

IMPACT OF HUMAN ACTIVITIES ON NUTRIENT LOADS IN THE LOWER DANUBE WATER BODIES

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ABSTRACT. Impact of Human Activities on Nutrient Loads in the Lower Danube Water Bodies. The paper analyzes the spatial and temporal variation along the Romanian stretch of the Danube River (upstream of the Danube Delta) for a set of water quality indicators reflecting one of the significant water management issues as well as the main pressures identified at the basin level and nutrient pollution. In this respect, an analysis of the point and diffuse sources of pollution has been done, considering the contribution of human agglomerations, agricultural activities and other sources along the Romanian territory. The quantification of the diffuse nutrient emissions from the Romanian analytical units bordering the lower Danube sector has been performed using the MONERIS model. The emission sources and pathways of pollution contributions have been estimated and the nutrient total specific emissions have been mapped.

The impact of these pollution sources on water quality has been evaluated through the results of the monitoring program done in the frame of the TransNational Monitoring Network (TNMN) which operates under the International Commission for the Protection of the Danube River (ICPDR). In regards to the concentrations of various forms of nitrogen and phosphorous, such as nitrates, nitrites, ammonium, orthophosphates and total phosphorous, the lower sector of the Danube has been characterized for a period of 10 years (2006-2015) in 6 monitoring sections/sites, outlining spatial and temporal trends. It has been thus observed that the water quality of the Danube River has improved due to the implementation of nutrient reduction pollution measures at the basin-wide level. In addition, the variation of nutrient loads (inorganic nitrogen and total phosphorous) calculated in 3 monitoring sites for the same 10-year period has been analyzed and interpreted from a time and space point of view. At the same time, the total nitrogen and total phosphorous loads transported by the Danube to the Black Sea have been evaluated in order to reach the target nutrient quantities (of 1960 level) agreed upon internationally in order to prevent the eutrophication phenomena of the Northern-Western shelf of the Black Sea.

Key words: monitoring network, water quality, nitrogen, phosphorous, water body, pollution sources, nutrient loads.

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1. INTRODUCTION AND RESEARCH HISTORY

From its source in the Black Forest Mountains and up to its discharging point into the Black Sea, the Danube River, with a length of approx. 2860 km and a hydrographic basin of approx. 817.000 sq. km drains – either partially or entirely – territories belonging to European countries, out of which 14 with territories greater than 2000 sq. km. The Danube River Basin is considered to be “the most international” hydrographic basin in the world, and amongst the countries through which it flows, Romania holds the biggest surface, with approx.28.7% of its river basin.

From a geographical perspective, gorges or gates delineate the Danube River into three sectors: the upper sector (alpine), the middle sector (Pannonian) and the lower sector (Pontic). The lower course (the Pontic or Romanian sector) is 1075 km long from Baziaș to the Black Sea. In this sector, the Danube River collects tributaries Timok (Serbia - Bulgaria), Ogosta, Iskar, Osam, Jantra, Lom (Bulgaria) on its right side and Romanian rivers, especially Jiu, Olt, Arges, Ialomita, Siret and Prut on its left side. Out of the total of 1075 km, the Danube River flows entirely through Romanian territory from Silistra up to its confluence with the Prut River – a section of 205 km – and forms natural borders with Serbia, Bulgaria, the Moldavian Republic and Ukraine for 905 km. The Danube Delta unfolds from Ceatal Chilia – situated between the continental and marine landscape, it is subjected to the alternative influence of both, thus being in a continuous evolutionary process; its landscape is typical for wetlands and is rich in biodiversity(Gâștescu and Țuchiu,2012).

Current European legislation of water management field strives to ensure sustainable development and an integrated water management at the level of the river basin, achieved through international cooperation taking into consideration the transboundary character of many river basins and river districts in Europe. Cooperation in regards to water management in the Danube River Basin is achieved in conformity with the Convention on cooperation for the protection and sustainable use of the Danube River (Sofia, 1994). The main objectives of the Danube Convention are: the sustainable and equitable management of water resources, the improvement of water quality and the conservation and restauration of aquatic ecosystems, the reduction of pollutants in the river basin as well as the reduction of pollutants transported to the Black Sea. In accordance with the Danube Convention, the International Commission for the Protection of the Danube River (ICPDR) was established in order to guarantee cooperation on basin-wide important and transboundary water management issues. In addition, ICPDR ensures the institutional and technical coordination framework for the implementation at the international level of the Water Framework Directive -

Directive 2000/60/EC and the Directive on floods risk assessment and management - Directive 2007/60/EC (Danube River Basin Management Plan – Update, 2015).

The first Danube River Basin District Management Plan was finalized in 2009 and tackles important water management issues, establishing the waters status as well as the measures necessary in order to improve the current status. This plan was updated in 2014-2015 and approved by the Water/Environment Ministers of the Danube countries in February of 2016.

In accordance with the Danube River Basin District Management Plan, long term visions/goals and management objectives have been set for each water management issue, in order to reducing the effects of anthropogenic pressures. The most important issues identified for surface waters are: organic substances pollution, nutrients pollution, hazardous substances pollution, and hydro-morphological alterations.

In regards to nutrient pollution, the defined goal is “the achieving of a balanced management of nutrient emissions from point and diffuse sources in the Danube River Basin so that the Danube and Black Sea waters will not be threatened or impacted by eutrophication”. Considering the eutrophication of the North Western shelf of the Black Sea occurred at the beginning of '70s, it is considered that the values of nutrients transported by the Danube into the Black Sea as recorded in '60s represent the goal to prevent the eutrophication of the Black Sea waters (approx. 300 kt N/yr. and approx.. 20 kt P/yr.)

The goal of the management objectives is to reduce nutrient pollution by ensuring wastewater collection systems and treatment plants for human agglomerations, the application of the best available technologies (BAT) in industrial and agro-industrial installations, the application of action programs for agricultural sources, the assurance of nutrient balance in a sustainable way and the reduction of diffuse pollution, as well as the reduction of phosphorus pollution through the use of phosphates free detergents (Danube River Basin District Management Plan, 2015).

These important aspects in regards to nutrient management in the Danube River Basin are grounded in a series of scientific studies whose results on nutrient emissions and loads, their impact on the Danube River and Black Sea waters, as well as the scenarios regarding future development have stood as basis for the decisions of the planning documents (Pinay et al., 1990; Behrendt et al., 2004; Vădineanu et al., 2003).

The Danube TransNational Monitoring Network – TNMN of the ICPDR was put into operation in 1996, with the initial objective of providing the analysis of the concentrations trends and relevant pollutant loads, the analysis and evaluation of water quality and the identification of important pollution sources share. In 2000, the main objective of TNMN was thus developed as to identify the

water status (according to the Water Framework Directive) and the long term water quality and constituents and pollutants loads for the Danube River and its main tributaries. In addition, pollutant loads carried by the Danube to the Black Sea are calculated based on monitoring data (Danube River Basin Monitoring Programs, 2007).

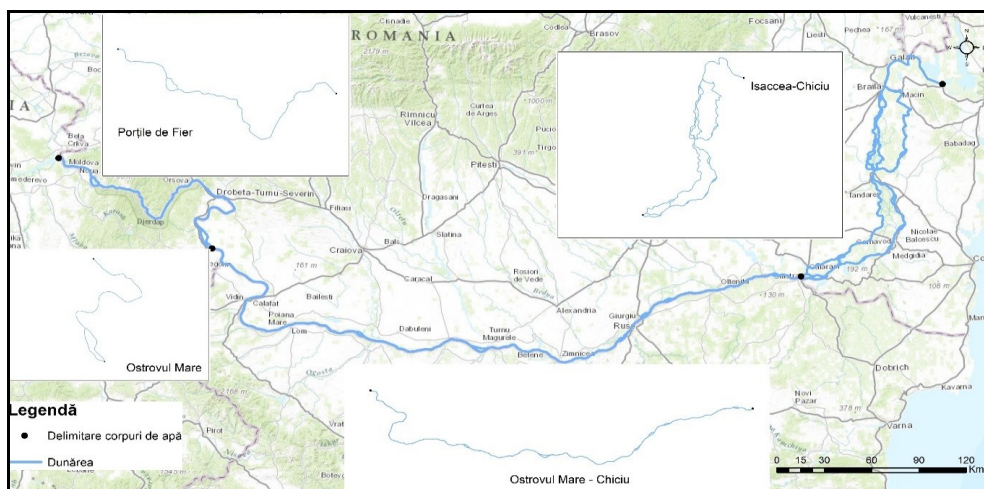


Fig. 1. Delineation of water bodies on the Danube River between Baziaș and Isaccea

In accordance to the implementation process of the Water Framework Directive, 4 bodies of surface water have been defined in the lower sector of the Danube (between Baziaș and Isaccea) out of which 2 water bodies are reservoirs (Portile de Fier/Iron Gates and Ostrovul Mare) and 2 are river water bodies (Ostrovul Mare – Chiciu and Chiciu - Isaccea) (Fig. 1) (Updated National Management Plan, 2016).

The goal of the study is the analysis of point and diffuse nutrient pollution sources in Romania by quantifying their emissions at the level of the 4 water bodies on the lower sector of the Danube (between Baziaș and Isaccea). In addition, a general evaluation of the water quality in the Romanian lower sector of the Danube River is made using a set of indicators/determinants relevant to the nutrients pollution. Moreover, nutrients loads transported by the Danube River on the studied stretch are analyzed from a spatial and temporal perspective, to be compared with the target values set and agreed at the international level.

2. METHODS AND MATERIALS

2.1. Analysis of anthropogenic pressures

In the Water Framework Directive it is foreseen that the Member States should analyze the type and extent of significant anthropogenic pressures to which water resources are exposed. In regards to nutrients pollution, these are:

- **Point pollution sources** from urban, industrial, or agricultural activities or other installations and activities, particularly those that fall under the scope of European directives (Council Directive 91/271/EEC concerning urban waste water treatment, Council Directive 96/61/EEC concerning integrated pollution prevention and control repealed by Directive 2008/1/EC), etc.

- **Diffuse pollution sources** from urban, industrial or agricultural activities or other installations and activities, particularly those that fall under the scope of all the European Directives stated above, as well as Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources.

For the analysis of pressures and impact, the concept of DPSIR (Driver-Pressure-State-Impact-Response) is be used; thus, it is necessary to include information on anthropogenic activities and changes produced at the level of water body status, as well as the response or measures taken to improving water bodies status (Guidance on Analysis of pressures and impacts, 2003).

According to the Water Framework Directive, significant pressures - pressures which produce a significant impact on water bodies – are to be taken into consideration, respective the ones that have as result the failure of reaching the environmental objectives of the respective water body. In order to identify the significant pressures, it is necessary to have an inventory of all anthropogenic pressures and significance criteria set, which corroborated with the specific characteristics of the water body and its catchment lead to the identification of the potential significant pressures (*Țuchiu, 2010*).

A national methodology regarding the identification of point and diffuse pollution sources and the evaluation of their impact on surface waters has been developed in Romania, following the principles and guidelines from the Guidance no. 3 “Guidance on Analysis of pressures and impacts”, developed at the European level within the Common Implementation Strategy of the Water Framework Directive.

Urban point pollution sources /human agglomerations contribute to the pollution of surface waters with suspended matters, organic matters, nutrients and other pollutants. Urban agglomerations need to respect the provisions of the Directive concerning urban waste water treatment (Directive 91/271/EEC), as well

as ensuring the adequate systems for the collection and treatment of urban wastewater. The biological treatment of wastewater should be assured for all urban wastewaters coming from human agglomeration of over 2000 population equivalent (PE). Due to the fact that the territory of Romania is sensitive to nutrient pollution (due to the eutrophication risk of the Black Sea), human agglomerations above 10,000 PE should ensure the nutrients treatment/removal before discharging into surface waters.

Industrial and agricultural point pollution sources contribute to the pollution of water resources through the discharge of pollutants specific to the type of activity undergone. In regards to nutrient pollution, industrial and agricultural point sources of pollution should respect the provisions of the Directive 2010/75/EC on industrial emissions (integrated pollution prevention and control) and the Nitrates Directive (91/676/EC).

In regards to **diffuse sources of pollution**, the MONERIS model (MODelling Nutrient Emissions in RIver Systems) is used to estimate emissions from these sources. The model was developed for and applied to the evaluation of nutrient emissions (nitrogen and phosphorus) in numerous river basins and districts in Europe, including the Danube River Basin. The model quantifies the contribution of various categories of pollution sources to the total nutrient emissions and the pathways by which diffuse pollution occurs (Venohr, Popovici, Țuchiu, 2010).

2.2. Assessment of anthropogenic impact and water quality from nutrient perspective

In accordance with the Water Framework Directive, the evaluation of the impact of various types of significant pressures is an important requirement, and the obtained results are utilized in the analysis of failing risk to meet environmental objectives, the evaluation of the water bodies' status, as well as estimating its trend in the future.

The spatial-temporal evaluation of the Danube River water quality from the nutrient point of view has accomplished using monitoring data for the period 2006 - 2015 in 6 monitoring sections (Baziaș, Gruia, Pristol, Oltenița, Chiciu and Reni) as seen in table 1. The set of indicators selected for the water quality evaluation included dissolved and total forms of nutrients such as N-NO₃, N-NH₄, N-NO₂, P-PO₄ and P total.

For nutrients, the primary monitoring data for the TNMN are produced on a monthly basis, with the exception of monitoring sections included in the program for pollutants loads calculation (Pristol, Chiciu și Reni) where the sampling frequency is twice per month (Table 1).

In accordance with the procedures for gathering of data for the TNMN, the main producers of primary data are the laboratories belonging to the water management authorities, research institutes as well as environmental protection agencies from the countries located in the Danube River Basin.

The quality of the TNMN data is guaranteed both by internal specific procedures of the laboratories and through their participation in the inter-comparison schema of the ICPDR.

2.3. Analysis of the Danube River nutrients loads

As it has been outlined above, one of the TNMN objectives is the monitoring of pollutant loads transported by the Danube from upstream to downstream, towards the Black Sea. In this context, starting with the year 2000 a procedure for the monitoring and calculation of physico-chemical parameters loads was developed. The monitoring sites on the Danube River were set for the monitoring and calculation of the pollutants loads of the Danube River. The pollutants loads calculated at Reni are transmitted annually by the International Commission for the Protection of the Danube River (ICPDR) to the Commission for the Protection of the Black Sea against Pollution (The Black Sea Commission) for the evaluation of the contribution of the Danube to marine pollution (TNMN Yearbook 2000-2015).

Table 1. Analyzed monitoring sections and their location on the Danube River (Danube River Basin Water Quality Database)

Monitoring section	Section code	Profile*	Km of river	Section altitude (m)	River basin surface (sq. km)
Bazias	RO1	L,M,R	1071	70	570896
Gruia	RO1	L,M,R	851	32	577.085
Pristol	RO2	L,M,R	834	31	580100
Amonte Argeş Oltenița)	RO3	L,M,R	432	16	676150
Chiciu	RO4	L,M,R	375	13	698600
Reni	RO5	L,M,R	132	4	805700

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

For the current paper, the analysis of nutrient loads was developed for a period of 10 years in 3 monitoring sections. The monitoring sections were selected out of the 6 Romanian sections which are part of the TNMN in the studied stretch; they are the 3 monitoring sections included in the program for pollutants loads calculation (Pristol, Chiciu și Reni). In these 3 quality monitoring sections, the

nutrients are monitored twice a month and the collected data have been used to calculate the annual average. The hydrological data from 3 gauging stations (Gruia, Chiciu-Călărași and Isaccea) have been used for flow values, where the flow is measured on a daily basis. For the calculation of annual nutrients loads (inorganic nitrogen and total phosphorus), the mean annual flow values from these 3 gauging stations have been utilized. It should be mentioned that the distance between qualitative monitoring sections and the gauging stations (g.s.) are relatively short (22.5 km between g.s. Gruia and Pristol, 4.6 km between Chiciu and g.s. Chiciu-Călărași and 31.8 km between Reni and g.s. Isaccea) and therefore there is no significant external flow between them (Table 2).

The calculation procedure of the annual pollutants loads and in selected monitoring sections is the following:

- For the monitoring sections in which multiple monitoring sites/profiles exist (left bank, middle, right bank), the three values of concentration are used for the calculation of daily mean concentration;

- In the case of concentration values below the limit of detection, the limit of detection value is utilized.

Table 2. The location of qualitative monitoring sections and gauging stations used for the calculation of the Danube River nutrient loads

Qualitative monitoring section	Gauging station
Pristol, km 834	Gruia, km 856.5
Chiciu, km 375	Chiciu-Călărași, km 379.6
Reni, km 132	Isaccea, km 100.2

The procedure consists of the following steps:

- The calculation of monthly mean concentration using the daily mean concentration and the daily mean flow through the following formula:

$$c_m (\text{mg/l}) = \frac{\sum c_i (\text{mg/l}) \times Q_i (\text{m}^3/\text{s})}{\sum Q_i (\text{m}^3/\text{s})}$$

in which i has values between 1 and n (n is the number of days in a month); c_i is the daily mean concentration and Q_i is the daily mean flow

- The calculation of monthly mean flow out of daily mean flow:

$$Q_m (\text{m}^3/\text{s}) = \frac{\sum Q_i (\text{m}^3/\text{s})}{n}$$

– The calculation of monthly load for each pollutant through the multiplication of monthly mean concentration with the mean monthly flow:

$$L_m \text{ (tons)} = c_m \left(\frac{\text{mg}}{\text{l}} \right) \times Q_m \left(\frac{\text{m}^3}{\text{s}} \right) \times n \text{ (number of days of the month)} \times 0,0864$$

– The calculation of annual load/quantity through the addition of monthly loads:

$$L_{\text{yr.}} \text{ (tons)} = \Sigma L_m \text{ (tons)}.$$

3. ANALYSES, RESULTS AND DISCUSSIONS

3.1. Identification and evaluation of nutrients pollution sources contributions to the water bodies on the lower Danube River sector

Through the application of the national methodology regarding the identification and assessment of anthropogenic pressures for the 4 water bodies on the lower sector of the Danube River (between Bazias and Isaccea), the following results have been found:

- **Point pollution sources**

The identification and evaluation of anthropogenic pressures has been done in 2015. Thus, urban agglomerations that evacuate urban wastewater in the 4 water bodies were taken into consideration – 19 human agglomerations, out of which 17 with over 2000 PE and 2 agglomerations under 2000 PE with centralized sewer systems. The main characteristics of urban pollution sources are as follows:

- **Water body 1 (Iron Gates)** – 3 agglomerations are identified and evaluated (Belobresca, Pojejena and Orsova), out of which only Orsova exceeds 2000 PE; all 3 agglomerations have a total of 12,500 PE, out of which approx. 50% of the PE is connected to the wastewater sewer and treatment systems. Urban wastewater is treated in mechanical and biological treatment plants and is discharged into the water body, with a mean flow of approx. 7 liters per second and significant quantities of suspended matters, organic matters and nutrients (approx. 7 tons of total nitrogen and 300 kg of total phosphorus - 2015 data).

- **Water body 2 (Ostrovul Mare)** – 1 human agglomeration (Drobeta Turnu Severin) is identified and evaluated, having a biodegradable organic load of 140,000 PE, out of which about 72% of the PE is connected to the sewer and wastewater treatment plant. Urban wastewater is mechanically treated and is discharged into the water body with a mean flow of approx. 210 l/s and significant quantities of pollutants (approx. 235 t of total nitrogen and approx. 29 t of total phosphorus in 2015). The Drobeta Turnu Severin wastewater treatment plant is

reported to the European Pollutant Release and Transfer Register (E-PRTR), as it has exceeded the 5 t total P per year threshold.

– **Water body 3 (Ostrovul Mare - Chiciu)** – 6 agglomerations with over 2000 PE (Calafat, Corabia, Turnu Măgurele, Zimnicea, Giurgiu, Oltenița) are identified and evaluated, with a total of 201,800 PE, out of which 72% of PE is connected to the wastewater collection and treatment systems. Urban wastewater is mechanically treated (Corabia), both mechanically and biologically (Calafat, Turnu Magurele and Zimnicea) and mechanically, biologically and tertiary (Giurgiu and Oltenita), discharging in the water body a mean flow of approx. 216 l/s. The nutrient emissions are approx. 166 t of total N and approx. 3.5 t of total P in 2015.

– **Water body 4 (Chiciu - Isaccea)** – 9 agglomeration with over 2000 PE (Ostrov, Călărași, Cernavodă, Turcoia, Măcin, Brăila, Galați, Luncavița, Isaccea) are identified and assessed, with a total of 773,600 PE, out of which 86% of total PE is connected to the wastewater collection and treatment systems. Wastewater is mechanically and biologically (Ostrov, Turcoia, Măcin, Brăila, Galați, Luncavița, Isaccea) and mechanically, biologically and tertiary treated (Călărași și Cernavodă), discharging into the water body a mean flow of approx. 1498 l/s. Significant quantities of nutrients are registered, with approx. 1098 t of total N and approx. 32 t of total P in 2015. Wastewater treatment plants of Galati and Braila are reported to the European Pollutant Release and Transfer Register (E-PRTR), Braila exceeding the thresholds of 50 t N per year, 5 t P per year and Galati exceeding the N total (50 t per yr.) and P total (5 t per yr.) thresholds.

- **Diffuse pollution sources**

Diffuse nutrient emissions in the lower Danube River have been estimated using the MONERIS model. The information and data used in modeling and estimating diffuse nutrient emissions, were those afferent to the analytical units delineated as sub-basins in the lower sector of the Danube River (Fig 2).



Fig. 2. Analytical units delineated as sub-basins in the lower sector of the Danube River

Through the application of the MONERIS model on analytical units, using data between 2009 and 2012, diffuse pollution pathways have been identified and quantified, such as atmospheric deposition, surface runoff, tile drainage flow, soil erosion, groundwater flow and urban systems flow for both Nitrogen and Phosphorus(Fig.3,4).

It can be observed that for Nitrogen, the greatest quantities come from groundwater flow (57.7%), surface runoff (19.4%) and flow from impermeable urban systems (11.8%) whereas for Phosphorus the main sources of diffuse pollution are from soil erosion (40.9%), groundwater flow (31.1%) and urban systems (22.3%).

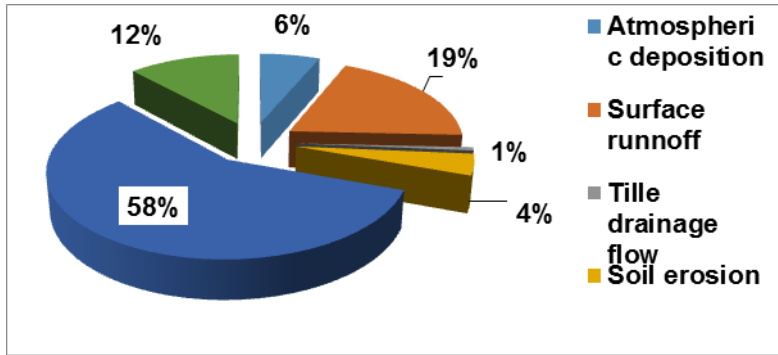


Fig. 3. Pathways of diffuse Nitrogen emissions in the lower sector of the Danube River

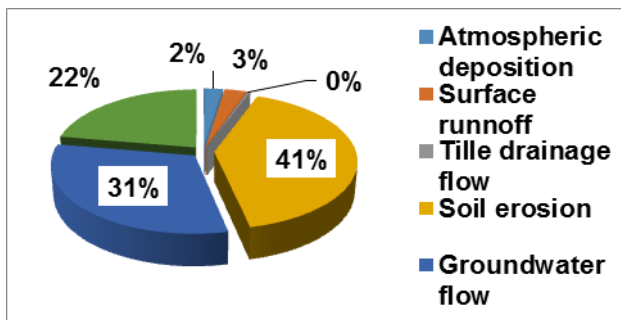


Fig. 4. Pathways of diffuse Phosphorous emissions in the lower sector of the Danube River

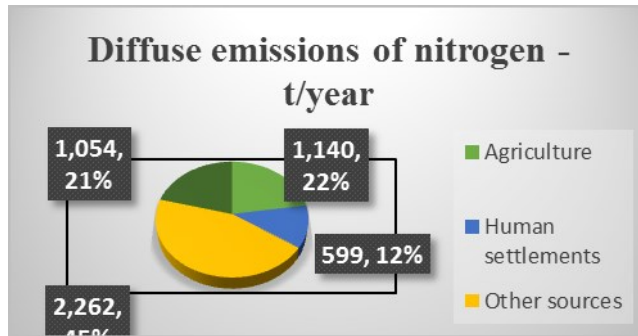


Fig. 5. Diffuse Nitrogen emissions on the lower sector of the Danube River

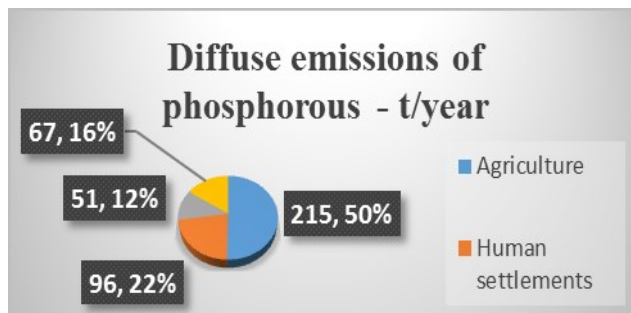


Fig. 6. Diffuse Phosphorus emissions on the lower sector of the Danube River

Through the selection of analytical units (sub-basins) from the Danube River catchment, the quantities of nutrients emitted by agriculture, human settlements and other activities (industrial and transport activities) have been estimated, as well as those that are naturally occurring (through atmospheric deposition for Nitrogen and the composition of rocks for phosphorus) (Fig. 5, 6).

Thus, the total diffuse emissions of nitrogen from the lower sector of the Danube is approx. 5054 t/year (the annual mean between 2009 and 2012), while for Phosphorus is approx. 428 t/year. In addition, it should be noted that for Nitrogen, industrial and transport activities (other sources such as fossil fuels combustion) have the biggest contribution (45%) followed by agriculture (22%). For Phosphorus, agriculture (50%) and settlements without wastewater collection systems (22%) have a significant impact. These results show that nutrients emitted by diffuse pollution sources reach the bodies of water with the aid of rainfall, by soil sediments being washed into the water (contamination with soluble nitrogen

and phosphorus compounds such as nitrates, nitrites, ammonium and orthophosphates), through suspended solids (containing organic forms of nutrients), as well contamination through air (which contains nitrogen compounds).

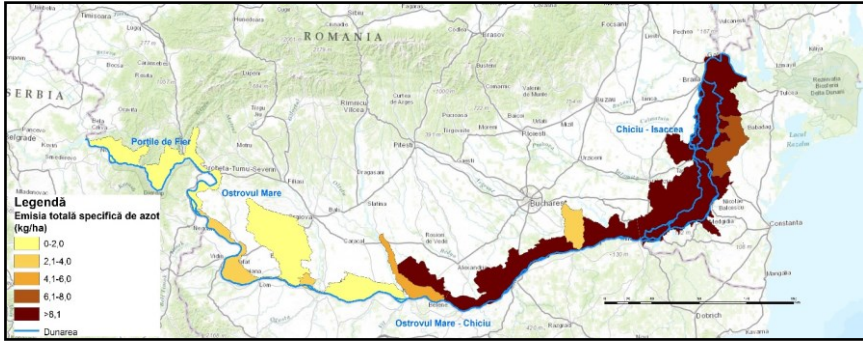


Fig. 7. Total specific Nitrogen emissions (point and diffuse sources)

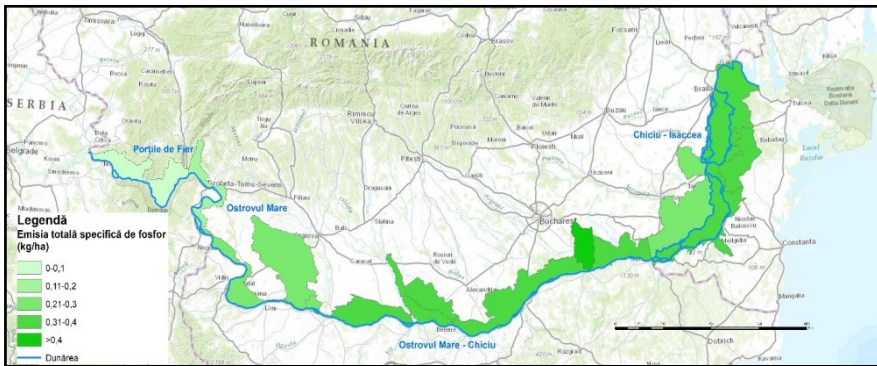


Fig. 8. Total specific Phosphorus emissions (point and diffuse sources)

Concerning specific emissions (quantities of Nitrogen and Phosphorus emitted per surface area from all point and diffuse pollution sources – kg per ha), through the application of the MONERIS model, the following specific mean emissions have been observed within the analytical units on the lower Danube River: 6.05 kg/ha for Nitrogen and 0.29 kg/ha for Phosphorus (Fig. 7,8).

It can be observed that the largest specific emissions can be found in water bodies 3 and 4 (downstream of the Olt River confluence to Isaccea).

3.2. Water quality evaluation on the Danube river on the studied section from nutrient point of view

The presence of nitrogen forms in water is dependent upon the concentration of oxygen in the water. Thus, in waters with a high concentration of oxygen, higher concentrations of nitrates can be found, and in the absence of oxygen or its presence in lower concentration, nitrites and ammonium can be found. Ammonium, nitrites and nitrates together form inorganic nitrogen; they are dissolved in the aquatic environment. Total nitrogen is the sum between inorganic nitrogen and organic nitrogen (amino acids, proteins, peptides, urea and nucleic acids).

In high concentrations, nitrates, nitrites and ammonium are toxic for human health and aquatic environment, and ammonium is toxic for aquatic organism in basic pH (over 7.4) when the ammonium-ammonia balance ($\text{NH}_4^+ - \text{NH}_3$) moves towards the formation of gaseous ammonia (NH_3).

In the case of lentic systems, the rise of nutrient concentrations leads to the eutrophication phenomenon (algae bloom), with negative effects on the water use (the apparition of unpleasant smell, the decrease in oxygen concentration, elevated turbidity, etc.) Nitrate concentration varies depending on season, being lower during summer and autumn due to algae development (consumption of primary producers) and higher during winter and spring seasons.

Total phosphorus is the sum of inorganic phosphorus (orthophosphates and polyphosphates) and organic phosphorus, the phosphorus dissolved and adsorbed by suspended particles and sediments.

Nutrients are present in surface waters from natural sources (through the decomposition of organic matter and especially nitrogen forms, as well as sedimentary rocks and soils rich in humus for phosphorus forms) and from anthropogenic sources of pollution.

Out of the various fractions of nutrients analyzed through the TNMN program, the following chemical species have been evaluated: N-Nitrates, N-ammonium, N-nitrites, P-orthophosphates, P total, during a period of 10 years (2006-2015).

- **Nitrates (NO_3^-)**

In regards to annual mean concentrations of N- NO_3^- , calculated for the analyzed period at the monitoring sections located in the lower sector of the Danube River, they have varied between 1.15 mg N/l (Baziaș) and 1.55 mg N/l (Chiciu). The lowest value measured within the 10 year span analyzed is below the limit of detection (0.003 mg N/l) and it was recorded in Oltenița (2009) and Reni (2011). The highest value was 4.04 mg N/l (la Chiciu, 2011).

The spatial variation (upstream – downstream) of multiannual mean concentrations of N- NO_3^- on the lower sector of the Danube River between 2006

and 2015 is increasing (1.15 mg N/l in Baziaş and 1.40 mg N/l in Reni) due to the nitrogen discharged by the pollution sources and the contribution of the Danube's tributaries.

In regards to spatial-temporal variation (2006-2015), the annual mean concentration of N- NO₃ in Reni is on a decreasing trend, as it is presented in figure 9 through the linear tendency equation, showing a reduction of pollution with nitrates on the lower sector of the Danube River, especially due to the treatment of industrial and municipal wastewaters, the reduction of agricultural emissions throughout the Danube's basin as well as the improvement of water quality in the Danube's tributaries.

The biggest annual mean value of N-NO₃ (1.83 mg N/l) was recorded in Pristol (2008). With the exception of this value, during the period analyzed, the biggest mean annual values were recorded in Chiciu. The result can be explain through the contribution of the Arges River and wastewater discharged from the Bucharest municipality (Fig.9.).

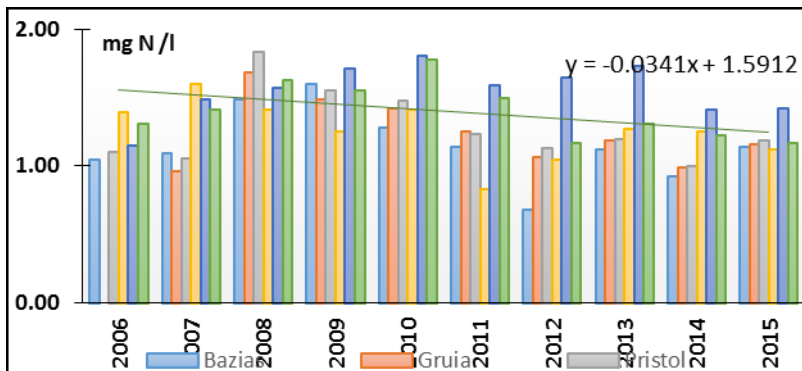


Fig. 9. Variation of annual mean values of N-NO₃ concentrations

- **Ammonium (NH₄⁺)**

For the monitoring sections on the lower sector of the Danube River, the N-NH₄ values measured have varied between the limit of quantification (0.008 mg N/l) and 1.476 mg N/l (extreme value registered in Baziaş in 2006). It can be observed that multiannual mean values of ammonium concentrations decrease from Baziaş to Gruia (from 0.137 to 0.103 mg N/l) and then rise to values of 0.167 mg N/l in Reni, due to the contribution of pollution sources downstream from the Ostrovul Mare reservoir(Fig.10.).

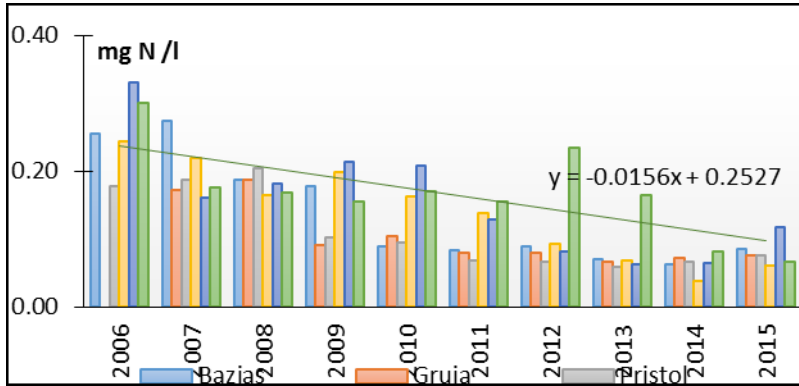


Fig. 10. Variation of annual mean concentrations of N-NH₄

Higher multiannual mean concentrations have been observed in monitoring sections Chiciu and Reni. The ammonium level recorded in these sections indicates the contribution of the Dambovită River through the Argeș River, the explanation being that similar to the case of other pollutants directly evacuated over a long period through the untreated wastewater in the Bucharest municipality.

From a temporal and spatial standpoint, annual mean concentrations of N-NH₄ have been on the decrease during the period between 2006 and 2015 in all stations of the lower sector of the Danube River.

All monitoring sections record a linear tendency to decrease, showing an improvement of the water quality of the Danube River, due to the reduction of economic activities and the continuous improvement and functioning of urban wastewater treatment plants. In addition, higher annual mean values have been recorded in 2006, when historically high flows have been recorded on the Danube River, the maximum values of the 1931-2016 period.

- **Nitrites (NO₂⁻)**

For nitrites, the multiannual mean values of N-NO₂ calculated for the analyzed period have varied between 0.020 (Baziaș and Pristol) and 0.063 mg N/l (Oltenița), the lowest value registered being under the limit of quantification (0.0015 mg N/l) and the highest being 2.152 mg N/l (Oltenița, 2011).

From a temporal standpoint, annual mean concentrations of N-NO₂ have been decreasing during the period between 2006 and 2015 at all monitoring stations in the lower sector of the Danube River, with the only exception being the Oltenița (upstream Argeș River) section, where it has been registered an increase in 2011 (Fig. 11). As shown in the chart, in the Reni section, a linear decreasing trend has been recorded, the cause being similar to other nitrogen forms.

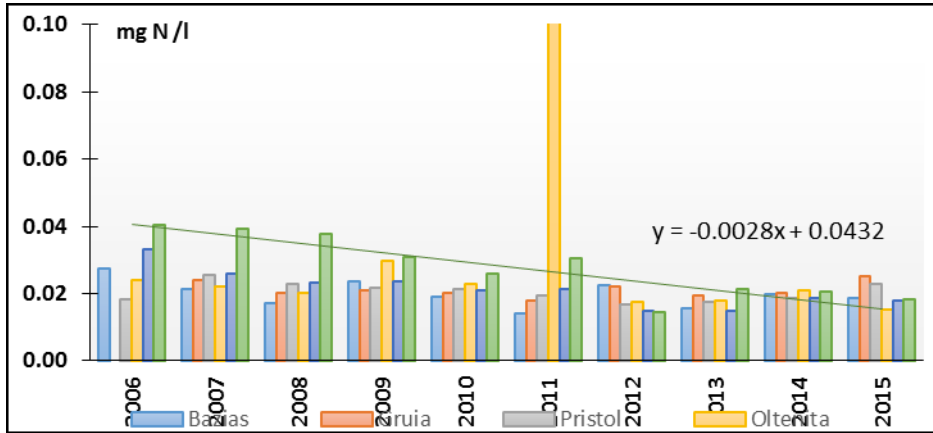


Fig. 11. Variation of annual mean concentrations of N-NO₂

In this context, the exceptional ammonium concentration value in the Oltenita section can be explained, under the conditions that it is not an analysis error, by the contribution of point pollution sources located between Pristol and Oltenita (e.g. the discharge of wastewater) and diffuse emissions.

- **Orthophosphates (PO₄⁻)**

In regards to the mean multiannual concentrations of P-PO₄ in monitoring sections in the lower sector of the Danube River in the period between 2006 and 2015 they have been generally decreasing from upstream to downstream, having the multiannual mean concentrations recorded between 0.041 mg P/l (Reni) and 0.098 mg P/l (Gruia).

The values of orthophosphates concentrations recorded in analyzed sections on the Danube River have varied between being under the limit of quantification (0.004 mgP/l) and 1.36 mg P/l (Pristol)(Fig.12).

Figure 12 shows the temporal and spatial variation of annual mean values of orthophosphates in the period between 2006 and 2015. From a temporal perspective, in the Reni monitoring section, a linear decreasing trend can be observed, as it can be seen from the tendency equation. In regards to the multiannual characterization, in the period between 2008 and 2009, the highest annual mean values have been recorded at Baziaș, Gruia and Pristol sections (higher than 0.2 mg P/l).

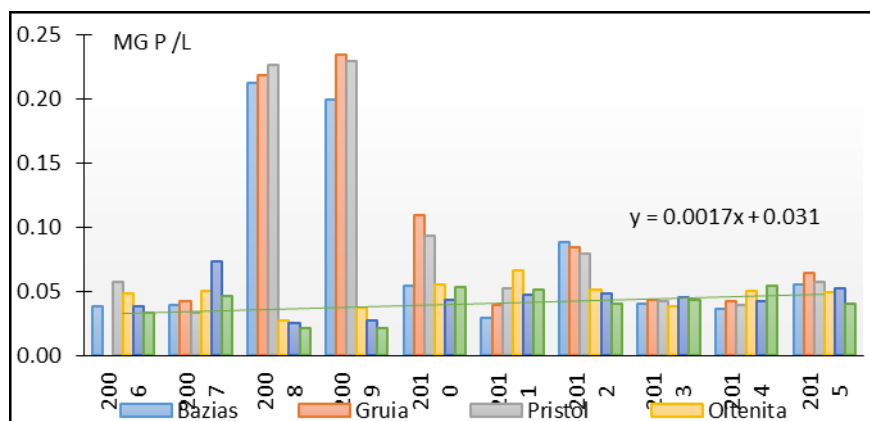


Fig. 12. Variation of annual mean concentrations of P-PO₄

• Phosphorus total

The determined concentrations of phosphorus total have varied between being under the limit of quantification (0.004 mg P/l) and 1.5 mg P/l (in Pristol).

Through the statistical analysis of multiannual mean concentrations of total phosphorus calculated for the analyzed period (2016-2015) in the monitoring sections of the lower sector of the Danube River, values have been registered to vary between 0.084 mg P/l (Oltenița) and 0.182 mg P/l (Gruia). The spatial variation (upstream – downstream) of the multiannual mean concentrations of total phosphorus on the lower sector of the Danube River during the analyzed period is on a decreasing tendency (from Baziaș – 0.135 mg P/l to Reni – 0.093 mg P/l). In comparison with Gruia and Pristol, Baziaș has recorded a smaller multiannual value of phosphorus total (0.135 mg/l) that can be explained by the phenomena of suspended solids sedimentation in the Iron Gates reservoir, particles in which the total phosphorus can be partially found, as well as by the consumption in algal bloom phenomena.

The tributaries from Bulgaria and Romania, such as Russenski Lom, Argeș, Iskar, Jantra, Siret and Prut have contributed with higher concentrations of phosphorus compared with the ones found in the Danube River and yet their influence is smaller than in the case of total nitrogen.

In regards to the spatial and temporal variation (2006-2015), the annual mean concentrations of total phosphorus at Reni is on a decreasing trend, as is shown in figure 13 through the linear trend equation, showing a reduction of pollution with phosphorus on the lower sector of the Danube River, due to the treatment of industrial and municipal wastewater, the reduction of agricultural

emissions throughout the Danube basin as well as the improvement of the water quality in the Danube tributaries.

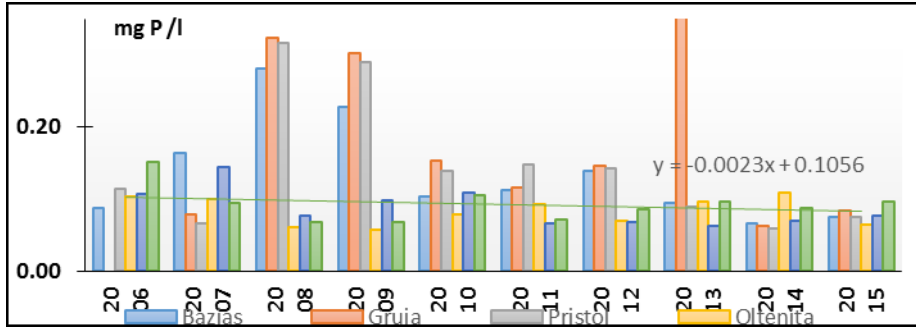


Fig. 13. Variation of annual mean concentrations of P total

3.3. The analysis of nutrient loads on the lower sector of the Danube River

Nutrients found in water are monitored and considered important for water management due to their contribution to eutrophication processes. For the Danube River Basin it is essential that the quantities of phosphorus be reduced in order to avoid both the eutrophication of the Danube River and most importantly of the Black Sea, especially the northwestern side which is heavily influenced by the water quality of the Danube River.

The analysis of nutrient loads transported by the Danube River has been done in monitoring sections Pristol, Chiciu and Reni, taking into consideration the method described above over a period of 10 years.

The 10 year period thus analyzed is characterized by a hydrologic regime of high waters (years 2006 and 2010), low waters (especially during 2011 and 2012) and normal or close to normal regime for the rest of the period, based on the annual mean flow values. In addition, as usual, annual mean flows rise from upstream to downstream, from the Gruia gauging station down to Isaccea gauging station.

It can be observed during the analyzed period that years 2006 and 2010 stand out with higher loads of *inorganic nitrogen* due to the extreme flows recorded (over 15,000 m³/s at Isaccea), as well as the high amounts of rainfall that have absorbed nitrogen oxides from the atmosphere, have drained and washed the catchment, as well as the agricultural fields with nitrogen surplus, dissolving nitrogen salts or gathering suspended particles containing nitrogen (Fig. 14).

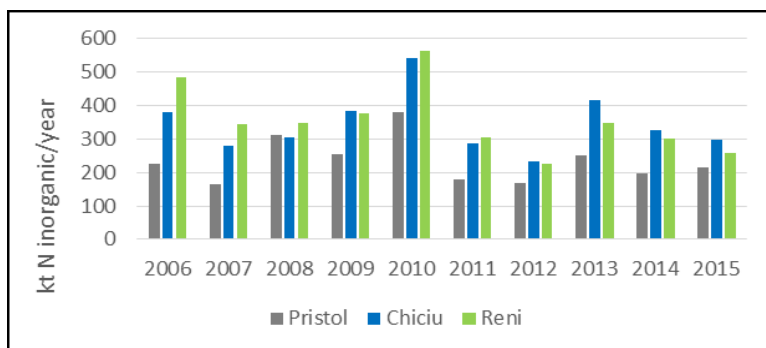


Fig. 14. Variation of inorganic nitrogen loads at the Pristol, Chiciu and Reni sections

For the years 2011-2012, lower loads of inorganic nitrogen can be observed due to the minimum/reduced flows recorded and the periods of drought during summer and the beginning of autumn (2200-2600 m³/s at Isaccea). The year 2013 stands out with higher loads of inorganic nitrogen. However, both the year 2013 and 2014 have been characterized by their periods of spring and the beginning of summer when maximal flows have been recorded (approx. 13,000 m³/s). For comparison it is stated that the multiannual mean flow entering the Danube Delta is approx. 6500 m³/s.

A general increase in the quantities of inorganic nitrogen transported by the Danube River can also be observed on a longitudinal profile from Pristol to Reni correlated with the increase of flow from upstream to downstream, with the contribution of the Danube tributaries and the contribution of the pollution sources. However, situations have been observed (during 2012-2015) when smaller quantities of inorganic nitrogen have been recorded at Reni in comparison with Chiciu. This can be explained by the nitrification-denitrification phenomena as well as through algal blooms and phytoplankton production.

Aside from the flow dependency of inorganic nitrogen loads, it can be observed that there is a decreasing trend of inorganic nitrogen from temporal point of view. In general, loads under 300 kt N_{inorganic}/year have been recorded, with the sole exception of the year 2013. As stated above, the vision agreed upon at the ICPDR level foresees the reduction of the quantities of nutrients transported by the Danube to the Black Sea to that of '60s. In the case of inorganic nitrogen, that quantity amounts to approx. 300 kt N/year. Seeing as organic nitrogen is added to inorganic nitrogen (approx. 25% in the case of the lower sector of the Danube River), it should be concluded that a further reduction of at least 25% in order to reach the goal and prevent further eutrophication of the Danube waters and the northwestern area of the Black Sea (Fig.15).

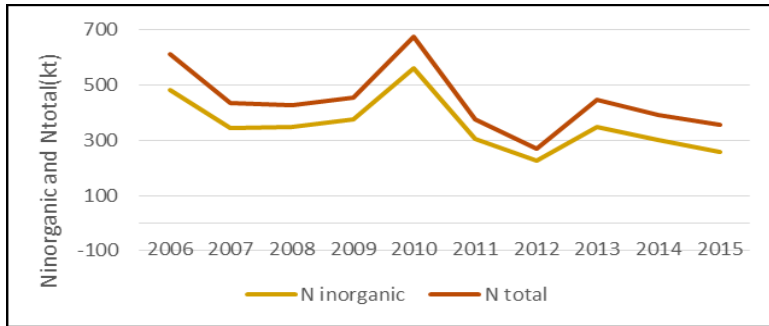


Fig. 15. Variation of inorganic nitrogen loads and total nitrogen at the Reni section

The further reduction of nitrogen entails the implementation of measures throughout the Danube River Basin for the reduction of nitrogen pollution, respective the tertiary urban wastewater treatment for human agglomerations of over 10,000 PE, the application of BAT and good agricultural practices, the ensuring of agriculture advisory services, the ensuring of buffer zones along rivers, other measures requested by European directives as well as additional measures which are beneficial to other means, such as rural development, the restoration of wetlands and floodplains, afforestation and others.

In regards to **total phosphorus**, it can be observed that for the analyzed period, unlike in the case of inorganic nitrogen, higher loads of total phosphorus total have been registered at Pristol in 2008 and 2009 as well as in 2006 and 2010 due to the maximum flows recorded. For the year of 2006 and 2010, large quantities have drained and washed the catchment, dissolving phosphorus salts or gathering suspended particles containing phosphorus (Fig. 16).

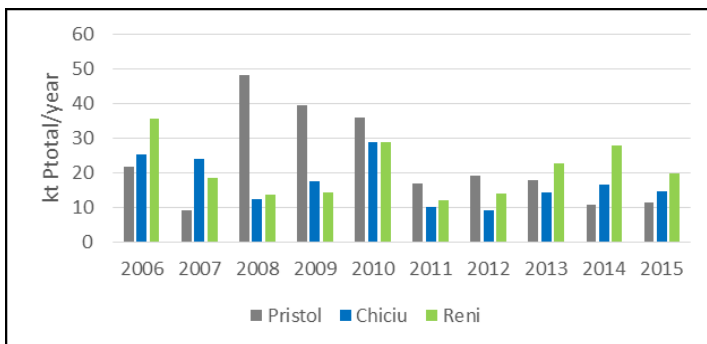


Fig. 16. Variation of total phosphorus loads at Pristol, Chiciu and Reni sections

As it is the case with inorganic nitrogen, lower phosphorus total loads can be observed during 2011-2012 due to the minimum/reduced flow recorded and drought periods.

Unlike it has been the case with inorganic nitrogen, no spatial increase can be observed with total phosphorus loads from Pristol to Reni. This can be explained through the phenomena of suspended solids sedimentation through which organic phosphorus is adsorbed, as well as algal blooms. The smaller concentration of phosphorus limits the process of eutrophication. In addition, due to the fact that the Pristol monitoring section is located downstream from the Ostrovul Mare reservoir, it is possible that the operation and management of the reservoir permit the fine sediments to be evacuated downstream, thus having adsorbed phosphorus and other pollutants.

A decreasing trend in the total phosphorus loads can be observed in the last 5 years, in comparison with the period between 2006 and 2010, due to the application of measures foreseen in the first Danube River Basin Management Plan. At the Reni monitoring section, the phosphorus loads have gradually increased from approx. 12.1 kt/year in 2011 to 28.1 kt/year in 2014, in correlation with the rise in the annual mean flow of the Danube River. In 2015, the load transported by the Danube River has been 19.8 kt/year, this reaching the goal established by the ICPDR of 20 kt/year, representing the approx. value recorded in 1960. Seeing as during years 2006, 2010, 2013 and 2014 there have recorded values exceeding the 20 kt/year threshold at Reni, the measures enumerated for nitrogen should be continuous implemented, along with the use of phosphates free detergents.

4. CONCLUSIONS

The analysis and assessment of anthropic pressures on the four water bodies of the lower Danube River sought to identify the potentially significant point pollution sources and to estimate their contribution in pollutant substances such as nutrients. Human agglomerations discharging wastewater into the 4 water bodies and influencing their quality with nutrients have been inventoried. Sources of diffuse pollution from urban, industrial, as well as other activities have been estimated and identified. In addition, the quantification of diffuse emissions of nitrogen and phosphorus in the sub-basins of the lower Danube River by applying the MONERIS model has been done analyzing polluting activities and the pathways of diffuse emission. Thus, for the total nitrogen diffuse emission, industrial and transport activities (other sources) are the biggest contributors to pollution, followed by agriculture. For phosphorus, diffuse emission comes primarily from agricultural activities and human settlements. According to the

analysis, the biggest point and diffuse emissions can be found in the water bodies between Ostrovul Mare and Isaccea.

The analysis of spatial and temporal variations of nutrients on the lower sector of the Danube reflect the impact of the main anthropic pressures identified for the period ranging between 2006 and 2015, in 6 monitoring sections (from Bazias to Reni). The variability of monitored concentration values were analyzed based on the multiannual minimum, average and maximum values, (2006-2015) for nitrogen and phosphorus forms, which were interpreted in regards to their interdependence, behavior and the aquatic transformations/reactions, as well as through the correlation of tributaries and pollution sources contributions. Variations on a longitudinal profile have been established, with the observation that nitrogen forms have a spatial trend towards increasing, while phosphorus forms show the opposite of this tendency.

From a temporal perspective, the majority of nutrients (with the sole exception of orthophosphates) have a trend of decreasing concentrations in the water and thus improving the water quality as a result of the reduction of anthropogenic pressures due to the construction of and functioning wastewater treatment plants for human agglomerations and industrial installations, the application of the best available technologies in the industry and good agricultural practices, the use of phosphates free detergents as imposed by the European and national legislation.

The analysis of annual nutrient loads (inorganic nitrogen and total phosphorus) of the lower Danube River has shown a variability dependent on the Danube River flow. Thus, in years of extreme hydrologic regime with extremely high flow have also been marked by larger nutrient quantities. From a spatial standpoint, in general, it has been observed that quantities of nutrients transported by the Danube River have the tendency to increase longitudinally from Pristol to Reni considering the rise in flow from upstream to downstream and the contributions of Danube's tributaries and pollution sources. Situations have been observed where due to the consumption of nutrients in algal blooms processes, of sedimentation processes and nitrification-denitrification phenomena on the lower sector of the Danube River, the nutrient loads decreased from upstream to downstream. In regards to temporal variation, a general tendency towards decrease can be observed for nutrients loads (especially inorganic nitrogen) in the Danube River, due to the implementation of measures to reduce pollution. Even so, it is still necessary that the measures for the reduction of nutrient discharges and emissions should continue, as the nutrient loads goal foreseen in order to prevent eutrophication of the Danube River and of the northwestern shelf of the Black Sea (levels recorded in '60s) have not yet been met.

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