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ANALYSIS OF THE STATE OF THE SURFACE WATERS OF THE PYASACHNIK DAM

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Abstract

An ecological monitoring survey of the freshwater ecosystem of the Pyasachnik Dam was carried out in the period 2011-2016. The main indicators of surface water quality such as temperature, transparency, electrical conductivity, dissolved oxygen, $N–NH_4$, $N–NO_2$, $N–NO_3$, orthophosphates P, total nitrogen, total phosphorus, and chlorophyll a content were monitored. Hereafter, the obtained results are discussed by years and seasons. The chemical status and ecological potential of the freshwater ecosystem were determined. The investigated surface waters are suitable for irrigation, but with a permanent mandatory monitoring.

Keywords: ecological potential, irrigation, physicochemical monitoring, chemical status, chlorophyll

INTRODUCTION

Pyasachnik Dam is located on the territory of Hisarya municipality, Plovdiv region, between the villages of Belovitsa and Lyuben, in the Upper Thracian lowland, on the southern slopes of the Mountain Sredna Gora. Its area is 9.1 km², and its volume is 103.7 million m³ (Georgiev & Vladev, 2007). It powers up the rivers Pyasachnik, Kalavaschitsa, Gerenska, and some others as well. It is fed by the atmospheric and underground waters in the area. No production and processing activities related to the wastewater discharge into the dam have been established. There are a lot of agricultural areas in the region and the main crops grown are cereals, technical crops, fodder, and oil crops. Adjacent agricultural areas with the agrotechnologies applied for crops' cultivation are a potential source of diffuse nitrate pollution in the dam's waters. At the same time, the Pyasachnik Dam is used by the company "Irrigation Systems" for irrigation activities by the municipalities of Hisar and Saedinenie (Appendix 1, Article 13, Item 1 of the Water Law, List of complex and significant dams under number 35). The dam and the surrounding area are attractions for camping, sport fishing, and recreation. On the other hand, the Pyasachnik Dam is distinguished by exceptional biological diversity. The freshwater ecosystem was declared under BG 0002010 "Pyasachnik Dam" as protected area according to the Birds Directive (Directive 2009/147/EC), as well as it is in close connection with the protected area BG 0000444 "Pyasachnik River" according to the Habitats Directive (Directive 92 /43/EEC) and the requirements of the Law on Biological Diversity (2002). Since 1997, a BirdLife International has declared thet the dam as an ornithologically important site under NATURA 2000. Since 1998, it has been adopted as a Corine site because it is a place where endangered bird species of European importance are located (NATURA 2000).

Until now, there are some scientific publications on its ecological potential. Cheshmedjiev et al. (2010) published data based on the phytoplankton. The study of Peycheva et al. (2014) was focused on the toxic and essential metal concentration of freshwater fish. Smilyanov et al. (2018) and Varadinova & Smilyanov (2020) worked on the biological element macrozoobenthos. However, there is a

lack of physicochemical monitoring of surface waters of the Pyasachnik Dam and chlorofil a content, according to Regulation Norm H-4/2012 and Water Framework Directive (2000/60/EC, WFD).

The current research aims to: 1) present the main results of the conducted physicochemical monitoring and research on the content of chlorophyll a for phytoplancton in the dam ecosystem; 2) analyze the state of the surface waters, and the possibilities of using the waters of the Pyasachnik Dam for crop irrigation.

MATERIALS AND METHODS

During 2011-2016, ecological monitoring studies of the freshwater ecosystem of the Pyasachnik Dam were carried out. Sampling was done at the Dams wall, marked as the Pyasachnik Dam-wall point (42.398566, 24.570536; Figure 1). The research was conducted during the spring, summer, and autumn seasons of all aforementioned years. The sampling was carried out at 5 m from the shore and from a depth of 1.5 m, according to the standard procedures (BDS ISO 5667-4 and VVLM 1013/2010). Water testing was according to the following standards: BDS 17.1.4.01, BDS EN 27888, BDS EN 26777, BDS EN ISO 5814, BDS EN ISO 14911, BDS ISO 7890-3, BDS EN ISO 6878, BDS EN 12260. The main physicochemical parameters suc as temperature (mercury thermometer), electrical conductivity (Multiparameter instrument, WTW Multi 340 i), dissolved oxygen (Microprocessor oximeter, Orion Star A223), content of $N–NH_4$, $N–NO_2$, $N–NO_3$, orthophosphates P (Spectrophotometer, DR 3900), total nitrogen (System for the determination of total and organic carbon and nitrogen, Multi N/C 2100), total phosphorus (UV-VIS Spectrophotometer, ThermoScientific UV-Visible) were analyzed using the relevant equipment showed in the brackets.

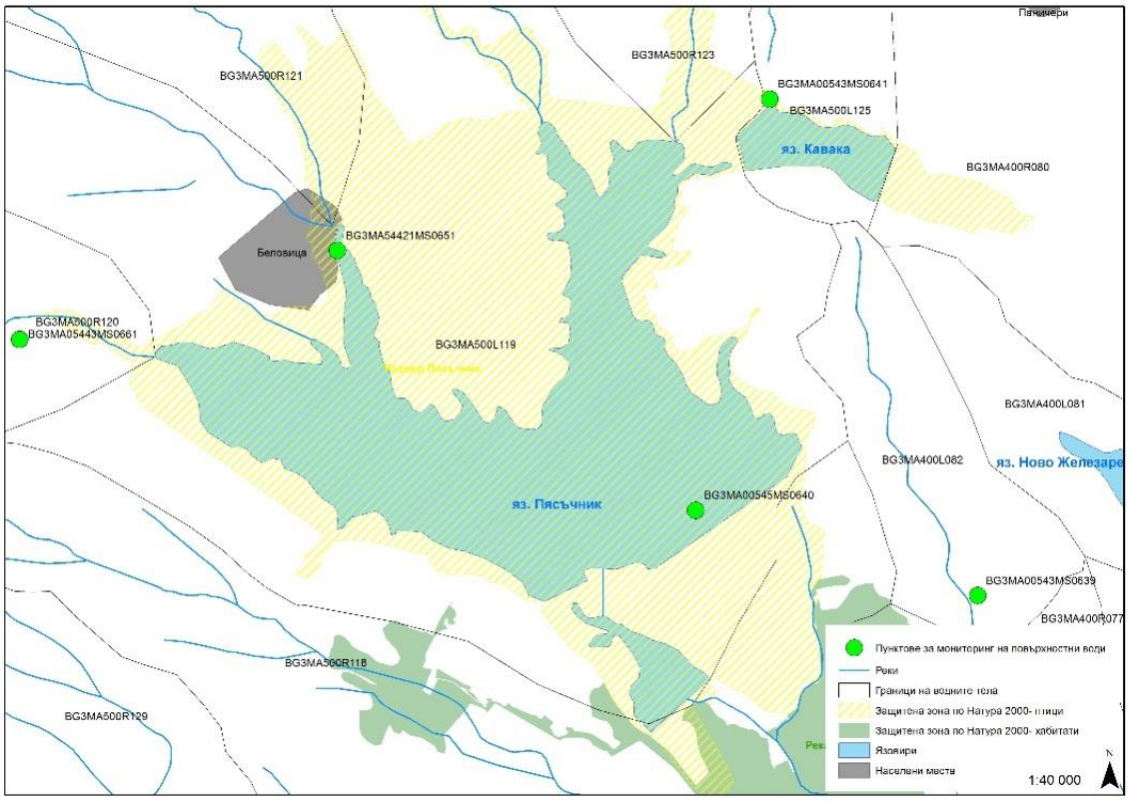

Figure 1. Pyaschnik Dam and location of the PyaschnikDam-wall sampling point

Water transparency (m) was determined visually, semi-quantitatively over 0.2 m by the method of Secchi (Davies-Colley & Smith, 2001) using a plastic or other material disc with a diameter of 20 cm, divided into four sectors oppositely colored in white and black. The amounts of chlorophyll a were determined according to BDS ISO 10260 by extraction with ethanol and measured spectrophotometrically (spectrophotometer Helios Alfa). The obtained results for the content of $N–NH_4$, $N–NO_2$, $N–NO_3$, and total nitrogen were analyzed with the indicators for orthophosphates, total phosphorus, transparency, and chlorophyll a. The suitability of the dams waters for irrigation have been evaluated according to Directive 91/676/EEC, the Rules for Good Agricultural Practice, and Regulation Norm No. RD-635/13.08.2013. The sampling frequency and the monitored indicators have been determined accordint to the requirements of the Water Framework Directive (2000/60/EC, WFD) and Regulation Norm H-4/2012.

A total of twenty-four samples for eleven indicators were processed. The analyzes was carried out in the Regional Laboratory - Plovdiv and the Regional Laboratory - Pazardzhik of the Environmental Executive Agency - Sofia. Statistical processing of data was done with Excel for Windows.

Determination of total phosphorus was done after peroxodisulphate oxidation according to BDS EN ISO 6878. The organophosphate compounds are converted to orthophosphates by acid mineralization with peroxodisulfate. The method used the reaction of the orthophosphoric ions (after oxidation) with an acidic solution containing molybdate and antimony ions to obtain an antimony phosphormolybdate complex, the intensity of which is measured spectrophotometrically at a wavelength of 880 nm.

Analysis of orthophosphates. The method consists in the reaction of orthophosphoric ions with an acidic solution containing molybdate and antimony ions to produce an antimony phosphormolybdate complex, the intensity of which is measured spectrophotometrically at a wavelength of 880 nm (or at 700 nm).

Nitrites analysis method is based on a reaction of the nitrite contained in the sample for analysis with 4-aminobenzenesulfonamide in the presence of orthophosphoric acid and a pH value of 1.9. A diazonium salt was obtained and simultaneous addition of N-(1-naphthyl-)-1,2-diaminoethane dihydrochloride gave a pink colored substance. Absorbance was measured spectrometrically at a wavelength of 540 nm.

Nitrates were estimated spectrophotometrically by the yellow-colored compound produced by the reaction of NO^{3-} with sulfosalicylic acid (formed by addition of sodium salicylate and sulfuric acid to the sample) after treatment with an alkaline base at a wavelength of 415 nm. Spectrometric measurement of a yellow compound of nitrates and sulfosalicylic acid (sodium salicylate + sulfur acid) after base treatment. Disodium EDTA (Na_2EDTA) is added simultaneously with the base to prevent precipitation of Ca^{2+}, Mg^{2+} addition of azide prevents the interfering effect of nitrites.

Ammonium was measured according to BDS EN ISO 14911. Spectrometric measurement of the blue coloration formed by the reaction of ammonium with salicylate and hypochlorite ions in the presence of sodium nitroprusside. Color intensity was measured spectrophotometrically at a wavelength of 655 nm. Spectrometric measurement at 655 nm of a blue compound obtained by the reaction of ammonia with salicylate and hypochlorite ions in the presence of Sodium nitrosopetnacyanoferrate (III) (sodium nitroprusside). – 1,3,5 – triazine -2,4,6 – (1H, 3H, 5H) – trione (sodium dichloroisocyanurate). The reaction of chloramine with sodium salicylate is carried out at pH 12.6 in the presence of sodium nitroprusside. Some chloramines present in the sample are quantified

as a result. Sodium citrate is added to the reagent to mask the effect of cations - Ca^{2+}, Mg^{2+}

According to Davies-Colley & Smith (2001) the Secchi transparency is a function of the reflection of light from the water surface and depends on the absorption characteristics of water, dissolved and suspended substances in it. There is also a relationship between dissolved organic matter concentration and transparency, but theoretical analyzes and empirical studies have shown that Secchi transparency is more related to the presence of suspended particles than to dissolved organic matter. Suspended particles can be microscopic algae or solids.

Table 1. Main indicators of surface water quality of the PyasachnikDam by years

Indicators	2011 Average±SD (Min-Max)	2012 Average±SD (Min-Max)	2013 Average±SD (Min-Max)	2014 Average±SD (Min-Max)	2015 Average±SD (Min-Max)	2016 Average±SD (Min-Max)
Temperature, °C	17.55±10.83 (6-29)	16.3±10.05 (4.2-26)	18.2±7.08 (10-27)	18.97±7.8 (11.5-26.4)	17.5±10.37 (5-27)	19.6±9.64 (5-30)
Transparency, m	-	G 1.87±1.55 (1-4.6)	V 1.15±0.77 (0.4-2)	V 1.05±0.3 (0.8-1.4)	V 1.26±0.38 (0.6-1.5)	V 0.88±0.19 (0.6-1)
Electrical conductivity, µS/cm	E 258±17 (243-283)	E 290±31 (260-330)	E 293±17 (268-310)	E 233±38 (196-286)	E 243±62 (184-324)	E 216±17 (200-248)
Dissolved O_2, mg/dm^3	E 8.7±2.38 (6.3-12)	E 8.5±2.37 (6.3-11.8)	E 9.8±3.05 (7.5-14)	E 8.93±3.49 (4.6-13.1)	E 9.6±1.36 (8.1-10.8)	E 9.2±1.99 (6.5-12.2)
N-NH_4, mg/dm^3	V 0.45±0.39 (0.1-1)	V 0.36±0.35 (0.037-0.8)	V 0.55±0.34 (0.22-1.03)	V 0.34±0.4 (0.05-0.91)	G 0.18±0.03 (0.14-0.21)	V 0.37±0.35 (0.11-0.88)
N-NO_3, mg/dm^3	E 0.15±0.06 (0.075-0.19)	G 0.67±1.06 (0.057-1.9)	E 0.25±0.11 (0.18-0.37)	E 0.21±0.18 (0.05-0.41)	G 1.01±1.11 (0.15-2.26)	•0.36±0.19 (0.11-0.57)
N-NO_2, mg/dm^3	E 0.02±0.02 (0.002-0.044)	E 0.005±0.004 (0.001-0.011)	E 0.019±0.005 (0.01-0.02)	-	-	-
N total, mg/dm^3	E 0.21±0.03 (0.19-0.23)	E 1.33±0.17 (1.2-1.45)	G 1.98±0.96 (1.4-3.4)	-	-	-
P orthophosphates mg/dm^3	V 0.15±0.1 (0.07-0.22)	V 0.14±0.11 (0.01-0.28)	V 0.12±0.09 (0.026-0.24)	V 0.09±0.1 (0.024-0.17)	V 0.07±0.05 (0.018-0.14)	G 0.04±0.02 (0.014-0.054)
P total, mg/dm^3	V 0.15±0.11 (0.07-0.22)	V 0.14±0.11 (0.039-0.3)	V 0.17±0.09 (0.086-0.26)	V 0.11±0.06 (0.062-0.19)	V 0.11±0.06 (0.036-0.17)	V 0.23±0.008 (0.05-0.067)
Chlorophyll a, µg/dm^3	B 30.38±43.04 (5.2-107)	16.44±14.37 (7.4-33)	V 68.45±67.87 (6.7-139)	B 29±15.43 (19-52)	V 108.7±91.5 (16.8-219)	B 25.27±11.79 (8.1-33)

Ecological status/potential:
Legend: E – excellent; G - good; - moderate; B - bad; V - very bad.

RESULTS AND DISCUSSION

The obtained results of the monitored main indicators of surface water quality of the freshwater ecosystem of the Pyasachnik Dam: temperature, transparency, electrical conductivity, dissolved oxygen, N–NH_4, N–NO_2, N–NO_3, orthophosphates P, total nitrogen, total phosphorus, as well and chlorophyll a for the period 2011-2016 are presented in Table 1 and Table 2 by season. The ecological potential of surface waters is presented using the adopted color marking according to the Water Framework Directive (2000/60/EC, WFD) and Regulation Norm H-4/2012. The chemical status is marked only as good or bad in blue or red. All results obtained in the present study correspond to a good chemical condition. Therefore, only the values for ecological potential are reflected in color in Tables 1 and 2.

Table 2. Main monitored water quality elements of the Pyasachnik Dam by seasons

Indicators	Spring	Summer	Autumn
Temperature,°C	6.95±3.04 (4.2-11.5)	25.68±2.37 (22-30)	15.56±5.66 (10.5-25)
Transparency, m	**G** 1.96±1.23 (0.6-2.7)	**V** 0.96±0.31 (0.6-1.5)	**V** 1.04±0.43 (0.4-1.6)
Electrical conductivity, µS/cm	**E** 286±46.11 (210-330)	**E** 236.75±35.09 (184-300)	**E** 256.12±39.01 (196-304)
Dissolved O_2, mg/dm^3	**E** 11±1.78 (8.1-13.1)	**E** 9.09±2.34 (6.3-14)	**E** 7.78±1.57 (4.6-9.4)
N-NH_4, mg/dm^3	**V** 0.35±0.31 (0.1-0.91)	**G** 0.25±0.29 (0.04-1)	**V** 0.6±0.35 (0.14-1.03)
N-NO_3, mg/dm^3	**E** 0.73±0.68 (0.19-1.9)	**G** 0.16±0.11 (0.05-0.4)	**E** 0.56±0.84 (0.07-2.26)
N-NO_2, mg/dm^3	**E** 0.025±0.02 (0.008-0.04)	**E** 0.005±0.005 (0.001-0.02)	**E** 0.009±0.001 (0.008-0.01)
N total, mg/dm^3	**G** 0.94±0.63 (0.23-1.40)	**G** 1.65±1.33 (0.19-3.4)	**G** 1.43±0.04 (1.4-1.45)
P orthophosphates, mg/dm^3	**V** 0.09±0.05 (0.078-0.144)	**G** 0.045±0.04 (0.014-0.144)	**V** 0.18±0.08 (0.054-0.28)
P total, mg/dm^3	**V** 0.09±0.04 (0.058-0.17)	**V** 0.08±0.07 (0.036-0.12)	**V** 0.19±0.08 (0.067-0.3)
Chlorophyll a, µg/dm^3	**G** 9.52±5.15 (5.2-16.8)	**B** 46.83±65.89 (8.9-219)	**V** 60.66±54.61 (7.4-146)

Legend: E – excellent; G - good; - moderate; B - bad; V - very bad.

The temperature differences were most significant when comparing to the individual seasons. In spring, it varies from 4.2-5°C to 10-11.5°C; summer from 22-30°C, etc. (Table 1-2).

Water purity also varied during the seasons of the study period. In spring, the transparency was between 1.5÷2-2.7 m, while in summer, it varied from 0.6-1.0 m to 4.6 m, and in the autumn - from 0.40-0.80 m to 1.4 -1.6 m. The average values showed good (1.87 m) for 2012, moderate (1.15-1.05-1.26 m) for 2013-2015, and poor (0.88 m) for 2016, with a norm for good ecological potential of 2.5 -1.5 m. The indicators of electrical conductivity of water show a good ecological potential at a norm of 650-750 µS/cm (Table 1-2) according to Regulation Norm No. H-4/2012 for the characterization of surface waters. Dissolved oxygen has a good ecological potential at 7.00-6.00 mgO_2/dm^3 rates. During spring, summer, and fall, the content of dissolved oxygen changed and ranged from 11-9.09-7.78 mgO_2/dm^3 (Table 1-2). The N–NH_4 content has a moderate ecological potential for the period 2011-2014, as well as for 2016, and it has a good ecological potential for 2015 (Table 1-2). The results thus obtained varied over the seasons, with a gradual increase observed in autumn, compared to the norms for good ecological potential (0.1-0.3 mg/dm^3). During the study period, 2011-2016, the values for N–NO_3 were of good ecological potential. Readings ranged from 0.15 to 1.01 mg/dm^3, compared to 0.6-1.8 mg/dm^3 norms. Values for N–NO_2 indicated a good ecological potential at rates of 0.03-0.06 mg/dm^3, with values of the quality trace element ranging from 0.005 to 0.019-0.02 mg/dm^3. Measurements for orthophosphates ranged from 0.04 to 0.15 mg/dm^3. The presented results showed a good ecological potential at norms of

0.025-0.050 mg/dm^3. The values for total nitrogen ranged from 0.94 to 1.65-1.43 mg/dm^3, showed a good ecological potential according to the standard (0.7-2.0 mg/dm^3). The total phosphorus results ranged from 0.09-0.08 to 0.19 mg/dm^3. They showed a moderate ecological potential at 0.025-0.050 mg/dm^3 (Table 1-2). During the studied period, thr content of chlorophyll a varied from 16.44 to 108.7 μg/dm^3, with values indicating good, moderate, and poor ecological potential for the spring, summer, and autumn seasons, respectively.

Correlation relationships (Spearman's correlation coefficient, rs) between major quality items were examined (Table 3).

Table 3. Correlation dependences (Spearman's coefficient, rs) between the contents of main quality elements

Correlation dependencies	rs	p
Chlorophyll a/ t^{o}C	0.19^{ns}	>0.05
Chlorophyll a/transparency	0.94****	<0.001
Chlorophyll a/dissolved O_2	0.99****	<0.001
Chlorophyll a/electrical conductivity	0.78**	<0.01
N-NH_4/chlorophyll a	0.48*	>0.05
N-NH_4/orthophosphates P	0.99****	<0.001
N-NH_4/P total	0.98****	<0.001
N-NH_4/transparency	-0.17^{ns}	>0.05
N-NO_3/chlorophyll a	-0.53*	>0.05
N-NO_3/orthophosphates P	0.53*	>0.05
N-NO_3/P total	0.31*	>0.05
N-NO_3/transparency	0.78**	<0.01
N-NO_2/chlorophyll a	-0.89****	<0.001
N-NO_2/orthophosphates P	0.73**	<0.01
N-NO_2/P total	-0.25^{ns}	>0.05
N-NO_2/transparency	0.99****	<0.001
N total/chlorophyll a	0.84***	<0.01
N total/orthophosphates P	-0.12^{ns}	>0.05
N total/P total	0.13^{ns}	>0.05
N total/transparency	-0.97****	<0.001

Legend: ns – non-significant correlation; * - moderate correlation; ** - significant correlation; *** - strong correlation; **** - very strong correlation.

Very strong correlations were found between chlorophyll content and those for transparency and dissolved O_2; between the N-NH_4 content and those for orthophosphate content P and P total; between the N-NO_2 content and that of transparency; between the total N content and that of transparency (Table 3). The values of the chlorophyll indicator were influenced by the content of N, P, and their compounds. Potential sources of pollution could be domestic wastewater from settlements without treatment facilities and agriculture.

From the physicochemical monitoring carried out, as well as on the basis of Regulation Norm No. RD-635/13.08.2013 of the Minister of the Environment and Water and Directive 91/676/EEC on the protection of water from pollution with nitrates from agricultural sources, the Rules for good agricultural practice are established that the surface waters of the Pyasachnik Dam meet the requirements of the

specified documents and can be used for irrigation but with permanent monitoring of the surface waters' quality.

According to the scientific literature, similar studies were carried out for other Bulgarian Dams as Dospat, Studen Kladenets, Ivaylovgrad, Koprinka, Zhrebchevo, Konush, and Srebarna Lake in carp fish breeding basins and others. Various correlations, trends and dynamics of phytoplankton, as well as other biological indicators of biological quality elements, accompanied by physicochemical and chemical quality indicators, have been tracked (Belkinova et al., 2012; Beshkova et al., 2014, Dochin & Stoyneva, 2016, Dochin & Ivanova, 2017, Dochin et al., 2017, Stoyneva, 1998, Terziyski, 2014, Hristov, 2013, Tsanev & Belkinova, 2008). The results obtained in this study can be used towards taking measures for water quality improvement and to protect components of the environment, biological diversity, and water resources.

CONCLUSION

As a result of the research carried out in the period 2011-2016 on the content of main elements for the quality assessment of the surface waters of the Pyasachnik Dam, it was established that the surface waters of the freshwater ecosystem were in good chemical condition. Excellent ecological potential was reported for electrical conductivity, dissolved O_2, N-NO_3 and N-NO_2, except for the N-NO_3 content during the summer period of the study (good ecological potential). Very strong correlations were found between chlorophyll a content, transparency and dissolved O_2; between the N-NH_4 content, orthophosphate content P and P total; as well as between the content of N-NO_2, total N and transparency. The surface waters of the Pyasachnik Dam have met the regulatory requirements in relation to the pollution from agricultural sources and can be used for irrigation but with permanent monitoring of their quality.

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