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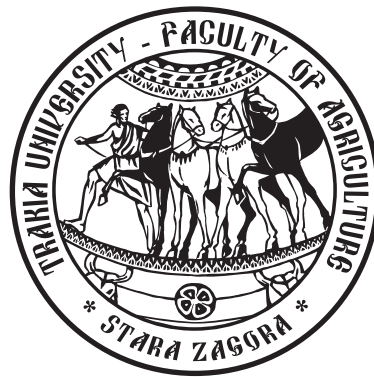
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Agriculture and Environment

Assessment of the physical-chemical status of surface water in lower part of Toundja river, Bulgaria

G. Mihaylova^{1*}, G. Kostadinova², G. Petkov²

¹Executive Environment Agency, Regional Laboratory, 6000 Stara Zagora, Bulgaria

²Department of Applied Ecology and Animal Hygiene, Faculty of Agriculture, Trakia University, 6000 Stara Zagora, Bulgaria

Abstract. The aim of the study was to assess the physical-chemical status of surface water in lower part of Toundja river (to the border with Turkey), on selected indicators of water quality (temperature, oxygen balance, pH, conductivity, ammonium nitrogen – N-NH₄, nitrite nitrogen – N-NO₂, nitrate nitrogen – N-NO₃, phosphates – P-PO₄, BOD₅) in accordance with the proposed Classification system (Consortium for Biomonitoring, 2010). The system is designed according to the Water Framework Directive (WFD) of the European Union 2000/60/EC, whose main objective is to achieve “good water status for surface water bodies by 2015”. The assessment was carried out at water body level, taking into account the results for three groups of indicators: general, nutrients and organic pollutants. For the investigated area was found a “good” status for surface water bodies of semi-river type R5. Achieving the goal of “good” state for surface water bodies of river type R12 (large lowland rivers) is mainly related to reducing pollution from phosphates and nitrite nitrogen. This leads to a real risk of not achieving the WFD objective of “good physical-chemical status” of surface water, used for irrigation in agriculture and other economic activities.

Keywords: Water Framework Directive, Toundja river, river water body type, physical-chemical quality indices, water quality status assessment

Introduction

Water Framework Directive 2000/60/EC (WFD) is the main document of the European Union's policy for managing the water sector, in response to growing demand for sufficient quantities of good quality water for all purposes. The implementation of the directive is challenging due to the introduction of a new integrated approach to sustainable water management based on river-basin.

Analysis and assessment of water quality and their ecological status raised many issues related to multicomponent, complex interaction between various elements and processes of the aquatic ecosystem and last, but not least, their variability under the influence of natural and anthropogenic factors. In determining the water quality is necessary to establish not only the content of one or another pollutant, but to assess the entire complex of pollutants in river water (Kostadinova, 2006; Gartsyanova, 2010; Georgieva, 2012). This requires the creation and implementation of methods for integrated assessment of river water quality by physical-chemical characteristics, based on which water can be categorized as water in “very good”, “good”, “moderate”, “bad” or “very bad” status. Furthermore, complex methods make it possible to perform comparative qualitative analysis of water in various areas of a river stream, or between river basins. In these methods, depending on the purpose of the study can be selected representative parameters (specific to a type of contamination), to assess the water quality. A key point in the implementation of an integrated method for assessing water quality is the selection of sufficient number and adequately representative physical-chemical parameters that most accurately reflect the degree of deviation of a given ecosystem from its natural state, due to anthropogenic pressure. Good status for the overall surface water status is determined by the basic physical-

chemical indices of water quality: temperature, oxygen balance, pH, conductivity and nutrients (nitrate nitrogen – N-NO₃, nitrite nitrogen – N-NO₂, ammonium nitrogen – N-NH₄; phosphates – P-PO₄), which should not exceed the levels specified in the classification system, and ensuring proper functioning of river type-specific ecosystem. Data for the country (RBMP, 2008) indicate that significant anthropogenic impact on water is in the lower parts of watersheds, particularly on urban areas and agricultural lands located in the lowlands. Usually in these areas is observed combined pressure of all sources of pollution – agriculture, industry, settlements, others. This pressure is measured in the total assessment of physical-chemical status of surface water bodies.

The purpose of this study was to assess the physical-chemical status of surface water from the lower part of Toundja river, by comparison of selected physical-chemical indicators of water quality with regulated values for these parameters in Classification system, proposed by the Consortium for biomonitoring (CB-1, CB-2, 2010).

Material and methods

Study area

Under the adopted typology of surface water bodies, Bulgaria is divided into two ecoregions: “East Balkans” and “Pontic Province” (Figure 1). Both basin areas, which naturally belong to the catchment area of the Black Sea – Danube and Black Sea are combined into one – N 12 Pontic Province. Both Mediterranean Basin regions in Bulgaria – East Aegean Region and West Aegean Region, form ecoregion East Balkans – N 7. East Aegean Region, including and catchment area of Toundja river is located entirely within ecoregion N 7 “East Balkans”. Designated (under the

* e-mail: gmihaylova@bv.bg

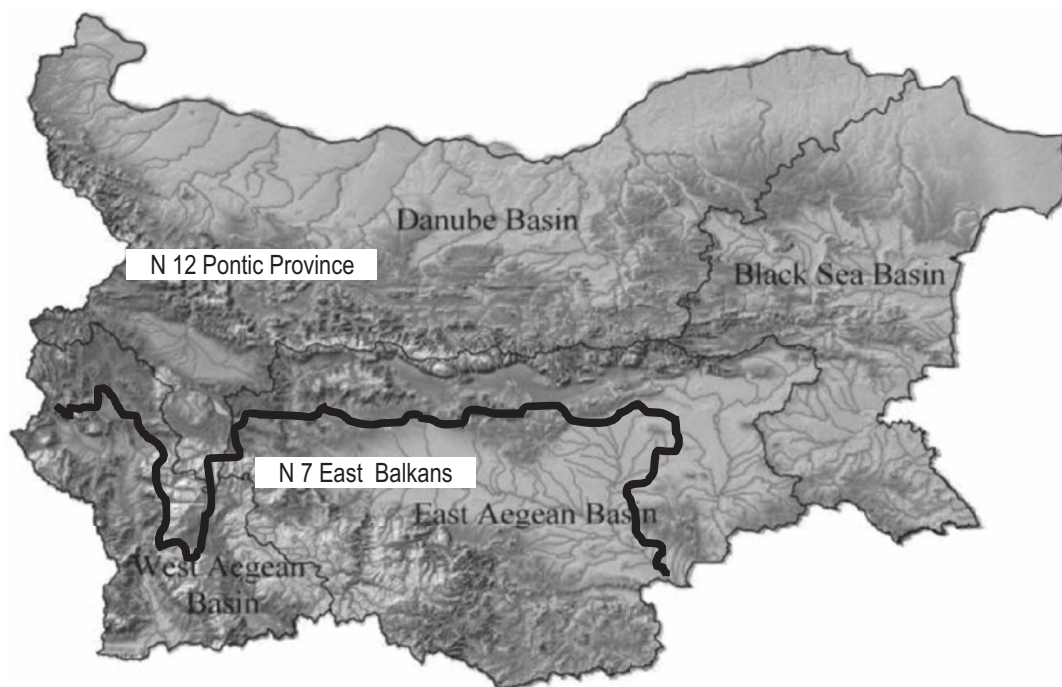


Figure 1. Map of Bulgaria with ecoregions – No 7 “East Balkans” and No 12 “Pontic Province”



Figure 2. Typology of surface water in Tundja river basin

typology) surface water bodies in category “River” in Toundja River Basin are presented in Figure 2.

Sources of pollution of Toundja river

Major pollutants of surface water in the lower part of Toundja

river are industrial enterprises, farms and settlements with sewerage systems, but without built wastewater treatment plants (WWTP) and settlements with built and acting, but technically outdated and in poor condition WWTP. Agricultural land used for intensive agriculture, which are treated with nitrogen and phosphate

fertilizers, pesticides and waste from livestock farms are one of the major sources of diffuse pollution (mainly nitrogen, phosphorus and biodegradable organics).

Monitoring points

To achieve the objectives of the study were used data from physical-chemical monitoring of surface water for the period 2004-2010, within 5 points of the lower part of the Toundja river (NEMS, Database "Surface water", 2004 - 2010) as follow:

- Point 1, Banya: river type R5 (semi-mountain type river);
- Point 2, Samuilovo: river type R12 (large lowland type river);
- Point 3, Hanovo: river type R12 (large lowland type river);
- Point 4, Elhovo: river type R12 (large lowland type river);
- Point 5, Srem: river type R12 (large lowland river).

Sampling and sample preparation

For sampling and sample preparation of water for analyses, international references (ISO 5667-2; ISO 5667-3; ISO 5667-6) and Bulgarian state standards (BSS) were used.

Physical-chemical parameters and methods for analysis

In monitoring points (*in situ*), with calibrated field equipment were measured standard physical-chemical parameters: temperature, reaction pH, dissolved oxygen and conductivity. All nutrients ($\text{NO}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$) and BOD_5 were determined in Regional Laboratory-Stara Zagora at the Executive Environment Agency, Sofia, in accordance with standards (Table 1).

Ecological assessment in respect of physical-chemical indices and river types

The interpretation of the physical-chemical monitoring results and assessment of the status of surface water were carried out in accordance with Classification system for assessing the ecological status and ecological potential of certain types of surface waters in the territory of Bulgaria (CB-2, 2010) (Table 2).

Statistical analysis of monitoring data, on selected physical-chemical parameters, were made with the construction of box – plots, summarizing the information of measured minimum and maximum values, number of analyzes (n), median (50-th), 25-th and

Table 1. Indices and standards for their analysis

No	Parameter	Standard
1.	Temperature, °C	ISO 10523
2.	pH	ISO 10523
3.	Conductance, $\mu\text{S}/\text{cm}$	BSS EN 27888
4.	Dissolved oxygen, mgO_2/l	BSS EN 25814
5.	Ammonium nitrogen (N-NH_4), mg/l	BSS ISO 7150-1
6.	Nitrite nitrogen (N-NO_2), mg/l	BSS EN 26777
7.	Nitrate nitrogen (N-NO_3), mg/l	BSS ISO 7890-3
8.	Orthophosphate (as phosphorus PO_4), mg/l	BSS EN ISO 6878
9.	Biological oxygen demand - BOD_5 , mg/l	BSS EN 1899-1,2

75-th percentile. This format allows comparison of the results for each monitoring point within the basin. If it is determined excess of medians, the surface water bodies are defined as bodies „at risk”.

Results and discussion

Water temperature (°C)

Values for water temperatures at all points in the river basin vary widely from 1.4 °C at point 3 (Hanovo) to 28.3 °C at point 5 (Srem) (Figure 3). The lowest temperatures were measured in February and the highest in August. The median values for water temperature ranged from 13.9 °C (point 1, Banya) to 17.6 °C (point 3, Hanovo). Interquartile ranges were 11.2 °C to 20.6 °C at point 2 (Samuilovo) and 8.8 °C to 23.8 °C at point 5 (Srem).

pH

Values for pH in water from all points in the river basin ranged from 6.81 at point 5 (Srem) to 8.9 at point 1 (Banya) (Figure 3). Median pH values ranged from 7.72 (point 3, Hanovo) to 8.37 (point 1, Banya). Interquartile ranges for pH were 7.85 to 8.06 at point 2 (Samuilovo) and 8.2 to 8.58 at point 1 (Banya). Figure 3 shows that the measured pH values for all observed points vary within limits 6.5-

Table 2. System for ecological assessment of water from different river types

Ecological status	Dissolved oxygen, mg/l	pH	Cond. $\mu\text{S}/\text{cm}$	N-NH_4 , mg/l	N-NO_3 , mg/l	N-NO_2 , mg/l	P-ortho- Po_4 , mg/l	BOD_5
Semi-river types - R5								
very good	10.5 ÷ 8.00	÷	700	< 0.04	< 0.5	< 0.01	< 0.02	< 1.2
good	8.00 ÷ 6.00	6.5 ÷ 8.5	750	0.04 ÷ 0.4	0.5 ÷ 1.5	0.01 ÷ 0.03	0.02÷0.04	1.2 ÷ 3
moderate	6.00 ÷ 5.00	÷	1000	0.4 ÷ 0.6	1.5 ÷ 3	0.03 ÷ 0.06	0.04÷0.06	3 ÷ 6
bad	5.00 ÷ 4.00	÷	1200	0.6 ÷ 0.8	3 ÷ 5	0.06 ÷ 0.09	0.06÷0.08	6÷12
very bad	< 4	÷	>1200	> 0.8	> 5	> 0.09	> 0.08	> 12
Lowland rivers types - R12								
very good	9.00 ÷ 7.00	÷	700	0.10	< 0.7	< 0.03	0.01 ÷ 0.025	< 2
good	7.00 ÷ 6.00	6.5 ÷ 8.5	750	0.1 ÷ 0.3	0.7 ÷ 2	0.03÷0.06	0.025 ÷ 0.06	2 ÷ 4
moderate	6.00 ÷ 5.00	÷	1000	0.3 ÷ 0.6	2 ÷ 4	0.06÷0.09	0.06 ÷ 0.08	4 ÷ 8
bad	5.00 ÷ 4.00	÷	1200	0.6 ÷ 1.5	4 ÷ 10	0.09	0.08 ÷ 0.1	8 ÷ 20
very bad	< 4	÷	> 1200	> 1.5	> 10	> 0.09	> 0.1	> 20

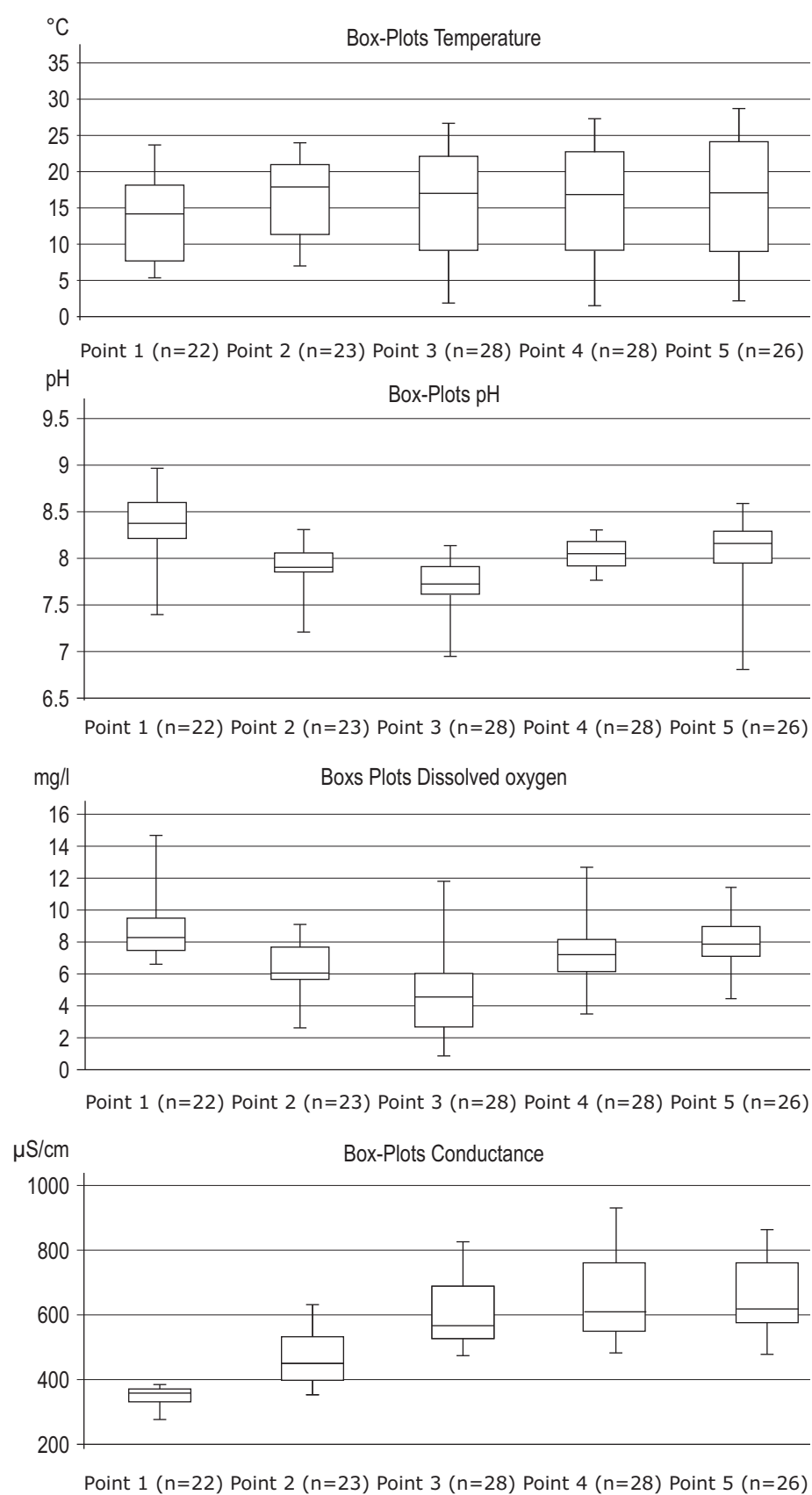


Figure 3. Temperature, pH, dissolved oxygen and specific conductance of water from different monitoring points of Tundja river –min, max, median, 25-th and 75-th percentiles

8.5 pH units. Water quality in lower part of Toundja river, assessed on the base pH values is defined as "good" in 100% of all cases.

Dissolved oxygen (mgO₂/l)

Dissolved oxygen concentrations in water from the different points ranged from 0.77 mg/l at point 2 (Samuilovo) to 14.64 mg/l at point 1 (Banya) (Figure 3). Median values ranged from 4.5 mg/l (point 3, Hanovo) to 8.2 mg/l (point 1, Banya). Interquartile ranges for dissolved oxygen concentrations were from 7.03 mg/l to 8.9 mg/l at point 5 (Srem) and from 2.6 mg/l to 5.9 mg/l at point 3 (Hanovo). The assessment of water quality in different monitoring points, in respect of dissolved oxygen, is based on the number of values for this indicator, recalculated in percentages and categorizing them according to classification system (Table 3). The analysis of Table 3 shows that in terms of dissolved oxygen, surface water are defined as water with "very good" quality in 55 % of all investigated samples (point 1, Banya) to 73 %, respectively at point 5 (Srem). Water status is defined as "moderate" for point 2 (Samuilovo) and "very bad" for point 3 (Hanovo) in 43 % of cases.

Specific conductance (μS/cm)

Values for specific conductance of water ranged from 279 μS/cm at point 1 (Banya) to 926 μS/cm at point 4 (Elhovo) (Figure 3). Median values ranged from 356 μS/cm (point 1, Banya) to 616

μS/cm (point 5, Srem). Interquartile ranges were from 334.75 μS/cm to 365.75 μS/cm at point 1 (Banya) and from 549.5 μS/cm to 759.75 μS/cm at point 4 (Elhovo). The assessment of water quality for different monitoring points, in terms of specific conductance, is presented in Table 3. The water status classified as "very good" in more than 60 % of all cases at points 4 (Elhovo) and 5 (Srem) to 100 % at points 1 (Banya) and 2 (Samuilovo).

Ammonium-nitrogen (N-NH₄)

Values for ammonium-nitrogen in water from all monitoring points of the river basin ranged from 0.01 mg/l at point 1 (Banya) to 3.13 mg/l at point 2 (Samuilovo) (Figure 4). Median values ranged from 0.04 mg/l (point 1, Banya) to 0.56 mg/l (point 2, Samuilovo). Interquartile ranges were from 0.02 mg/l to 0.09 mg/l at point 1 (Banya) and from 0.22 mg/l to 0.9 mg/l at point 3 (Hanovo). The assessment of water quality in different monitoring points, in terms of ammonium-nitrogen, is presented in Table 3. The status of surface water is defined as "good" in 50 % of all cases at point 1 (Banya) and point 5 (Srem), and "bad" at point 2 (Samuilovo – 37 %) and point 3 (Hanovo – 40 %).

Nitrite-nitrogen (N-NO₂)

Content of nitrite-nitrogen in water from all points in the river basin ranged from 0.004 mg/l at point 1 (Banya) to 0.83 mg/l at point

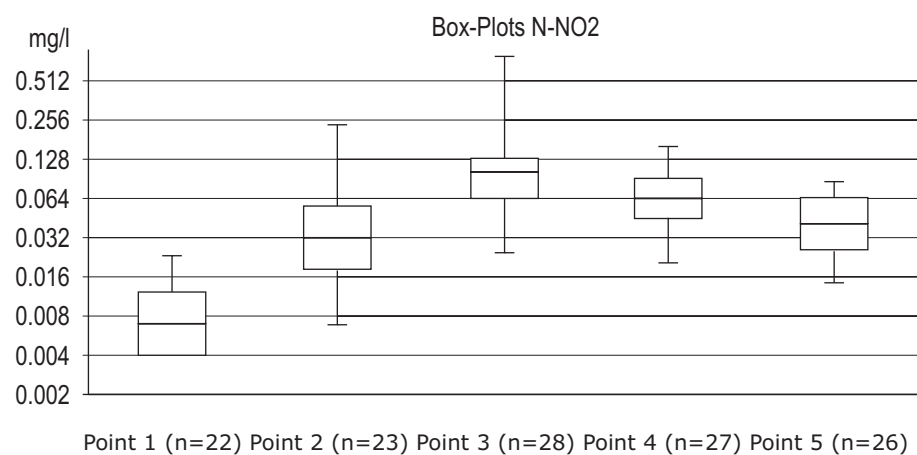
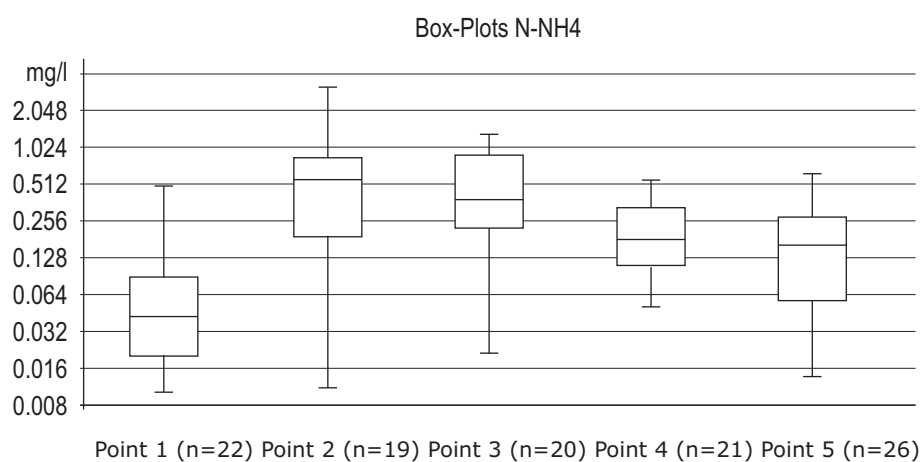
Table 3. Water quality of Toundja river at investigated points and indices (in % of all cases)

Ecological status	Point 1 (Banya)	Point 2 (Samuilovo)	Point 3 (Hanovo)	Point 4 (Elhovo)	Point 5 (Srem)
Dissolved oxygen, mgO ₂ /l					
very good	55	39	1r1	50	73
good	45	9	14	25	12
moderate	-	43	14	11	4
bad	-	-	18	11	11
very bad	-	9	43	3	-
Specific conductance, μS/cm					
very good	100	100	82	64	65
good	-	-	7	4	8
moderate	-	-	11	32	27
bad	-	-	-	-	-
very bad	-	-	-	-	-
Ammonium-nitrogen (N-NH ₄), mg/l					
very good	45	16	15	24	38
good	50	21	30	48	50
moderate	5	16	15	28	8
bad	-	37	40	-	4
very bad	-	10	-	-	-
Nitrogen-nitrite (N-NO ₂), mg/l					
very good	68	48	4	4	31
good	32	26	18	41	31
moderate	-	13	14	22	31
bad	-	-	-	4	7
very bad	-	13	64	29	-

Nnitrogen-nitrate (N-NO ₃), mg/l					
very good	50	25	22	4	4
good	50	75	59	65	58
moderate	-	-	19	27	38
bad	-	-	-	4	-
very bad	-	-	-	-	-

Phosphate (P-PO ₄), mg/l					
very good	64	21	-	-	4
good	32	11	7	-	-
moderate	4	5	-	7	-
bad	-	16	4	3	4
very bad	-	47	89	90	92

Biological oxygen demand (BOD ₅), mg/l					
very good	50	17	4	4	12
good	45	39	57	70	69
moderate	5	31	36	26	25
bad	-	9	3	-	4
very bad	-	4	4	-	-



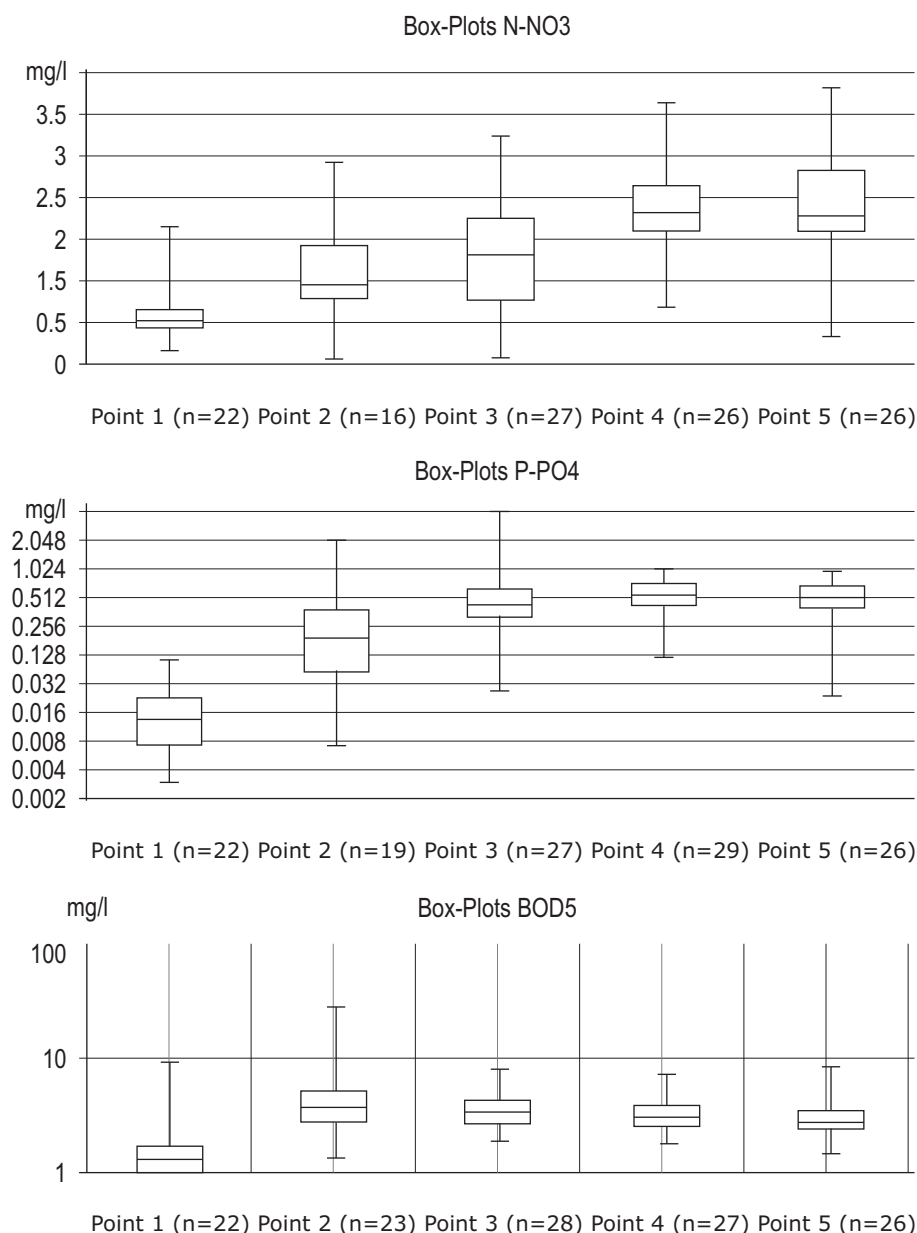


Figure 4. Content of N-NH₄, N-NO₂, N-NO₃, P-PO₄, BOD₅ in water from different monitoring points – min, max, median, 25-th and 75-th percentiles

3 (Hanovo) (Figure 4). Median values ranged from 0.007 mg/l (point 1, Banya) to 0.11 mg/l (point 3, Hanovo). Interquartile ranges were from 0.004 mg/l to 0.01 mg/l at point 1 (Banya) and from 0.07 mg/l to 0.14 mg/l at point 3 (Hanovo). The status of surface water classified as “very good” (68% of all cases) and “good” (32 % of all cases) only for point 1 (Banya) and “very bad” (64 % of all cases) for point 3 (Hanovo) and point 4, Elhovo (29 % of the cases) (Table 3).

Nitrogen-nitrate (N-NO₃)

Nitrogen-nitrate concentrations in water from the investigated points of the river basin ranged from 0.024 mg/l at point 2 (Samuilovo) to 4.2 mg/l at point 4 (Elhovo) (Figure 4). Median values ranged from 0.5 mg/l (point 1, Banya) to 1.79 mg/l (point 4, Elhovo). Interquartile ranges were from 0.41 mg/l to 0.62 mg/l at point 1 (Banya) and from 0.75 mg/l to 1.71 mg/l at point 3 (Hanovo). Surface water quality in all monitored points over 50 % of all cases is defined as “good” ecological status in terms of nitrogen-nitrate (Table 3).

Phosphate(as phosphorus–P-PO₄)

Values for phosphate at all points in the river basin vary widely from 0.003 mg/l at point 1 (Banya) to 2.00 mg/l at point 3 (Hanovo) (Figure 4). The median values for phosphate ranged from 0.01 mg/l (point 1, Banya) to 0.27 mg/l (point 4, Elhovo). Interquartile ranges were from 0.008 mg/l to 0.023 mg/l at point 1 (Banya) and from 0.19 mg/l to 0.35 mg/l at point 5 (Srem). Surface water quality, in terms of phosphate indicator is defined as “very good” (64 % of all cases) and “good” (32 % of all cases) only for point 1 (Banya) and “very bad” (47 % to 92 % of all cases) in all other locations, due to incomplete treatment of waste water from large settlements (Sliven, Yambol, Elhovo) (Table 3).

Biological Oxygen Demand (BOD₅)

Values for BOD₅ in water from different points ranged from 1.00 mg/l at point 1 (Banya) to 1.92 mg/l at point 3 (Hanovo) (Figure 4).

Median values ranged from 1.34 mg/l (point 1, Banya) to 3.73 mg/l (point 2, Samuilovo). Interquartile ranges were from 1.03 mg/l to 1.73 mg/l at point 1 (Banya) and from 2.76 mg/l to 5.12 mg/l at point 2 (Samuilovo). The assessment of water quality in the river, in terms of BOD₅ indicator, for different monitoring points is presented in Table 3. The data show that the status of surface water in terms of BOD₅ is defined as "good" in 39 % to 70 % of all cases.

Conclusion

Assessment of water quality in the lower part of Toundja river, based on selected physical-chemical indices (temperature, pH, dissolved oxygen, conductivity, NO₃-N, NO₂-N, NH₄-N, PO₄-P and BOD₅), determined the surface water bodies of semi-river type R5 (point 1 – Banya) in "good" ecological status. The reason is that around this monitoring point there are no significant anthropogenic pressure. Assessment of water quality in water bodies from river type R12 (large lowland rivers), monitoring points - Samuilovo, Hanovo, Elhovo and Srem, determined the water status as water "at risk" with respect to achieving good physical and chemical condition. The main reason for that are the combined effect of various significant anthropogenic impacts on this part of the river (discharge of untreated sewage from cities, diffuse pollution from agricultural land treated with nitrogen and phosphate fertilizers, composting operations and the use of organic manure from livestock farms). Failure to reach a "good" status of river water bodies is mainly associated with excess amounts of phosphate, except point 1 (Banya) and by nitrite-nitrogen, except point 3 (Hanovo).

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Todorov N and Mitev J, 1995. Effect of level of feeding during dry period, and body condition score on reproductive performance in dairy cows, IXth International Conference on Production Diseases in Farm Animals, Sept. 11 – 14, Berlin, Germany, p. 302 (Abstr.).

Thesis:

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