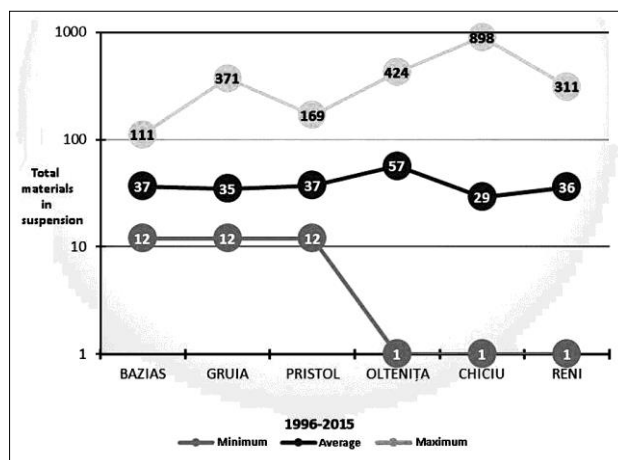


Fig. 4. Variation of multiannual minimum, average and maximum suspended matter concentration

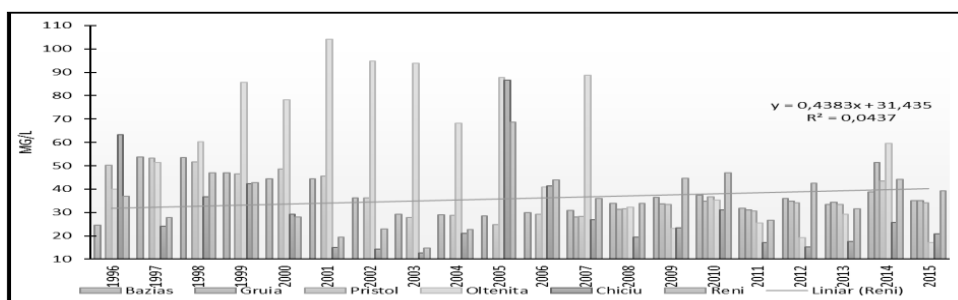


Fig. 5. Variation of annual average suspended matter concentration

The concentration of hydrogen ions (pH) varies depending on the chemical water content (the content of acids, salts and other substances) due to the erosion processes and the content of the rock and pollution sources. The water pH measures the ability of the aquatic environment to buffer acidic solutions (eg. acid

rain) or alkaline solutions due to the presence in the aquatic environment of weak acids and bases, as well as salts.

The pH level indicates a slightly alkaline environment in the lower Danube sector. The lowest measured values (<6,5) in the period 1996-2015 were 6.2 (recorded at Baziaş in 1996), 6.45 (Oltenița in 2014) and 6.3 (at Reni in 2002, respectively 2005). The maximum value for the analysed period was 9.47 (recorded at Chiciu in 2014). Spatial variation indicates a slight increase in the minimum and maximum pH values from Baziaş to Reni.

Slightly basic values in the lower sector are determined by the presence of sodium, calcium and potassium bicarbonates and carbonates, also showing the influence of primary productivity (production of phytoplankton) in conjunction with oxygen level and organic matter loading, as well as a good buffering capacity.

Alkalinity is conferred by the content of bicarbonates, hydroxides and, to a lesser extent, by the concentrations of phosphates, silicates, borates or acid sulphides in water. The water alkalinity reflects its ability to neutralize hydrogen ions and can be defined by excess positive loads over negative ones, being affected by the dissolution of bicarbonates. Generally, an alkalinity above 0.5 mmol/l shows a very good water buffering capacity.

For the period 1996-2015, according to the results of the monitoring, the multiannual average values of alkalinity in the Romanian Danube river sector are in the range 3.0 mmol/l (at Baziaş, Gruia, Pristol and Reni) and 3.1 mmol/l Oltenița and Chiciu), having a quasi-constant spacial profile.

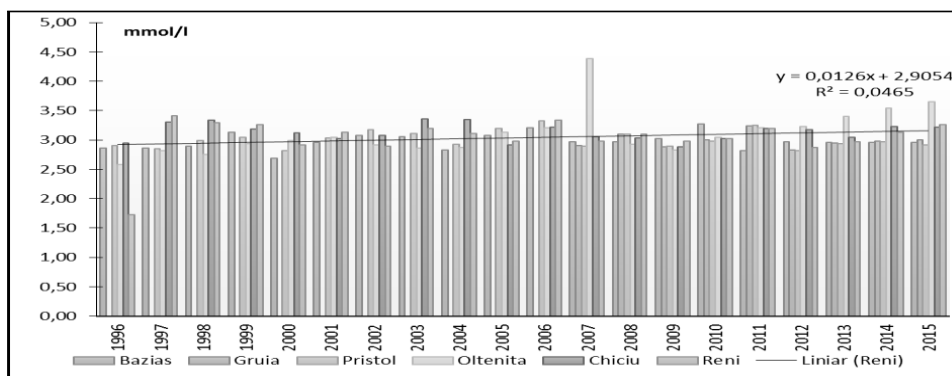


Fig. 6. Variation of annual average alkalinity values

Also, the multi-annual minimum alkalinity values for the same period range from 0.1 mmol/l at Reni and 2.4 mmol/l at Gruia, maximum values ranging from 4.0 mmol/l (at Gruia) to 18.7 mmol/l. The value of 18.7 mmol/l is an extreme value, recorded on 21.09.2007 at Oltenița (at a $Q_{\text{daily average}} = 6600 \text{ mc/s}$) measured in the middle profile, was validated by two other values of 18.6 mmol/l recorded in

the same section in the left and right bank profiles. On the same date, on the Arges River, there was an alkalinity value of 18.9 mmol/l and an ammonium value of 7.42 mgN/l, extreme values also.

From the space-time point of view, Fig. 6 shows that the Reni monitoring section presents an increasing trend of the annual average values for alkalinity in the period 1996-2015, according to the equation of the linear trend. Also, higher levels of annual mean alkaline values occurring in the Chiciu monitoring section are observed in 2007 and 2013-2015.

Cations (sodium, potassium, calcium and magnesium). The cations together with the anions (chlorides, sulfates, bicarbonates) form the major dissolved chemical constituents of the water and give it mineralization.

Sodium is found in water in the form of dissolved salts, especially chlorides and sulphates. The main source of sodium in surface waters is volcanic and sedimentary rocks from the river basin, which are washed by precipitation and drainage. At the same time, groundwater can contribute to increasing the sodium content of surface water. Also, water pollution from household wastewater and industrial wastewater (chemical, chlor-sodium, food, etc.) can lead to increased sodium levels in surface water.

From the data analysis of the period 1996-2015 it is observed that the value of the multiannual average **sodium** concentration in the lower Danube sector is spatially increasing from Baziaș to Chiciu (from 16.8 to 21.3 mg/l), then slightly decrease in Reni section (19.6 mg/l).

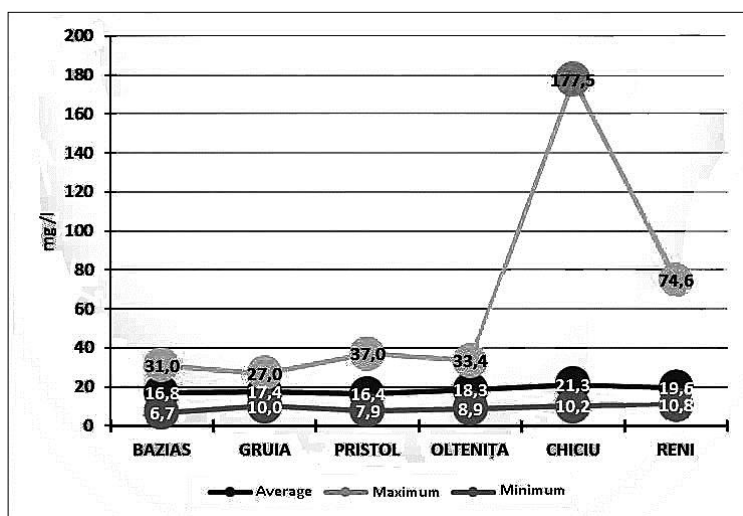


Fig. 7. Variation of multiannual minimum, average and maximum sodium concentration values

The maximum annual value of 177.5 mg/l (extreme value) was recorded at Chiciu in 2006 (23.08.2006), on the left bank profile, while on the right bank and in the middle were measured values of 171,4 mg/l. The minimum value recorded during the analysed period was 6.7 mg/l at Baziaş in 1999 (Fig. 7).

From a temporal aspect, Fig. 8 shows that in the Reni monitoring section there is a decreasing trend of the annual average values of sodium for the period 1996-2015, according to the equation of the linear trend. Also, a higher level of the annual average of sodium in the Chiciu monitoring section is observed in 2006.

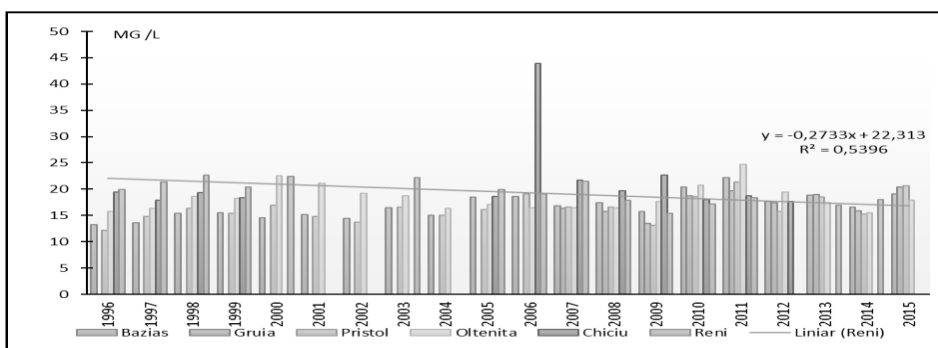


Fig. 8. Variation of annual average sodium concentration values

Potassium - like sodium, is found in water in the form of dissolved salts, the source being the soluble salts in the rocks (feldspar and mica). Due to reduced mobility, potassium is found less in water than sodium. Also, water pollution with domestic sewage and industrial wastewater, as well as diffuse pollution (surface drainage on fertilized soils, irrigation of potassium-containing soils) leads to increased potassium concentrations in surface water.

The variation in the mean multiannual potassium concentration values over the 20-year period analysed in the sections on the lower Danube sector is in the range of 2.3 mg/l (Gruia) and 3.1 mg/l (Reni). The minimum multiannual values range from 0.1 mg/l (Pristol) to 1.2 mg/l (Reni) and the maximum values fluctuate between 4.4 mg/l (Bazias) and 16.4 mg/l (Reni). The analysis of the multiannual values shows an increasing spatial variation on the Romanian Danube sector.

In the analysed period, the temporal variation of annual average potassium concentration at Reni has a linear decreasing trend, as shown in Fig. 9. The highest annual average potassium levels were recorded between 1996 and 2003, especially in the year 1996 at Reni, where the average annual value was 7.5 mg/l.

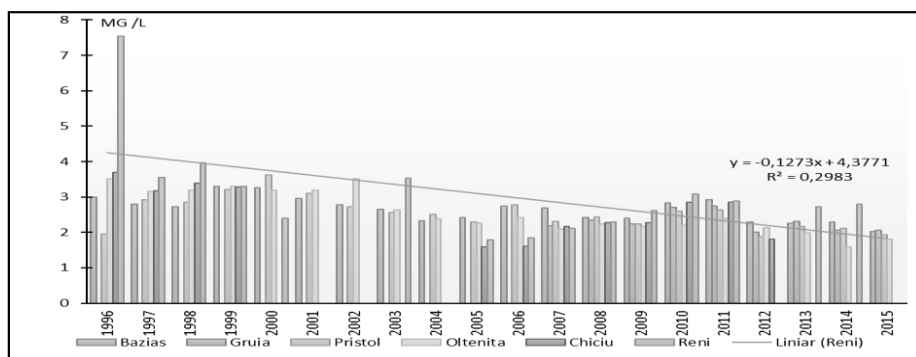


Fig. 9. Variation of annual average potassium concentration values

Calcium ion in surface water originates in particular from the dissolution of calcium carbonates, chlorides and sulphates which are present in significant quantities in sedimentary rocks. The content of calcium and magnesium bicarbonate, chlorinated, sulphate and nitrate salts imparts water its hardness properties. While calcium and magnesium bicarbonates give temporary hardness, sulphates, chlorides and calcium and magnesium nitrates give permanent water hardness.

For the same period, according to the monitoring results, the annual average values of **calcium** ion in the sections analysed on the Danube's lower sector are 49.1 mg/l (Bazias) and 59.4 mg/l (Oltenița). It is also noted that the minimum multiannual values vary a lot, with 1 mg/l at Bazias (2009) and 29.2 mg/l at Gruia (2009), and the maximum multiannual values - 76.7 mg/l at Reni (1998) and 96.5 mg/l at Pristol (2012) (Fig. 10).

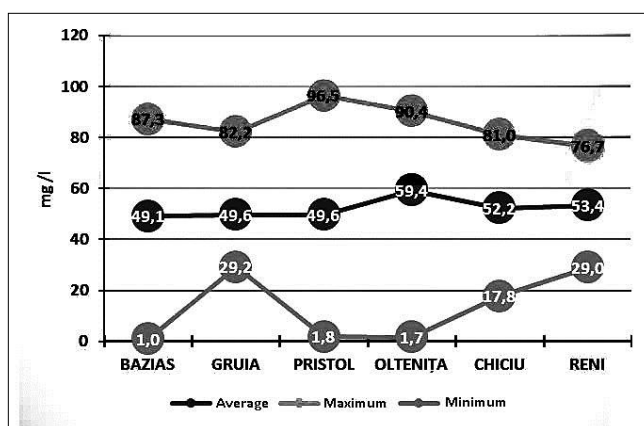


Fig. 10. Variation of multiannual minimum, average and maximum calcium concentration values

Fig. 11 shows the temporal and spatial variation of the annual average calcium values over the period 1996-2015. From time to time, there is a decreasing linear variation at the Reni monitoring section, as can be seen from the trend equation. From the point of view of multiannual characterization, the highest annual average values were registered between 2000-2006 in the Oltenita section.

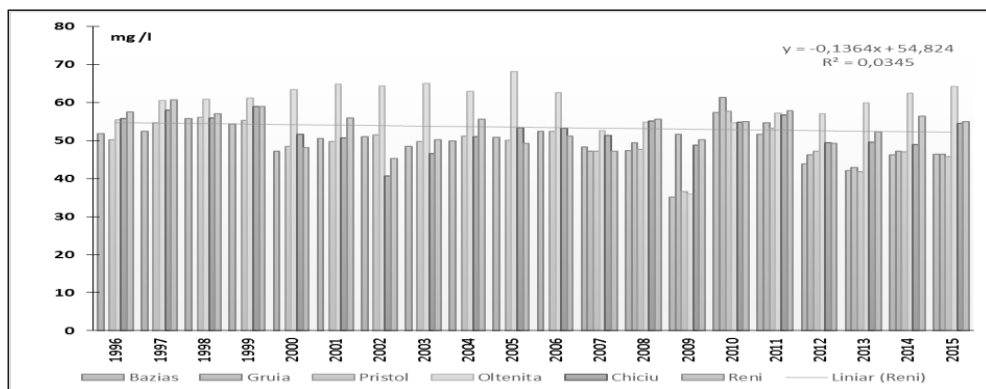


Fig. 11. Variation of annual average calcium concentration values

Magnesium ion in surface water comes mainly from the dissolution of magnesium carbonates, chlorides and sulphates found in sedimentary rocks. From the multiannual average values of *magnesium*, there is an increasing spatial variation from 14.8 mg/l at Baziaș to 19.8 mg/l at Reni.

The monitoring results from the period 1996-2015 varied between 3.7 mg/l (Baziaș, 1998) and 89.1 mg/l (Chiciu, 2004) (Fig. 12).

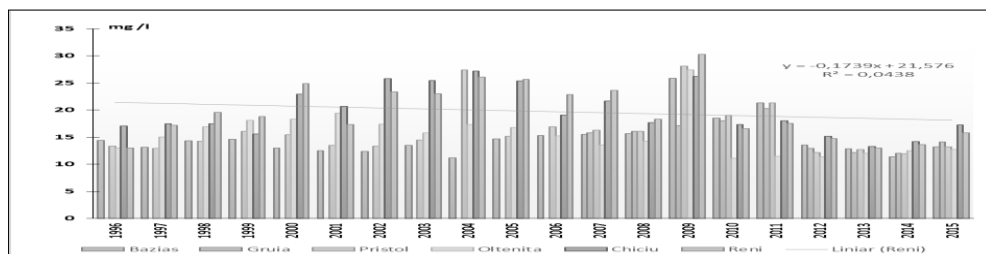


Fig. 12. Variation of annual average magnesium concentration values

The temporal variation trend of magnesium ion is decreasing at Reni, and the highest annual average values (over 25 mg/l) were recorded at Baziaș in 2009, Pristol in 2004 and 2009, Oltenita in 2009, Chiciu in the years 2002-2005, respectively Reni in 2004, 2005 and 2009. The lowest annual average values

(below 12 mg/l) were recorded at Baziaș in 2004 and 2014, Pristol in 2014 and Oltenita in 2010- 2012.

As a general conclusion for all the cations analysed, they have normal values for the Danube lower sector, being no subject to pollution, although there may be local increases whose causes are hardly detectable.

Anions (chlorides and sulphates). As well as sulfates, chlorides meet in all categories of surface water, coming from fields and soils, from underground waters, but also from domestic and industrial pollution sources. Higher chlorides concentrations are measured in the water courses during minimum drainage.

Chlorine concentrations (average, minimum and maximum multiannual values for the period 1996-2015) generally have an increasing trend from upstream to downstream on the Danube, with average values ranging from 19.1 (Gruia) and 31, 9 mg/l (Reni). For the sections analysed on the Danube, the minimum values of recorded chloride concentrations were 5.4 mg/l at Baziaș and 13.6 mg/l at Reni and the maximum values ranged from 29.8 mg/l at Gruia and 179.2 mg/l at Reni, the last value being recorded in 2000 (September 5). At that time, the relatively high concentration of chloride ion is explained by the very low daily flow rate, ie 3820 mc/s at the Isaccea hydrometric station (km 100.2).

Fig. 13 shows the variation in annual average values over the 20 years analysed, and higher values were recorded at Chiciu (2003) and Reni (1998 and 2004) sections, where average values above 40 mg/l were recorded. The relatively high values of the average concentrations of chlorides in 2003 are explained by the low flow rates recorded at the Chiciu - Călărași station (eg. on 29.09.2003 the measured chlorine concentration was 63.9 mg/l and the average daily flow rate was 2565 mc/s). As stated in Chapter 2, 2003 had a flow chart characteristic of dry hydrologic regime, the year in which the most severe drought at the level of the Danube river basin in the last decade occurred.

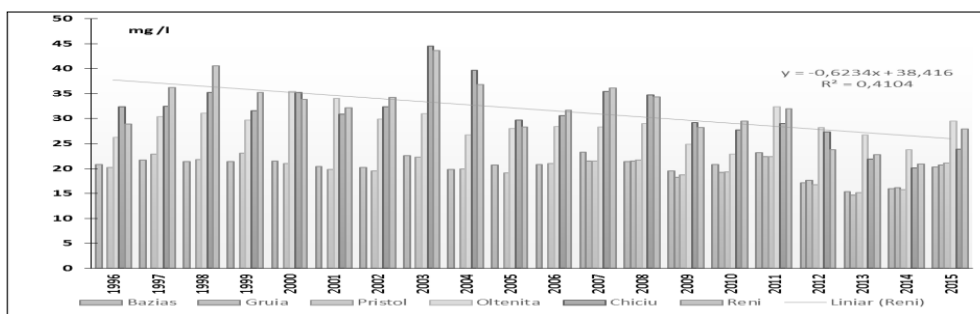


Fig. 13. Variation of annual average chlorides concentrations

The variation in chloride concentration is inversely proportional to flow rates, so that chlorides concentrate on small waters. Also, temporally it is observed

that the linear trend calculated in the Reni section is decreasing for the period 1996-2015.

Sulfur ions are present in almost all categories of water, their main source being the processes of chemical degradation and dissolution of sulphur-containing minerals, in particular gypsum, and the oxidation of sulphides and sulphur. Another source is the underground groundwater which, during certain periods (to small water) supplies surface waters. Sulphates may also come from the degradation of aquatic and terrestrial plants as well as aquatic organisms.

In the lower Danube sector, the measured sulphate concentrations ranged from 3.4 mg/l at Baziaş (2001) and 140 mg/l at Pristol (2010). The average multiannual value of sulphates (1996-2015) varied spatially in the range of 32.7 mg/l (Chiciu) and 59.5 mg/l (Oltenita), so the multiannual average sulphate concentrations have an increasing trend upstream Oltenita and then down to Reni. The minimum multiannual values for the 6 sections analysed in the lower sector show a variation of 3.4 mg/l at Baziaş, 17.8 mg/l at Oltenita and 9 mg/l at Reni, while the maximum multiannual values show a variation of 106.8 mg/l at Bazias, 140 mg/l at Pristol (value recorded on 17.03.2010 at a relatively high daily average flow, respectively 8210 m³/l calculated at Gruia - km 856 hydrometric station, 5).

As noted in Fig. 14, the trend of temporal variation is decreasing at Reni, and the highest annual average sulphates values (over 80 mg/l) were recorded at Oltenita between 2003 and 2007. The lowest annual average (22.3 mg/l) was recorded at Gruia in 2007 (a year with relatively small annual average flow - 4530 mc/s at the Gruia hydrometric).

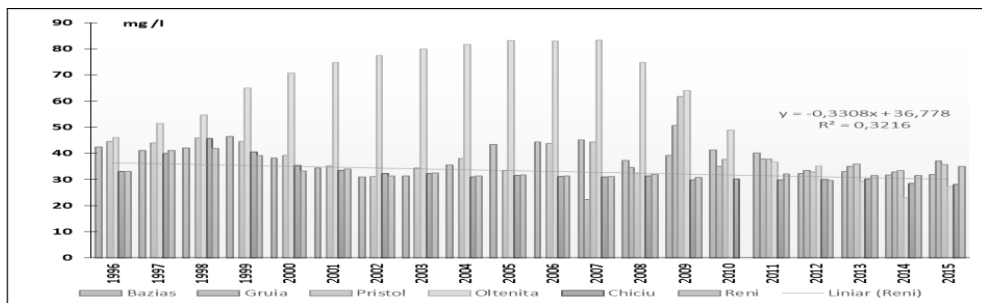


Fig. 14. Variation of annual average sulphates concentration values

3.1.2. Oxygen regime

Dissolved oxygen is a very important indicator in assessing the water quality and condition. Its concentration depends on: water temperature, atmospheric pressure, amount of oxidizable organic substances, photosynthetic plant content, transparency and turbulence (flow character). Water temperature greatly influences the dissolved oxygen content, as the higher the water

temperature, the lower the dissolved oxygen concentration in the water is. In winter, high concentrations of oxygen are recorded due to the low water temperatures that favour the dissolution of oxygen in water and the reduction of oxidation processes in the aquatic environment. Pollution of water with oxidizable organic matter from urban waste water and industrial waters (especially the chemical, agro-food, animal husbandry) leads to the reduction of oxygen content, with negative effects on the self-cleaning capacity of surface waters, but also with a negative impact on aquatic organisms, especially on benthic invertebrates and ichthyofauna, leading to fish mortality.

The multi-annual average dissolved oxygen concentrations (1996-2015) calculated in the sections analysed in the lower Danube sector varied between 8.7 mg/l (Pristol) and 9.2 mg/l (Oltenița and Reni), the lowest measured value (multiannual minimum) of 2.0 mg/l (registered at Chiciu on 30.04.2004 at a relatively high average daily flow rate of 11020 mc/s) and the highest (multiannual maximum) being 15.2 mg/l (at Chiciu in 2001) (Fig. 15).

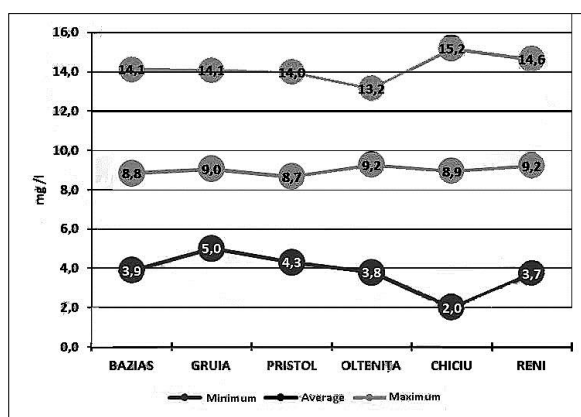


Fig. 15. Variation of multiannual minimum, average and maximum dissolved oxygen concentration

In terms of temporal variation (1996-2015), the annual average concentration of dissolved oxygen at Reni has a linear increasing trend, showing a reduction in organic matter pollution in the lower Danube sector, due to the treatment of municipal and industrial wastewater, as well as improving the quality of the tributary waters (eg. Argeș River by building the Bucharest wastewater treatment plant). The lowest annual average value of dissolved oxygen (7.2 mg/l) was recorded in Chiciu (1996) and Reni (2000).

Biochemical Oxygen Consumption (CBO₅). This indicator indirectly measures the level of contamination with organic matter by determining the amount of oxygen required for oxidative biodegradation by bacteria of organic

substances in 5 days. By measuring CBO_5 , the content of biodegradable organic substances is determined, namely the assessment of the pollution with biodegradable organic substances originating in particular from discharges of urban waste water, industrial waters (cellulose and paper, agro-food, zootechnics, etc.) and from diffuse sources of pollution (agricultural sources, landfills, etc.).

Larger multiannual mean concentrations of biodegradable organic matter (CBO_5) were observed in the upstream section of Argeş / Oltenita (3.38 mg O_2/l), and the lowest average concentrations were recorded at Gruia (1.85 O_2 mg /it). From the data analysis it is observed that the CBO_5 multiannual average concentration drops slightly from Baziaş to Gruia (from 2,48 to 1,85 mg O_2/l), then increases in Oltenita section (to 3,38 mg O_2/l) to drop back to 2.09 mg O_2/l at Reni. From the point of view of the minimum multiannual values these are 0.25 mg/l in all sections, except Oltenita section where a minimum value of 1.7 mg O_2/l was recorded. The maximum multiannual values range from 3,4 mg O_2/l (at Gruia in 2010) and 7,4 mg O_2/l at Baziaş (1997) and Pristol (1998).

From the temporal point of view, the average annual concentrations of CBO_5 decreased during the period 1996-2015 at all the lower Danube downstream sectors, with the exception of the Oltenita section (upstream Argeş) which increased during 2010-2015 (Fig. 16).

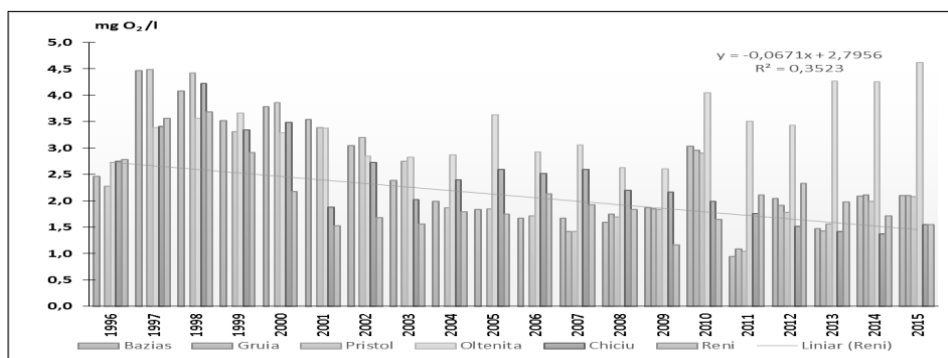


Fig. 16. Variation of annual average values of CBO_5 concentrations

In Chiciu and Reni sections there is a linear decreasing trend, mainly due to the improvement of the water quality of Argeş River with the operation of the Bucharest wastewater treatment plant.

The Olteniţa section has high CBO_5 values due to the quality of the tributaries in Bulgaria, especially Russenski Lom (with an average value of 8.65 mg O_2/l and a maximum value of 21 mg O_2/l for the period 2007-2014). Vit (average value of 5.74 mg O_2/l and maximum value of 32 mg O_2/l for the period 2007-2014), Iskar (average value of 5.91 mg O_2/l and maximum value of 24.6 mg O_2/l for 2007-2014) and Jantra (mean value of 3.20 mg O_2/l and maximum value of

17 mg O₂/l for the period 2007-2014). To these are added the tributaries from Romania with less contribution of CBO₅, respectively Jiu (average value 4.2 mg O₂/l and maximum value 13.3 mg O₂/l for the period 2007-2014) and Olt with a small contribution average 1.58 mg O₂/l and maximum value 4.06 mg O₂/l for the period 2007-2014). Also, the contribution of point sources (mainly municipal) pollution sources in Romania and Bulgaria is also neglected.

3.1.3. Nutrients

The presence of nitrogen in water depends on the concentration of oxygen present in water. Thus, in high-oxygenated waters, nitrates are present in higher concentrations, and in the absence of oxygen, or in the presence of nitrogen, nitrates and ammonium are present in lower concentrations. Ammonia, nitrites and nitrates together form inorganic nitrogen, being species dissolved in the aquatic environment. Among the forms of nitrogen in water, the most stable species is nitrate, and the presence of ammonium shows a recent pollution. The nitrite form is an intermediate form in the nitrogen cycle, between nitrate and ammonium, and occurs due to nitrogen reduction or bacterial oxidation of ammonia. In high concentrations nitrates, nitrites and ammonia are toxic to human health and the aquatic environment, and ammonium is toxic to aquatic organisms at basic pH when ammonium-ammonia equilibrium is displaced to form ammonia gas.

In the case of lentic systems (natural and accumulation lakes), increased nutrient concentrations lead to eutrophication (algae blossoming) with negative effects on water use (unpleasant odours, decreased oxygen content in water, high turbidity, etc.). Nitrate concentrations vary seasonally, being low in summer and autumn due to its absorption by algae and higher in winter and spring.

Nutrients are present in surface water from natural sources (from the decomposition of organic matter, especially of nitrogen, sedimentary (apatite) and humus-rich soils for phosphorus forms) and from anthropogenic sources of pollution. Pollution sources contributing to the increase of nutrient content in water are classified in: diffuse sources (from agricultural sources - application of synthetic fertilizers, animal growing), urban sources (lack of sewage and landfill and landfill, as well as atmospheric deposition) and point sources (urban, industrial and agricultural wastewater).

Nitrates (NO³⁻) are a stable chemical species in the aquatic environment, and the level of concentrations found depends on a number of aspects related to the water body category (river, natural lake, reservoir lake), the degree of water oxygenation, sewage discharges / emissions from pollution sources, the existence of water algae (phytoplankton and phytobenthos), seasons, the interdependence of surface waters with nitrate polluted groundwater, etc. Nitrogen concentrations are measured in waters by methods spectrophotometric.

From a statistical point of view, the mean **N-NO₃ multiannual nitrogen** concentrations calculated for the analysed period at stations located on the lower

section of the river varied between 1,199 mg N/l (Bazias) and 1,631 mg N/l (Chiciu) . The lowest value measured over the 20-year period analysed is below the limit of detection/limit of quantification (0,003 mg N/l) recorded at Oltenita (2009), Chiciu (2000) and Reni (2011) of 6 mg N/l (Oltenita - left bank, 27.04.2000, where the average daily recorded flow was 11800 mc/s). The spatial variation of N-NO₃ (upstream / downstream) multi-annual average concentrations in the lower Danube sector over the period 1996-2015 is increasing (at Bazias 1,199 mg N/l and Reni 1,557 mg N/l).

From the point of view of the spatio-temporal variation (1996-2015), the annual average nitric nitrogen concentration at Reni tends to decrease, as shown in Fig. 17 through the linear trend equation, showing a reduction in nitrate pollution on the lower sector of the Danube, due to the cleaning of municipal and industrial waste water, the reduction of agricultural emissions throughout the Danube basin, as well as the improvement of the quality of the Danube's tributaries.

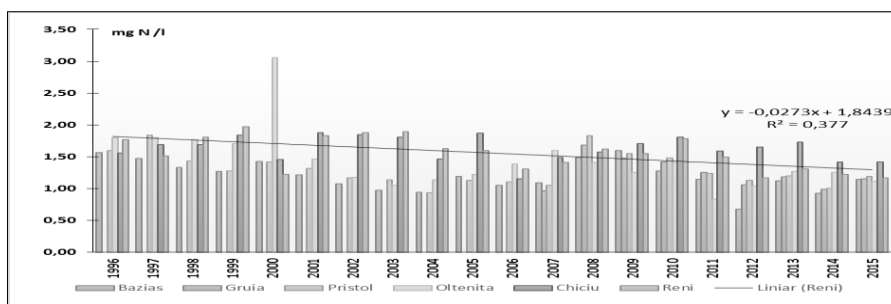


Fig. 17. Variation of annual average N-nitrates concentrations

The highest annual average nitrogen content of nitrogen (3.05 mg N/l) was recorded at Oltenita (2000). Excluding this value, the highest annual average values were recorded at Chiciu and Reni, this being explained by the contribution of the Argeş River which for the analyzed period contributed with a multiannual average nitrate value of 2.04 mg N/l, respectively a maximum value of 10.8 mg N/l (recorded at Clăteşti on 27.04.2000).

Orthophosphates (PO₄-) As for the multi-annual average concentrations of **phosphorus in ortho-phosphates** in the monitoring sections located on the lower Danube River sector in the period 1996-2015, they generally tend to decrease from upstream to downstream, with average concentrations ranging from 0.043 mg P/l (Reni) and 0.098 mg P/l (Gruia).

The maximum concentration values of ortho-phosphates measured in the sections analysed on the Danube fluctuated between 0.21 mgP/l (Oltenita) and 1.36 mg P/l (Pristol).

Fig. 18 shows the temporal and spatial variation of the annual average values in the period 1996-2015. From time to time, there is a decreasing linear variation in the Reni monitoring section, as can be seen from the trend equation. From the point of view of the multiannual characterization, the highest annual average values were recorded in the Oltenita section during 2001-2003, and in the 2008-2009 period in Baziaș, Gruia and Pristol sections (higher than 0.2 mg P / it).

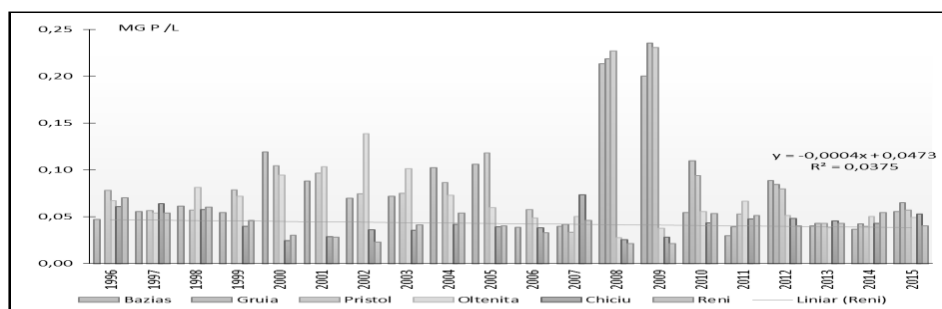


Fig. 18. Variation of annual average of P - ortho-phosphates

4. CONCLUSIONS

From the analysis of Danube water quality in the lower sector, the following conclusions can be drawn in the 6 monitoring sections:

The minimum, average and maximum multi-year values for the determinants that described the degree of variability of the monitored concentration values for the period 1996-2015 were analysed. Also, the values obtained were interpreted, in particular, from the perspective of the interdependence between these parameters, their behaviour, the aquatic transformations / reactions, as well as the correlation with the contribution of tributaries and sources of pollution;

Most determinants have an increasing spatial trend on a longitudinal profile (upstream), except for ortho-phosphates, with decreasing trend, and alkalinity with a quasi-constant spatial profile;

All determinants analysed in terms of time trends (especially in the Reni section) were evaluated, showing a decreasing trend, namely the improvement of water quality due to the closure of many industrial and agricultural pollution sources, the reduction of agriculture intensity, reduction of the number and magnitude of accidental pollution and, last but not least, pollution abatement measures, namely the construction of sewage treatment plants for human agglomerations and industrial installations, the application of the best technologies in industry and agricultural practices, the use of phosphorus-free detergents, European and national legislation.

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