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THE ANTHROPOGENIC IMPACT ON THE CHEMICAL AND MICROBIOLOGICAL PROFILE OF THE PASĂREA RIVER, ROMANIA

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Abstract. This study reported the chemical and microbiological composition of a sector of Pasărea River, Romania, comprising the Dimieni Bridge (DB) and Tunari Dam (TD) sites, in relation with the chemical and microbiological pollution of this tributary of River Dâmbovița. The amount of sulfate-reducing bacteria (5.75x10^7 cells/mL at DB and 5.5x10^7 at TD), nitrite and nitrate bacteria (3x10 cells/mL at DB and 3x10^3 at TD), total coliforms (2,5x10 C.F.U./mL at DB and 2.25x10 at TD) and faecal streptococci (5x10^3 C.F.U./mL at DB and 1.4x10^2 at TD) revealed a relatively high cell density of microbial groups considered indicators of microbiological pollution. The analysis of the chemical composition highlighted the presence of chromium, cerium, aluminium and barium oxides in the 10 – 20 % range at DB in winter and in the 20 – 70% range at TD during spring confirming the chemical pollution of the analysed river sector. These contents were in accordance with values that could sustain the development of a polluting microbial community. Based on the corroborated data, the current survey proposed a set of criteria for establishing standards for the microbiological and chemical pollution of fresh water relative to drinking water values.

Keywords: Pasărea River, polluted water, microbial and chemical composition.

Rezumat. Impactul antropogen asupra produselor chimice și microbiologice ale râului Pasărea, România. Acest studiu a prezentat compoziția chimică și microbiologică a unui sector al râului Pasărea, România, cuprinzând siturile Podul Dimieni (DB) și Barajul Tunari (TD), în relație cu poluarea chimică și microbiologică a acestui afluent al râului Dâmbovița. Cuantificarea bacteriilor sulfato-reducătoare (5,75x107 celule/mL la DB și 5,5x107 la TD), bacterii nitriți și nitrați (3x10 celule/mL la DB și 3x103 la TD), coliforme totale (2,5x10 C.F.U./mL la DB și 2,25x10 la TD) și streptococii fecali (5x103 C.F.U./mL la DB și 1,4x102 la TD) au relevat o densitate celulară relativ mare a grupelor microbiene considerate indicatori ai poluării microbiologice. Analiza compoziției chimice a evidențiat prezența oxizilor de crom, ceriu, aluminiu și bariu în intervalul 10 – 20 % la DB iarna și în intervalul 20 – 70 % la TD în timpul primăverii confirmând poluarea chimică a sectorului fluvial analizat. Aceste conținuturi erau în concordanță cu valori care ar putea susține dezvoltarea unei comunități microbiene poluante. Pe baza datelor coroborate, studiul actual a propus un set de criterii pentru stabilirea standardelor de poluare microbiologică și chimică a apei dulci în raport cu valorile apei potabile.

Cuvinte cheie: Râul Pasărea, apă poluată, compoziție microbiană și chimică.

INTRODUCTION

The biological activity of any type of ecosystem would not be possible without the existence of the microbial component. This establishes the balance between organic and inorganic substances, respectively between living and non-living matter. Flowing waters represent a particular environment from a microbiological point of view because their microbial composition undergoes fundamental changes from the springs to the confluence of the river with other flowing waters, or with the river-sea system (McCABE, 2011; KRAUSE et al., 2022). This composition is influenced by the hydrographic basin, by the input of the tributaries, the physical-chemical and climatic conditions, but mostly by the anthropogenic impact. Human communities have developed in the proximity of water reserves (flowing waters, lakes, seas, oceans) with a significant impact on them (BURIAN et al., 2000). Residue discharges resulting from industrial, agricultural, recreational or other human activities produce significant changes in the physical-chemical and microbiological composition of water (SINTON et al., 1993; HOLCOMB & STEWART, 2020). Water plays an essential role for all life forms on Earth, its quality having a major impact on all human communities. Throughout history, human communities have developed in the vicinity of rivers using water resources for various activities, which has led to an increase in anthropogenic impact on water quality (MILLER et al., 2017). This composition in turn influences the community of microorganisms in the anthropized aquatic ecosystem with direct effects on the cyclical rhythm of the biogeochemical cycles (ABBOTT et al., 2018).

In general, there is no system based on which water could bbe considered polluted or unpolluted, the classification being based on certain human perceptions. For example, water is considered sweet, brackish or salty according to taste, a threshold of 3g/L NaCl being arbitrarily chosen to separate a sweet water from a salty one (ENACHE et al., 2017). There are normative systems that classify water into several quality classes, a classification that allows the use of water in certain types of activities. Arbitrarily, in this study it was considered that the investigated running water can be considered polluted or unpolluted depending on the physical, chemical and microbiological parameters established for the quality of drinking water provided for the socio-economic systems along the investigated area.

The microbiological component is essential for the functionality of an ecosystem (aquatic, terrestrial) in terms of flow of matter, energy, information and biogeochemical cycles (AZAM et al., 1983). Changes in the physical and chemical composition of the ecosystem are reflected in its microbiological activity. Water reserves are of fundamental importance for daily human activities, so that knowledge of their biological and chemical structure is of particular importance. In the present study, a sector of the Pasărea River was investigated, located in the vicinity of some fundamental economic units for the normal development of daily activities, but also of a strongly developed human community with a significant anthropogenic impact on this sector of the river. The Pasărea River (Fig. 1) is part of the Argeș River hydrographic basin, being a typical lowland river with its sources in the Otopeni forest at an altitude of 91 meters, crossing the city of Bucharest in the northeast. This river merges with the Dâmbovița river (in the town of Fundeni), at an altitude of 40 meters, after a course of 48 km, with a meandering course with a sinuosity coefficient of 1.5 and after collecting the waters of the Sindrilita tributary (11 km long) with which it drains an area of 254 km^2. The meandering course makes it difficult for water to drain and favors the appearance and development of swamp vegetation. Water runoff is defined by average annual flows of less than 1m^3/s, the speed of the water current being low as a result of the low slopes. In this regard, the river bed was modified, according to the sector investigated in this study, with 24 ponds used for fish farming and irrigation, including Tunari, with an area of 21 ha (COCOŞ, 2006).

The study also aims to establish some general criteria by which a sector of a flowing water can be considered polluted or not, considering the biological capacity of a river to recover qualitatively as a result of the biological activity closely correlated with the physical and chemical composition.

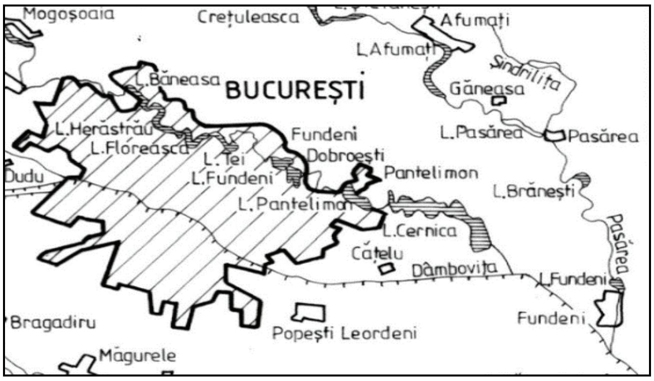

Figure 1. The location of the Pasărea River in the hydrographic basin of Bucharest area (COCOŞ, 2006).

MATERIALS AND METHODS

Water samples were collected seasonally during summer, autumn and winter of 2020, and spring of 2021 from two locations identified as the Dimieni Bridge (DB) and the Tunari Dam (TD).

A series of *physical and chemical parameters* of the river water was measured *on site* counting pH, salinity, total dissolved solids (ppm), conductivity 1 (µS/cm), conductivity 2 (µS/cm^2), salinity (PSU), total dissolved oxygen (mg O_2/L), turbidity (NTU), water temperature (ºC).

The chemical composition of water samples was determined by X-ray fluorescence spectrometry, using WD-XRF (Rigaku, Japan) equipment (NEAGU et al., 2021).

Microbiological analyses were performed from the samples and decimal dilutions for the main groups of microorganisms involved in the carbon, nitrogen, sulphur circuits as well as the groups of microorganisms indicating pollution following culture media and growth conditions as described in a previously papers (***. APHA 1998; LUCACI et al., 2019; NEAGU et al., 2021). The composition of culture media was used for different groups of microorganisms corresponding for ammonifying, denitrifying, coliforms, heterotrophic, streptococcus and sulphate reducing bacteria (***. APHA 1998; BERNASCONI et al., 2003; JANELIDZE et al., 2011).

Pollution criteria for flowing water were proposed relative to standards for drinking water (***. CD - 98/83/EC; ***. STAS 3001-91) and previous data (MESSLEY & KINGSBURY, 1973; SINTON et al., 1998; RAJI et al., 2015; SELVAM et al., 2015; WANG et al., 2016; HOLCOMB & STEWART, 2020; NEAGU et al., 2021; PODOSU et al., 2021a, b; BĂTRÎNESCU-MOTEAU et al., 2022; RUGINESCU et al., 2022).

RESULTS AND DISCUSSIONS

The physical and chemical parameters of Pasărea River water samples. The areas selected for the study, being controlled by the Pasărea river dam system, varied in terms of physical and chemical parameters.

This control system is reflected in significant values for turbidity, conductivity and total dissolved solids (DB – Fig. 2 and TD – Fig. 3). Indirectly, the rest of the parameters investigated on site were influenced by this system, as a positively correlated factor with turbidity and dissolved oxygen, for example. Regarding the spatial and temporal characteristics of the parameters, factors that varied significantly between ecosystems and factors that varied seasonally were highlighted. Similar behaviors were also reported in some studies for Georgian Black Sea coastal ecosystem (JANELIDZE et. al., 2011).

Water temperature varied between 4 ºC for the Dimieni Bridge and 7 ºC for the Tunari Dam in winter and 29 ºC in summer for both sites (Figs 2; 3), indicating small variations between the two locations. These moderate temperatures in the range of the tolerance limits for metabolic processes (LAZĂR et. al., 2017) could sustain the development of microbial communities during all seasons.

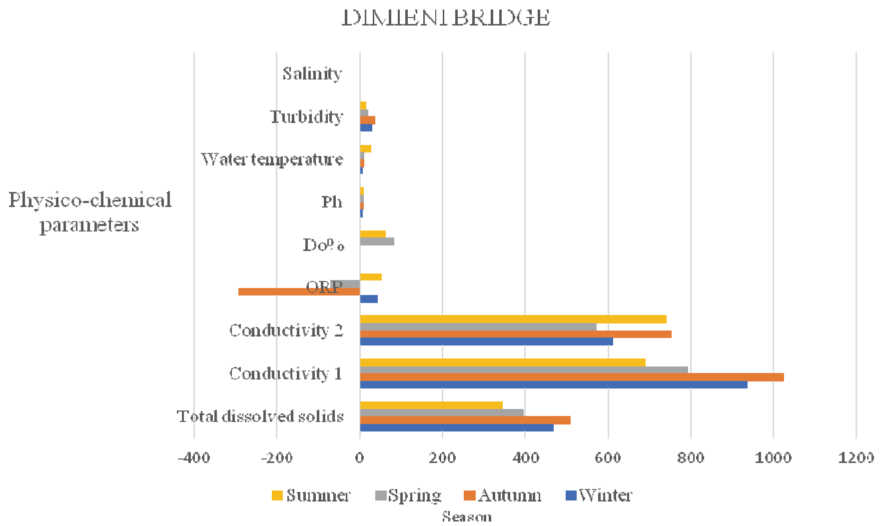

Figure 2. Parameters for the Dimieni Bridge: Total dissolved solids (ppm); Conductivity 1 (µS/cm), Conductivity 2(µS/cm^2); Salinity (PSU); Total dissolved oxygen (mg O_2/L); Turbidity (NTU); Water temperature (ºC).

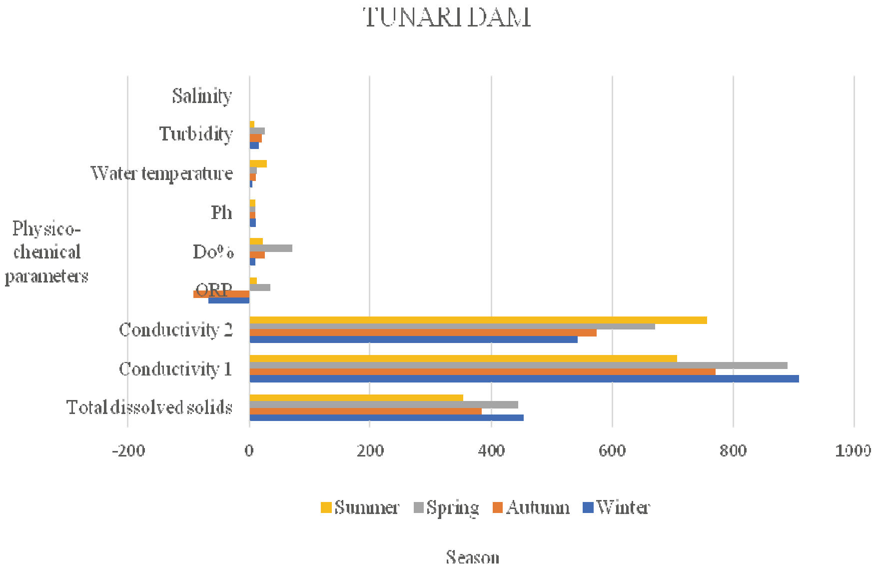

Figure 3. Parameters for the Tunari Dam.

The pH values of the water samples from the Dimieni Bridge site (Fig. 2) ranged between 6.82 in the winter season and 8.44 in the summer season, while for the Tunari Dam, the recorded values were higher, in a slightly alkaline range, varying between 8.27 during summer season and 9.55 in winter (Fig. 3). These relatively limited variations around a neutral pH during winter times have minor bactericidal effect by protein denaturation of hydrolysis, while the more alkaline values (8.44 and 9.55, respectively) could be responsible for modelling de composition of the river microbiome (LAZĂR et al., 2016).

Oxid Reducing Potential (ORP). The ORP measuring the electrical charge of the water revealed negative values for all analysed samples (Figs. 2 and 3), indicating an antioxidant potential that contributes to the neutralization of water acidity. As a parameter correlated with pH values, negative ORP values corresponded to higher pH values observed during autumn in both locations. Thus, the ORP value for the Dimieni Bridge (-293 mV) was in accordance with the higher pH value (8.27) at 11 ºC (Fig. 2), while for the Tunari Dam, the negative ORP (-92 mV) correlated with a higher pH value (9,16). Moreover, during winter season, the negative ORP (-66.7 mV) value is supported by the higher pH value (9,55) (Fig. 3).

Dissolved oxygen (O_2%). The oxygen saturation (DO%) measured in the two locations of the Pasărea River was highly different, varying also with the season. At the Tunari Dam, the DO content ranged from 9.2% in winter to 70.6% in spring (Fig. 3), while at the Dimieni Bridge the DO was 0 during both winter and autumn seasons, and varied between 62.2-83.5 in summer and spring (Fig. 2). The measured oxygen content of the river water in the mass of water was in accordance with supporting the development of aerobic microorganisms. Moreover, these recorded DO values corroborated with those of the corresponding oxid reducing potential ones (Figs. 2 and 3) could explain the absence of microorganisms involved in the nitrogen biogeochemical cycle, considering diminishes nitrate processing in the anthropized water flow (AZIZIAN et al., 2017).

The microbial content of the Pasărea River. During the four seasons, the number of microbial colony-forming units/ml obtained from water samples collected from the two locations of the Pasărea River showed a variation with both the type of microorganisms and the season (Figs. 4 and 5). In the case of the Dimieni Bridge, these values ranged from 3.22×10^5 (summer) to 4.5×10^4 (spring) (Fig. 4). For the sample, from the Tunari Dam, considering figure 5, the highest number of colony-forming units/ml was highlighted in the sample taken in the winter season, 1.7×10^5 and recorded a decrease in the spring season, respectively 1.4×10^2 CFU/ml. In temperate zones, the development of heterotrophic bacteria is dependent on the seasonal temperature variations, while low temperatures inhibit microbial growth (POMEROY & WIEBE, 2001). In this context, the data obtained for the Dimieni Bridge water samples suggest the constant presence of the food source in all four seasons. For the Tunari Dam, the highest microbial content (1.7×10^5 UFC/ml) was recorded during winter season, in accordance with the high TDS value (454 ppm) indicating an uptake of organic matter of exogenous origin.

The presence of total coliforms, faecal coliforms and faecal streptococci is frequently associated with the faecal-household contamination of ecosystems (KOLAREVIC et al., 2011). In this study, the presence of total coliform bacteria was confirmed during the four seasons for the water sample from the Dimieni Bridge, the highest number of CFU/ml (6.2×10^3) being determined for samples collected in autumn (2020). The number of UFC/ml was constant during the following winter (1.85×10^3 UFC/ml) and spring ($1.8x10^3$ UFC/ml).

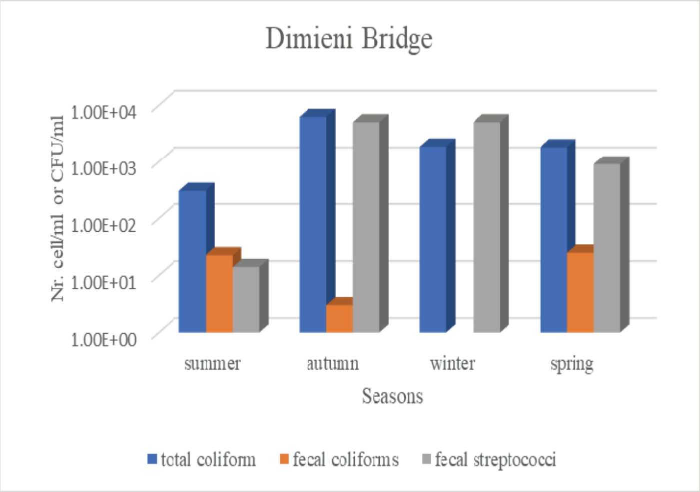

Figure 4. Microbial content of the Pasărea River during various seasons. The cell density (CFU/ml) of total coliforms, fecal coliforms and fecal streptococci was determined as indicated in Methods for water samples colected from the Dimieni Bridge and the Tunari Dam.

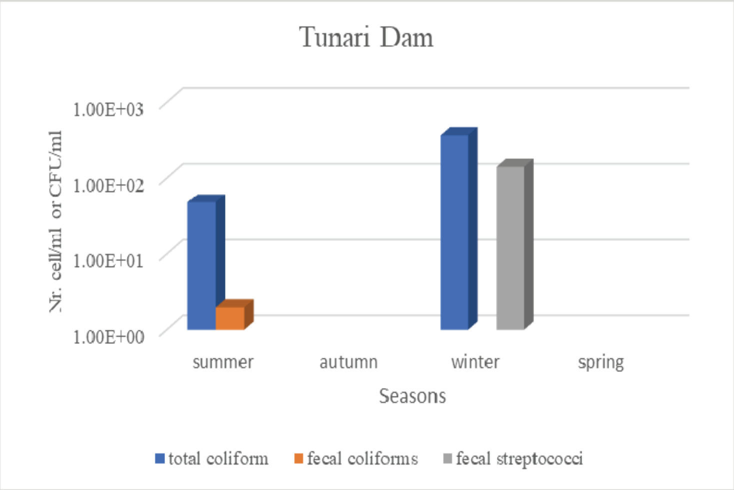

Figure 5. Groups of microorganisms, pollution indicator for the Tunari Dam.

A slightly reduced content of total coliforms, (3.03×10^{2} CFU/ml), was determined in the water samples collected during the warm season (summer 2020). For the Tunari Dam samples, the specific faecal coliforms and streptococcal colonies were present only in the summer season (2020) with a recorded cell density of 4.8 × 10 UFC/ml that increased 10-fold (3.65×10^{2} UFC/ml) during winter (2021). For the samples collected in autumn (2020) and spring (2021), no total coliform bacteria were identified (Figs. 4 and 5)

Faecal coliform bacteria were scarcely present during the seasonal sampling, for the water sample from the Dimieni Bridge in winter (2.5×10 UFC/ml), summer (2.25×10 UFC/ml), and autumn (3 UFC /ml) seasons, while absent during winter. The Tunari Dam water samples revealed the presence of only 2 UFC/ml faecal coliform bacteria during summer season, and absence of these pathogens during the other seasons. The faecal streptococci content at the Dimieni Bridge varied depending on the season, ranging from 5×10^{3} UFC/ml during autumn and winter to 1.4×10 UFC/ml in summer, with an intermediate value (9×10^{2} UFC/ml) during spring (Fig. 4). Meanwhile, for the Tunari Dam location, faecal streptococci were recorded only during the winter season (1.4×10^{2} UFC/ml) (Fig. 5).

Sulphate-reducing bacteria are an indicator of ecosystem pollution with organic substances, being able to reduce the microbial biomass due to the accumulation of H_2S toxic for aquatic organisms (LAZĂR et al., 2017). The high content of sulphate-reducing bacteria recorded in water samples from the Dimieni Bridge (Fig. 6) suggested a high anaerobic activity for organic matter degradation, with maximum (5.75×10^{7} cells/ml) reached during the spring period. For the Tunari Dam (Fig. 7), the cell density of aerobic heterotrophs varied between 7.5×10^{5} cells/ml in winter and 2.25×10^{5} cells/ml during summer season, with 10^{2}-10^{3}-fold lower values during autumn and spring, respectively. At this site, the number of sulphate-reducing bacteria registered the highest content during the winter season (5.5×10^{7} cells/ml), with a large drop during summer (5.5×10^{4} cells/ml) and a lower presence in spring and autumn (4.75×10^{2} cells/ml) (Fig. 7).

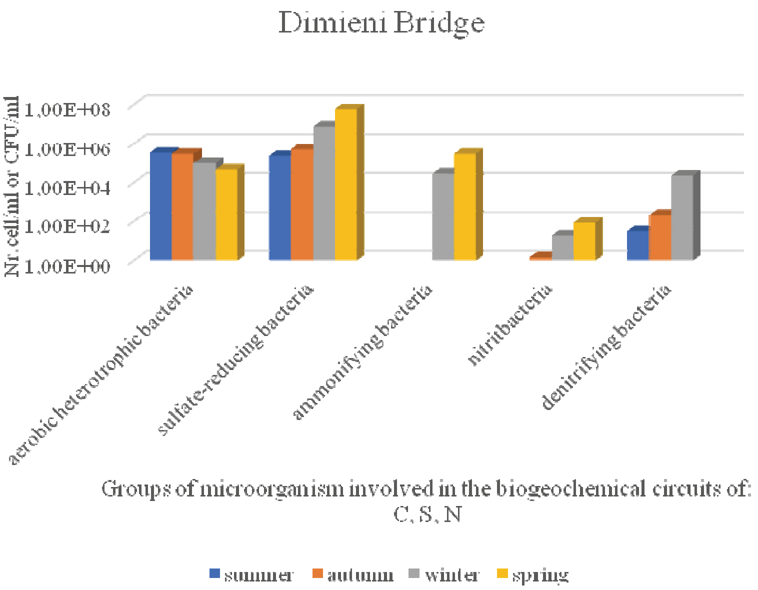

Figure 6. Groups of microorganisms involved in the biogeochemical circuits of carbon (C), nitrogen (N), sulphur (S) identified in the Dimieni Bridge site.

Bacteria involved in ammonification and nitrification (nitrite bacteria and nitrate bacteria) processes were present at te Dimieni Bridge site only in summer at a calculated content of 3x10 cells/ml (Fig. 7), possibly related with the lowest content of total dissolved solids (345 ppm) recorded during this season (Fig. 2). During autumn, nitrite and denitrifying bacteria were identified at this River site at a 1.4 cells/ml and 2.2×10^{2} cells/ml content, respectively. The increased number of denitrifying bacteria could be justified by the highest content of total dissolved solids (510 ppm) recorded during autumn season (Fig. 2). Moreover, the absence of ammonifying bacteria and nitrate bacteria was also noted during this period of time (Fig. 7). For the same sampling point, an increased number of bacteria involved in ammonification (2.8×10^{4} cells/ml), of nitrifying bacteria (1.8x10 cells/ml) and denitrifying bacteria (2.2×10^{4} cells/ml) was identified during the winter season, while nitrate bacteria were absent. In spring, only ammonifying bacteria (2.8×10^{5} cells/ml) and nitrite bacteria at low density (8×10 cells/ml) were identified among the nitrogen metabolizing microorganisms (Fig. 7).

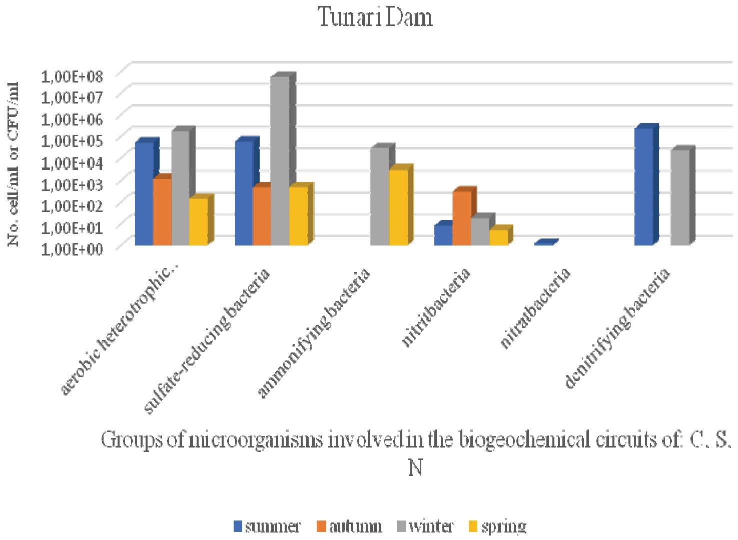

Figure 7. Groups of microorganisms involved
in the biogeochemical circuits of carbon (C), nitrogen (N), sulphur (S) identified in the Tunari Dam site.

At the Tunari Dam, ammonifying bacteria were absent during the summer season, and only a low number of nitrite bacteria (8 cells/ml) and nitrate bacteria (1.18 cells/ml) were identified, while the denitrification process was highly present (2.2×10^5 cells/ml). A comparison of the seasonal microbial content involved in the nitrogen cycle indicated the dominance of denitrifying bacteria during summer (8x10^4), the sole presence of nitrite bacteria (3×10^2 cells/ml) during autumn, an intensification of the processes underlying the nitrogen biogeochemical circuit during winter represented by ammonifying (3×10^3 cells/ml), nitrite (1.8x10 cells/ml), and denitrifying (2.2×10^4 cells/ml) bacteria, and a conserved ammonifying bacteria content while reduced presence (5 cells/ml) of bacteria involved in the nitrification process during spring season. The increased number of bacteria identified in the three stages of the cold season could be due to the highest values of the TDS content that was recorded at this location during this year interval. The reported data suggests an incomplete biogeochemical nitrogen cycle occurring at the two locations of the Pasărea River (ZARNEA, 1994; ARDELEAN, 2012; LAZĂR et al., 2016). Moreover, the determined physical and chemical parameters of the water samples from these investigated sited suggested the presence of polluted factors with an inhibitory effect on specific enzymatic activities involved in nitrogen biogeochemical transformations.

The chemical composition of the water in the Pasărea River. The chemical composition of the investigated Dimieni Bridge and Tunari Dam zones of the Pasărea River (Fig. 8) showed a large variation based on the sampling season. During summer, both sites contained SiO_2 (15-18 % mass), and lower content of K_2O, CaO, Fe_2O_3, As_2O_3, Cl, Al_2O_3, while >35% mass TiO2 was present at the Tunari Dam, and 14% mass of Tb_4O_7 and Lu_2O_3 at the Dimieni Bridge. Water samples collected during autumn (November 2020) showed a low content of SiO_2, K_2O, CaO, As_2O_3 and Cl as compared to the summer season, with <10% in the water collected from the Tunari Dam, and < 5% at the Dimieni Bridge. In addition, 67% BaO and 3-6% of HO_2O_3, Gd_2O_3 and Cr_2O_3 to were detected at the Dimieni Bridge, and 30% Nd_2O_3, 11% ReO_2, 9.7% Fe_2O_3, 8.1% Tb_4O_7 and 4.7% SrO at the Tunari Dam (Fig. 8).

During the winter season (February 2021), high concentrations of BaO (80% by mass) were identified at the Tunari Dam and Dimieni Bridge (35%), respectively, followed by lower mass percentages (<6) of Fe_2O_3, SiO_2, CaO, K_2O and Cl. Sm_2O_3 (16% mass), Tb_4O_7 (10% mass), Gd_2O_3 (8% mass) determined at the Dimieni Bridge (Fig. 8).

The chemical composition during spring (April 2021) revealed an increase of the BaO mass percentage (73%) at the Dimieni Bridge, while only 20% at the Tunari Dam, as in the other seasons, and lower percentages (<5%) of SiO_2, K_2O and CaO. Water samples from the later location also showed a high content of CeO_2 (30%), followed by Fe_2O_3 (8.6%), As_2O_3 (6.12%), GeO_2 (4.85%) and SeO_2 (3.4%) (Fig. 8).

Microbial and chemical criteria for the polluted water of the Pasărea River. Based on current standard for drinking water quality (***. Law 458/2002), and previous studies of water pollution (SELVAM et al., 2015; NEAGU et al., 2021), the current data were interpreted in the frame of criteria for polluted flowing water considering the presence of (i) sulphate reducing bacteria, nitrite and nitrate bacteria independent of their content, and (ii) Cr, Ce, Al and Ba oxides or salts at various concentration, including traces. Meanwhile, the presence of total coliforms and fecal streptococci confirmed that the analysed water sample was microbiologically polluted. Regarding the pollution origin, a ratio >1 between fecal coliform bacteria and fecal streptococci indicated anthropogenic pollution, while values <1 corresponded to animal pollution (MESSLEY & KINGSBURY, 1973 SINTON et al., 1998; RAJI et al., 2015; MILLER & HUTCHINS, 2017). For the Pasărea River, the corroboration of the presence of these factors indicated a highly polluted water sample, while the partial occurrence of these factors corresponded to a slow or moderate pollution of the flowing water.

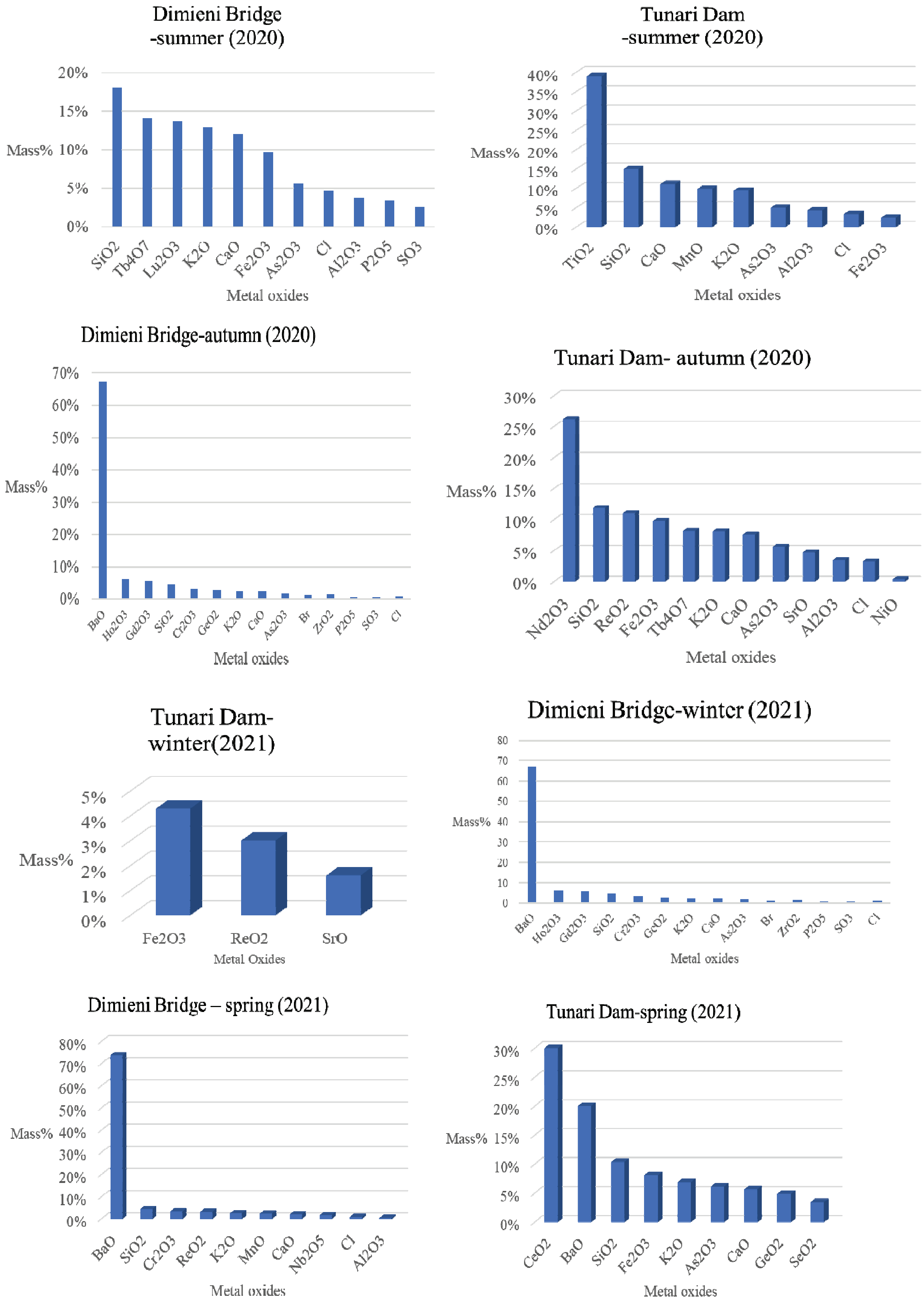

Figure 8. Season variation of the chemical composition of the water in the Pasarea River at DB and TD sites.

CONCLUSIONS

The physical and chemical parameters of the Pasărea River water indicated a variable pollution degree in two analysed sectors depending on the season. Suspended materials present at both sampling sites during the four seasons showed an increase in the electrical conductivity, with the highest values recorded at the Dimieni Bridge during autumn. The pH values ranged between 6.82 (winter - Dimieni Bridge) and 9.55 (winter - Tunari Dam), slightly exceeding the limits established in Order 161/16.02.2006, and suggesting an anthropogenic impact in the investigated areas.

The chemical composition of water highlighted the presence of oxides of rare metals such as Sm_2O_3, Gd_2O_3, Tb_4O_7, CeO_2, Nd_2O_3, Lu_2O_3, TiO_2, Cr_2O_3. Microbiological analyses revealed the presence of faecal streptococci and total coliforms during the four seasons in the sample of the Dimieni Bridge, and faecal coliforms during summer, autumn and spring. For the Tunari Dam, the microbial pollution was due to microbial groups comprised total coliforms and faecal coliforms during summer, and total coliforms and faecal streptococci in winter. Barium-based compounds were present at high concentrations, in support of chemical and biological pollution of the investigated areas.

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