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## Agro-Ecological Assessment of Ovcharitsa Dam (Bulgaria) Water Used For Thermal Power Plant Cooling

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Abstract. Ecological (as a natural source) and agricultural (as a resource for fish farming and irrigation of crops) assessment of Ovcharitsa Dam water, used for thermal power plant (TPP) cooling was carried out in one monitoring point by measurement of 12 physicochemical parameters (temperature, transparency, pH, EC, DO, COD, BOD<sub>5</sub>, unionized NH<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub>, total N and P-PO<sub>4</sub>), one biological parameter (chlorophyll-a), 9 pesticides and volatile organic compounds /VOC/ (atrazine, simazine, diuron, 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene, tetrachloroethane, trichloromethane, hexachlorobutadiene) and 6 microbiological parameters (aerobic mesophilic microorganisms, coliforms, total coli titer, Escherichia coli counts, E. coli titer, Salmonella spp. counts), stipulated in Bulgarian legislation in 2016-2017 (REGULATIONS: No. 4, 2000; No. 18, 2009; On EQS for priority substances and certain other pollutants, 2010 and No. H-4, 2012). The water samples were taken periodically during a two-year period: for physicochemical and biological analysis - in February, April, June, August and November; for microbiological observation - in June, August and November; for pesticides and VOC - in April. Water sampling, sample preparation and analysis were performed according international ISO and BSS standards. It was found that: a) the dam water ecological status was determined as "poor" by chlorophyll-a content and "very poor" by orthophosphates content based on the lowest estimates for the monitored parameters; b) with regard to the content of pesticides and VOC, the dam water was defined as water "in good chemical status"; c) the values of all monitored parameters were within the ranges (recommended and mandatory) for carp fish water with exception of temperature and unionized NH<sub>3</sub>, which exceeded the norms during some months of the year; d) according to measured water transparency, the trophic state of dam water was determined as hypereutrophic; e) the microbial status of the analyzed water demonstrated that it was not suitable for irrigation because it exceeded norms for total coli-titer and E. coli-titer, and due to the presence of intestinal pathogens (Salmonella spp.), which are not allowed in the water for irrigation.

**Key words:** dam water, physicochemical and microbiological parameters, priority pollutants, water quality, natural source, fish farming, irrigation.

#### Introduction

On the territory of Bulgaria around 2200 dams are built. These surface water bodies have different ecological characteristics due to the different environmental conditions and level of anthropogenic pressure. According to Water Framework Directive (WFD) 2000/60/EC (EC, 2000) all water bodies had to achieve a "good status" and "good ecological potential" up to 2015. To date, for a number of reasons legislative, political, absent or deficient enforcement mechanisms and effective control, insufficient funding, etc., this goal has not been achieved yet in Bulgaria. Despite the existing tendency towards improving surface water quality during the period 1996-2016, there are still water bodies at risk (NRSPEB, 2018). Such an object is the Ovcharitsa Dam, one of the 25 largest dams in the country. It is rather different from the other dams as its water is used mainly for thermal power plant (TPP) cooling and also for fish farming, fishing sport and irrigation of agricultural crops. Despite the strong anthropogenic pressure on the dam, its location (on the flyway of migratory birds), suitable climate conditions and warm water make it an appropriate habitat for many birds (native and migratory) and fish species.

Ovcharitsa Dam as a part of the protected area (43.062 ha) of the National Ecological Network NATURA 2000 (No. BG0002023) is an important habitat for 76 species (of which 22 are included in the Red of Bulgaria) of migratory Book and waterfowl (about 45,700 birds annually) (SG, 2008). It is one of the suitable places in the world where the great cormorant (Phalacrocorax carbo L., 1758), the Dalmatian Pelican (Pelecanus crispus Bruch, 1832) and the big White-fronted Goose (Anser albifrons Scopoli, 1769) stay for the winter. Moreover, the lake is inhabited by more than 18 fish species, such as common carp (Cyprinus carpio silver L., 1758), carp (*Hypophthalmichthys* molitrix Val., 1844), bighead carp (Hypophthalmichthys nobilis Rich., 1845), grass carp (Ctenopharyngodon idella Val., 1844), black carp (Mylopharyngodon Rich., piceus 1846),

European catfish (Silurus glanis L., 1758), channel catfish (Ictalurus punctatus Raf., 1818), pike-perch (Sander lucioperca L., 1758), perch (Perca fluviatilis L., 1758), pike (Esox lucius L., 1758), Prussian carp (Carassius gibelio Bloch, 1782), bream (Abramis brama L., 1758), bleak (Alburnus alburnus L., 1758), pumpkinseed (Lepomis gibbosus L., 1758), vimba bream (Vimba vimba L., 1758), chub (Squalius cephalus L., 1758), roach (Rutilus 1758), rudd rutilus L., (Scardinius erythrophthalmus L., 1758), etc. The basin also harbors different species of mollusks, of which the commonest is the invasive "Zebra" mussel (Dreissena polymorpha Pall., 1771).

During the last 10 years, a number of studies have been carried out on many surface water bodies in the country, including Ovcharitsa Dam. They were focused on different aspects of water monitoring and water quality assessment but did not provide an integral picture for their state. In the summer 2009 CHESHMEDJIEV et al. (2010) investigated 80 lakes/reservoirs on the basis of four main metrics (phytoplankton biovolume, Algae Groups Index, transparency, chlorophyll-a) and found that more than half of the them were in compliance with the WFD (EC, 2000) good requirements for ecological state/potential, and Ovcharitsa Dam was determined being "moderate" as in ecological status.

In the period 2012-2013, large-scale studies were conducted on the abiotic and biotic parameters of the Ovcharitsa Dam water and the area around it, with the aim to develop and implement in 2013 a Plan for the management of the dam as a protected area (DULEV et al., 2013). Data on the physicochemical indicators of water, the qualitative and quantitative composition of phyto- and zooplankton and benthos, the species composition and the status of fish stocks and populations of amphibians and birds have been collected and processed. Based on the obtained results the water quality status was determined as "moderate",

despite the measured above-threshold values for phosphates and transparency (TRAYKOV, 2013; UZUNOV, 2013).

ATANASOV et al. (2012) established high concentrations of heavy metals (Fe, Mn, Cu, Cr, Ni, Zn, Pb and Cd) in water and liver of carps (Cyprinus carpio L.) from dams with high anthropogenic pressure in Stara Zagora District, incl. Ovcharica dam. VALKOVA et al. (2015) found the highest Cd content in the sediment followed by aquatic plants, water and muscles of carps from different surface water bodies in Stara Zagora region (Bedechka River, Sazliyska River, Tundzha River, Jrebchevo Dam). In two other papers VALKOVA (2014; 2015) reported significantly higher levels of Zn, Pb, Cd and Ni in the muscle of "Zebra" (Dreissena polymorpha) from Ovcharitsa Dam than in the water, allowing the author suggesting the use of this mussel as an indicator of heavy metals pollution of surface water bodies. The studies of DOCHIN (2014), DOCHIN et al. (2015) and DOCHIN & IVANOVA (2017) in dams with different levels of anthropogenic load (Kardzhali, Dospat and Konush dams) revealed that the most significant abiotic factors affecting the quantitative, seasonal and spatial distribution of phytoplankton in water were pН, DO, transparency and electrical conductivity.

All these studies, for the most part, concern the water quality and assessment of the surface water bodies as a natural resource. There is no up-to-date integral scientific information on water bodies, heavily modified by strong anthropogenic pressure, used for different human activities. Ovcharitsa Dam falls into this group and the above mentioned argument motivated the present study, whose purpose was to assess the dam water quality by means of physicochemical, biological and microbiological parameters in three aspects - as a natural source, as a resource for fish farming and as a resource for irrigation of agricultural crops.

### **Materials and Methods**

*Study area.* The study was carried out during 2016-2017 in Ovcharitsa Dam (altitude 135 m, area 6550 acres, water volume 62.4 million m<sup>3</sup>, fed by Ovcharitsa River) located in ecoregion 7 (Eastern Balkan), the East Aegean River Basin, Southeast Bulgaria, Stara Zagora district, 50 km southeast from town of Stara Zagora. According to Regulation H-4 (2012) for characterization of surface water in the country, the Ovcharitsa Dam type is a L15 – large planar medium deep dam. The dam water is used for cooling of the TPP "Maritza East 2" EAD (1630 MW) in the largest energy complex of Bulgaria.

Sampling and sample preparation. Water samples were collected from surface water in one Monitoring Point (MP) - N42.263781° E26.146924° in the same months for the two years of the study as followed: 5 times for physicochemical and biological parameters August (February, April, June, and November, n=10), 3 times for microbiological parameters (June, August and November, n=6) and once for priority substances (pesticides and VOC) - April, n=2. For water sampling and sample preparation for analyses, international references (ISO 5667-1, 2, 3; ISO 27828) were used. The samples for physicochemical analysis were collected in dark containers with chemically pure glass beakers (3 L) and for microbiological analysis were taken in sterile bags.

Parameters and methods for analysis. The following parameters, characterizing surface determined: water quality were physicochemical parameters - temperature (T, °C) by Bulgarian State Standard (BSS) 17.1.4.01:1977, transparency by Secchi (TS) by Routine laboratory method (RLM)-2010, pH by ISO 10523, electroconductivity (EC) by BSS EN 27888 and dissolved oxygen (DO) by BSS ISO 25814 - in situ, with field Multi-340i/SET meter; COD by ISO 15705, BOD<sub>5</sub> by BBS EN 1899-2, unionized NH<sub>3</sub> by BSS 17.1.4.10, nitrite (NO<sub>2</sub><sup>-</sup>) by BSS EN 26777, nitrate (NO<sub>3</sub><sup>-</sup>) by BSS 17.1.4.12, total nitrogen  $(NH_3, NO_2^-, NO_3^- and N_{org.})$  by BSS EN 12260 and orthophosphates /P-PO<sub>4</sub>/ by BSS EN ISO 6878; biological parameter - chlorophylla by BSS ISO 10260; pesticides and volatile

organic compounds (VOC) - pesticides containing nitrogen and phosphorus by RLM 1026/2014, alkylurea pesticides by ALM 1026/2014, VOC by BSS EN ISO 15680; microbiological parameters aerobic mesophilic microorganisms (AMO) (MORITA, 2003), sanitary indicator microorganisms (Escherichia coli, total coliforms) and pathogens (Salmonella spp.) were determined by plating of 1 mL of the sample solutions or appropriate dilutions on selective, chromogenic culture sheets medium (Rida<sup>®</sup>Count Total; Rida<sup>®</sup>Count E. Rida<sup>®</sup>Count coli/Coliforms; Salmonella/ Enterobacteriaceae, **R-Biopharm** AG, Germany). The sheets were inoculated in duplicate, incubated at 35 °C for 24-48 h and the colonies were counted. Specific microorganisms form colonies of different colour on the specific test cards. To confirm the results for Salmonella spp., suspected colonies were subcultured onto Bismuth sulfite (BS) agar (HiMedia, Mumbai, India) at 35 °C for 24 hours. If typical colonies were present (brown, gray, or black sometimes with a metallic sheen), 2 or more of them were transferred onto triple sugar iron (TSI) agar (HiMedia, Mumbai, India) and lysine iron agar (LIA) (HiMedia, Mumbai, India). If, atypical reactions were observed after 24 h of incubation the result was considered as negative for Salmonella spp. The results are expressed in colony forming units (CFU/ml).

*Water quality assessment.* It was carried out in three aspects: the dam water as a natural source, as a resource for fish farming and as a resource for irrigation by requirements of Bulgarian standards (Regulation No. 4, 2000; Regulation No. 18, 2009; Regulation on EQS for priority substances and certain other pollutants, 2010 and Regulation No. H-4, 2012).

*Statistical analysis.* All data were analyzed by STATISTICA 6.0 for Windows (StatSoft Inc., 2001).

### **Results and Discussion**

*Ovcharitsa Dam water quality as a natural source* 

*Physicochemical parameters*. This group includes 12 parameters (Table 1). The monitored parameters demonstrated different dynamics of variation during the different months of the year as followed:

*Temperature.* The water temperature of Ovcharitsa Dam depended on the season and largely on the mode of TPP operation. As expected, the lowest temperatures were measured in February (10.4-12.5 °C), and the highest - in summer – June and August (28.3-31.0 °C). These higher temperatures and the continuous flow of warm water prevent the dam from freezing and make it unique for wintering fauna (DULEV *et al.*, 2013).

Transparency. Transparency values varied within a very narrow range for both years – from 1.0 to 1.2 m, with higher values in 3 out of 5 months for 2016 and in 4 out of 5 months in 2017. As the indicator is directly related to the phytoplankton quantity, it can concluded that amount be the of phytoplankton increased during the summer (June and August 2016 and August 2017) compared to other seasons. According to the data for this indicator, the status of the "moderate". waters was defined as CHESHMEDIJEV et al. (2010) assessed the Ovcharitsa Dam water quality on the same metric as "good" in July-September 2009 at water transparency 2.3 m.

*pH*. The distribution of surface water pH by months was relatively even – from pH 7.20 to 8.83, 2016 and from pH 7.51 to 9.02, 2017. The pH values in February, June, August and November for 2016, and in August and November 2017 fell within the range corresponding to "good" ecological status of the water (pH 6.5-8.7) are.

*EC.* The results obtained determined the water quality for this parameter as "moderate" for all monitored period. Highest levels of EC were measured in April followed by slight decrease in following months. TRAYKOV (2013) explained the dynamics in EC values during the different seasons with the dying of "flowering" in the spring and subsequent decomposition of the

biomass, that releases a large amount of soluble compounds into the water.

DO. This parameter indicated the level of eutrophication and depends on various factors: abiotic (temperature, vertical and horizontal circulation of water) and biotic (development of photosynthetic organisms, putrefactive processes, etc.). The maximum DO values were measured in February (10.5-11.2 mg/l) at lowest water temperature (10.4-12.5 °C) and the minimum DO values in August - 7.6 mg/l (2016) and June - 7.5 mg/l (2017) at highest water temperatures (30.0-31.0 °C). similar А relationship between dissolved oxygen and water

temperature was reported by TRAYKOV (2013) and UZUNOV (2013) again for Ovcharitsa Dam in 2012-2013. Our results characterized water quality by DO content as "excellent" in June, August and November 2016 and in April, June, August and November 2017.

*COD*. This is not a standard indicator of surface waters quality, but it gives an idea of their pollution, especially with substances that are not biodegradable. The parameter's values varied significantly (12-22 mg/l, 2016 and 14-25 mg/l, 2017) with a fluctuating trend towards decrease from February-April to November during the surveyed period.

**Table 1.** Physicochemical and biological parameters of Ovcharitsa Dam water, 2016 – 2017. *Legend:* \* R - Recommended norms; M - Mandatory norms (for carp water); \*\* MPC - Maximum permissible concentrations; *Ecological status: E* – excellent, *M* –moderate, *G* – good, *P* –poor, *VP* – very poor.

Parameters	Years	Parameters values and Ecological water status by months			RegulationRegulationH-4/2012No.4/2000		tion 100	Regulation No.18/2009 MPC**		
		II	IV	VI	VIII	XI		R*	<b>M</b> *	
Physicochemical parameters										
т°С	2016	10.4	20.5	29.0	30.0	15.1	_	28.0	10.0	28.0
I, C	2017	12.5	24.7	31.0	28.3	17.9	-	20.0	10.0	28.0
Transpa-	2016	1.2	1.2	1.0	1.0	1.2	1.0-2.0			
rency, m	2017	1.2	1.2	1.2	1.0	1.2	М	-	-	-
рН	2016	8.65	8.22	8.83	8.62	7.20	6.5-8.7	6	0	6.9
pm	2017	8.71	9.02	9.01	8.34	7.51	G	0-	-9	0-9
EC,	2016	750	770	760	756	759	> 750	-		2000
μS/cm	2017	790	821	763	800	765	М			2000
DO,	2016	11.2	10.1	9.1	7.6	7.9	9.00-7.00	> 8	>7	> 2
mg/l	2017	10.5	9.1	7.5	8.1	7.8	Е	- 0	- 1	~ 2
COD,	2016	22	18	20	17	12		-		100
mg/l	2017	19	25	16	14	16	-			100
BOD <sub>5</sub> ,	2016	1.5	1.3	2.2	2.7	1.8	2-4	16		25
mg/l	2017	1.7	2.8	2.5	2.9	3.5	G	<b>&lt;</b> 0	-	25
Unionized NH mg/l	2016	0.076	0.077	0.025	0.072	0.020	< 0.1	<0.05 <0.025		5
Onionized W13, mg/1	2017	0.092	0.150	0.031	0.064	0.030	Е	<0.00 <0.020	<0.02J	5
$NO_2^-$ ,	2016	0.005	0.005	0.006	0.003	0.015	< 0.03	<0.03 -		
mg/l	2017	0.007	0.002	0.006	0.006	0.030	Е			-
NO <sub>3</sub> -,	2016	0.54	0.49	0.32	0.17	0.30	< 0.8	-		
mg/l	2017	0.73	0.03	0.05	0.18	0.21	Е			20
Total N,	2016	1.28	1.21	0.92	1.15	0.92	0.7-2.5	-		
mg/l	2017	1.34	0.89	0.76	1.06	1.27	G			
P-PO <sub>4</sub> ,	2016	0.07	0.08	0.10	0.10	0.12	> 0.06, P	0.4		3
mg/l	2017	0.08	0.08	0.10	0.19	0.16	> 0.10, VP	0.4	5	
Biological parameter										
Chlorophyll-a, µg/l	2016	10	7	30.6	17	10	10.1 <b>-</b> 20.0, M			
	2017	6	12	32	20	9	20.1-50.0, P			-

 $BOD_5$ . The measured  $BOD_5$  values also varied significantly (1.3-2.7 mg/l, 2016 and 1.7-3.5 mg/l, 2017), but at relatively low levels throughout the monitored years. The water organic load was higher in 2017 compared to 2016, from 1.07 times in August to 2.15 times in April, revealing that this parameter was time-dependent. With regard to this characteristic, water quality was defined as "good" throughout the study period.

Biogenic elements. Nitrogen compounds (Unionized NH<sub>3</sub>, NO<sub>2</sub>, NO<sub>3</sub> and total N). Unionized NH<sub>3</sub> values varied significantly (0.020-0.150 mg/l) with higher levels in February and April compared to the other monitoring months (June, August and November). The  $NO_2^-$  concentrations also demonstrated large fluctuations throughout the year (0.002-0.030 mg/l), but with higher levels in November than in other months. The established  $NO_2^-$  levels in the water, as an intermediate product between the oxidized and reduced nitrogen states can be defined as low. NO<sub>3</sub><sup>-</sup> concentrations showed a similar monthly dynamics as unionized  $NH_3$  and  $NO_2^-$  concentrations. The measured  $NO_3^-$  values were much higher in February than in other months, especially in 2017. Significant fluctuations of the three indicators confirmed the influence of many environmental factors, among which most important are probably the processes of nitrification and denitrification. The content of unionized NH<sub>3</sub>,  $NO_2^$ and  $NO_3^$ determined the quality of dam water as "excellent".

Total N values varied between 0.76 and 1.34 mg/l during the different months of the two years of the study (Table 1). The highest levels were measured in February and the lowest - in June and November (2016) and in June (2017). According to the results for this parameter, the water quality was assessed as "good".

*Orthophosphates (P-PO*<sub>4</sub>). The parameter values fluctuated from 0.07 to 0.16 mg/l and showed an upward trend from February to November, more pronounced in 2017 compared to 2016. The water quality

assessed on the basis of orthophosphates was determined as "poor" in February-August 2016 and in February-June 2017, and as "very poor" in November (2016) and August and November (2017).

The location of the dam (on lands contaminated or at risk for pollution by biogenic elements, Order No. RD-146/2015) and the recirculation of the water used to cool the TPP contributes not only to the accumulation but also to the increase in the concentrations of the pollutants in the water body. In the same time, the concentrations of nitrogen compounds were maintained low, which determined the "good" and "excellent" water quality of the dam, while the content of orthophosphates was high and determined a "poor" and "very poor" water quality. According to TRAYKOV (2013) and UZUNOV (2013), the main reason for this contradiction is the higher temperature of the water as a result of TPP cooling. Higher water temperature, especially during the summer months, accelerates the metabolic degradation of the accumulated organics, especially of nitrogen compounds and enhances the processes of denitrification. This leads to a decrease in the concentrations of the various forms of nitrogen without substantially altering the amount of phosphorus. The results show that the nitrogen compounds were more environmentally sensitive, as they are converted more quickly than orthophosphates. Therefore, practices to limit contamination of the dam with biogens should be implemented.

*Biological parameter*. The values of the only determined biological parameter - chlorophyll-a, showed similar and significant dynamics of variation over the different months of the studded period (Table 1). The lowest levels of chlorophyll-a were determined in February and November (6-10  $\mu$ g/l), the highest - in June and August (17-32  $\mu$ g/l) and intermediate – in April (7-12  $\mu$ g/l) (Table 1). The established seasonal differences in the amount of chlorophyll-a are logical, being determined by the seasonal

dynamics in the amount of phytoplankton. During the warmer months of the year, especially in the summer, the biogenic elements accumulated in the water body from the catchment area of the dam and by the organic wastes from the two fish farms and other human activities, combined with the higher water temperatures, create conditions for intensive development of phytoplankton, respectively the amount of chlorophyll-a.

On the basis of chlorophyll-a content, the ecological status of Ovcharitsa dam water was determined as "moderate" in February and November 2016/2017 and in April 2016, and as "poor" in June and August 2016/2017, and in April 2017. In July-September 2009 CHESHMEDJIEV *et al.* (2010) assessed the dam water quality on this metric as "good" (chlorophyll-a =  $7.32 \mu g/l$ ).

Based on the estimates for all physicochemical and biological metrics monitored, the majority of which were in the ranges between "moderate" and "excellent" status, the final estimate for Ovcharitsa dam water for the period 2016-2017 was "poor" by chlorophyll-a content and "very poor" by orthophosphates, i.e. on the lowest estimates according to the Regulation H-4 (2012).

When comparing the results obtained in the present study and the estimates for the monitored indicators with those established by DULEV (2013), TRAYKOV (2013) and UZUNOV (2013) on the same parameters for Ovcharitsa Dam water in 2012-2013, no significant differences were found. The estimates authors' for the different parameters varied between "moderate" and "very good", with exception of the phosphates and transparency, characterizing the water quality as "poor". Therefore, it can be concluded that phosphorus compounds and, to a lesser extent, the other biogens continue to be a problem for dam water quality.

*Pesticides and volatile organic pollutants.* The dam water contained negligibly low concentrations of some of the pesticides and volatile organic pollutants (Table 2). Their levels were much lower than the permissible of the average annual values limits according to Regulation on EQS (2010) as followed: for atrazine by 12 times; for simazine by 100 times; for 1,2,3-, 1,2,4- and 1,3,5-trichlorobenzene by 4 times; for trichloromethane by 6.25 times and for hexachlorobutadiene by 15 times (calculated by MPC). Ovcharitsa Dam water quality, in terms of all these priority pollutants was defined as water "in good chemical status". This assessment is an indirect indicator for the good operation of the local waste water treatment plant at the TPP "Maritza East 2" EAD, which is a source of priority and priority hazardous substances. The National System for Environmental Monitoring of Water has neither found an excess of the individual emission norms for pollutants and priority substances in the treated waste water from the TPP in 2017 (RSSW-EAB, 2017).

*Ovcharitsa Dam water quality as a resource for fish farming* 

Dam water quality assessment as a resource for fish farming according to Regulation No. 4 (2000) was made based on the analysis of data obtained for physicochemical parameters, pesticides and volatile organic compounds (Tables 1, 2). Here, we included additionally coliform counts, which is a required microbiological indicator (Table 3) and water transparency, which is not regulated by the standard, but is important indicator for fish water quality. In this case, we used the legislation for carp fish farming because the water temperature of the Ovcharitsa Dam is more suitable for cyprinids rather than for salmonids or acipenserids. The dam water is inhabited by various carp species such as common carp, silver carp, bighead carp, grass carp, bleack carp and Prussian carp, as well as some other bottom and warm-loving fish species - European catfish, channel catfish bream, bleak, pumpkinseed, vimba bream, chub, roach, rudd, etc.

**Table 2.** Content of pesticides and volatile organic compounds (VOC) in Ovcharitsa Dam water, 2017. *Legend:* \* MPC - Maximum permissible concentrations (norms for carp water); \*\*AAV-EQS: Average annual value - Environmental quality standards; \*\*\*MPC- EQS: MPC - Environmental quality standards.

	Concentration	Regulation	<b>Regulation on EQS/2010</b>					
Parameter		No. 4/2000	AAV-	MPC-				
	μg/I	MPC*	EQS**	EQS***				
C. Nitrogen and phosphorus containing pesticides, n = 2								
Atrazine	< 0.05	-	0.6	2.0				
Simazine	< 0.01	-	1.0	4.0				
D. Alkylurea pesticides, n = 2								
Diuron	< 0.03	-	0.2	1.8				
E. Volatile Organic Compounds, n = 2								
1,2,3-trichlorobenzene	< 0.1	0.4	0.4	Not applied				
1,2,4-trichlorobenzene	< 0.1	0.4	0.4	Not applied				
1,3,5-trichlorobenzene	< 0.1	0.4	0.4	Not applied				
Tetrachlorethane	< 0.4	-	-	-				
Trichloromethane								
(chloroform)	< 0.4	12.0	2.5	Not applied				
Hexachlorobutadiene	< 0.04	0.1	-	0.6				

**Table 3.** Microbiological parameters of Ovcharitsa Dam water, 2016 – 2017. *Legend:* \* R - Recommended norms; \*\*Maximum permissible concentrations.

Parameters	Years	C <sub>x</sub> ±SD (n=3)	$C_{min}$	C <sub>max</sub>	#Regulation No. 4 R*	Regulation No. 18/2009 MPC**
Aerobic mesophilic	2016	$22000\pm3606$	19000	26000		
microorganisms, CFU/ml	2017	$23000 \pm 3606$	20000	27000	-	-
California CEU/100 ml	2016	$3300 \pm 361$	2900	3600	10.000	-
Conforms, CFU/100 mi	2017	$3400 \pm 300$	3100	3700	10 000	
Total coli titor ml	2016	-	0.01	0.01		< 0.1
	2017	-	0.01	0.01	-	
Escharichia coli CEU/100 ml	2016	$130 \pm 52$	100	190		-
	2017	$150 \pm 40$	100	190	-	
Ecclerichia coli titor ml	2016	-	1	0.1		< 1.0
Escherichia con-inter, ini	2017	-	1	0.1	-	
	2016	$1200 \pm 100$	1100	1300		Not allowed
Saimonella spp., CFU/100 ml	2017	$1300 \pm 173$	1200	1500	-	

The values of the most monitored parameters were within the range of the norms (recommended and mandatory) for carp fish as followed: pH – between 7.20 and 9.02, with exception of two cases in April and June 2017,

when the values were slightly over the upper limit, pH = 9.02; DO levels were over the minimum permissible value (> 7 mg/l), from 1.07 to 1.6 times; BOD<sub>5</sub> values were lower than the permissible limit for recommended norm (< 6 mg/l, from 1.71 to 4.61 times; NO<sub>2</sub><sup>-</sup> and P-PO<sub>4</sub> concentrations were lower than the allowable limits for recommended norms (< 0.03 mg/l and 0.4 mg/l) up to 15 times and from 2.10 to 5.71 times, respectively; trichlorobenzene (1,2,3-; 1,2,4and 1,3,5-), tetrachloroethane, trichloromethane and hexachlorobutadiene levels were more than 4 times, 30 times and over 2.5 times, respectively lower than the relevant maximum allowable concentration; coliform counts were 2.70 to 3.45 times lower than the maximum permissible counts.

Deviations from the norm were demonstrated by temperature and unionized  $NH_3$ values. The water temperature exceeded the upper permissible limit in the summer months (June-August), by 1.0-2.0 °C in 2016 and by 0.3-3.0 °C in 2017 (Table 1). The elevation of water temperature above the upper limit was not high, except during the summer months and probably did not affect significantly the carp fish diversity and populations. On the other hand, attention should be paid on the fact that biota and some physicochemical processes (oxygen solubility, hydrophobic interactions) are particularly sensitive to temperature changes (MIHAYLOVA *et al.*, 2012).

The unionized ammonia content in water exceeded the recommended and mandatory norms in February, April and August in 2016 and in February, April, June (only the mandatory norm), August and November (only the mandatory norm) in 2017 (Table 1, Fig. 1).



**Fig. 1.** Content of unionized ammonia in Ovcharitsa Dam water by months and years.

The presence of unionized ammonia in levels exceeding the norm in combination with low and normal concentrations of nitrites are indicative of fresh fecal water pollution (most likely from both fish farms) well as for subsequent as rapid ammonification that reduces the ammonia concentration by transforming it in nitrite (possibly the warm water and the large number of the water microorganisms contribute to this rapid effect).

Water transparency is an indirect parameter characterizing the water quality for fish. It depends on the amount of particles (inorganic - sediment and organic algae, phytoplankton, zooplankton, etc.) in the water. The transmission of light through the body of water is extremely important since the sunlight is the primary source of energy for all biological phenomena. Water transparency directly is related to orthophosphates and chlorophyll-a content in water and it is used for determination of the trophic state. In our case, the parameter's values varied between 1.00 and 1.20 m, which determined the trophic state of dam as hypereutrophic (RMB, 2019).

Some studies revealed relationships between water transparency and aquatic organisms that depend on vision for foraging, intra-species mating, or communication (HEUBEL & SCHLUPP, 2006; KARACAOGLU et al., 2006; LJUNGGREN & SANDSTRÖM, 2007). DE MELO et al. (2009) established a positive and highly significant correlation between water transparency and abundance, and distribution of the Cynodontidae Bananal species in the floodplain, Mato Grosso, Brazil. These results give reason to carry out such studies in Ovcharitsa dam and other surface water bodies in the country. Perhaps it's time to include this parameter to the national standard of water quality for fish.

*Ovcharitsa Dam water quality as a resource for irrigation* 

The controlled parameters, characterizing the water quality for

irrigation of agricultural crops (total 12) fall into three of the five groups of indices according to Regulation No. 18 (2009): salinity (EC), sanitary indicator microorganisms (total coli-titer, *Escherichia coli* titer and enteric pathogens – *Salmonella* spp.) and miscellaneous (T °C, pH, DO, COD, BOD<sub>5</sub>, unionized NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and P-PO<sub>4</sub>).

Salinity. EC. This is the basic parameter, characterizing the water salinity, respectively the total salt concentration of the water. By years of measurement EC values were very close; their fluctuation between both years of the investigation was on the average 1.04 times (Table 1). The results obtained (750.0-821.0 µS/cm) were similar to EC values of Sazliyka River water (654.3–912.2 µS/cm, ZHELEV et al., 2015) which through Ovcharitsa River receives water from Ovcharitsa Dam, and much higher than the EC values of Maritsa River water (at Mirovo village, Stara Zagora district) - 296.0-378.0 µS/cm (KOSTADINOVA et al., 2017), left tributary of which is Sazliyka River. A probable cause of reduced EC while the water passes from a smaller to a larger surface water body (as in our case) is likely associated with increased water amount in each successive water body while the amount of dissolved salts remains relatively constant.

On the basis of this parameter the Ovcharitsa Dam water quality meets the requirements for irrigation of agricultural crops as all values were 2.43 to 2.67 times lower than the MPC for irrigation water (<  $2000 \mu$ S/cm), (Table 1).

Sanitary indicator microorganisms. This group includes parameters stipulated in Regulation No. 18 (2009) - total coli-titer, Escherichia coli titer and enteric pathogens – Salmonella spp., as well as some additional parameters - aerobic mesophilic microorganism (AMO), total coliforms and E. coli (Table 3). The values of all investigated microbiological parameters varied in different ranges within years and between the two years of the surveyed period. By years the parameters values varied more significantly as followed: for AMO - 1.37 times in 2016 and 1.35 times in 2017; for coliforms – 1.24 and 1.19 times and for Salmonella spp. - 1.18 and 1.25 times, respectively; for E.coli - 1.9 times for both vears; for total coli-titer and E.coli titer without fluctuations. Significantly narrower value ranges demonstrated the parameters when the two years of the observed period were compared: for AMO - 1.05 times at minimum and 1.04 times at maximum values; for coliforms - 1.06 and 1.03 times, and for *Salmonella* spp. – 1.09 and 1.15 times, respectively; for E. coli, total coli-titer and E.coli titer the values did not change. Relative persistence in those microbiological parameters of the water was observed during the two years of monitored period. This gives reason to assume that the factors of the environment in the dam water that affect the microorganism's diversity and populations are also relatively constant over the years.

The content of microorganisms in the water of the final water intake of the water of the Ovcharitsa Dam (on the country's territory) - Maritsa River, was drastically lower than in the dam water: for AMO 18-138 CFU/ml vs. 19000-27000 CFU/ml; for coliforms 155-340 CFU/ml vs. 2900-3700 CFU/ml; for Salmonella spp. 21-66 CFU/ml vs. 1100-1500 CFU/ml (KOSTADINOVA et al., 2017). Three main reasons for these substantial differences in the counts of the different microorganisms between the Ovcharitsa Dam water and the Maritsa River identified. water can be First, the temperature of the dam's water was higher than the temperature of the river water (the dam's water is used for cooling of TPP); second, the amount of dam water was less than that of the river water, it creates conditions for enrichment of the dam water with organic substances/wastes to a greater extent than for the river water due to the two fish farms for intensive rearing of fish and from the other hydrobionts living in the dam); and third, the dam water remains in the dam for a longer period of time compared to the water in the river, which entails slower change in the environmental conditions in dam water in comparison to river water. All this creates more favorable conditions for the survival and increasing of the microbial populations in the dam water.

Quality assessment of Ovcharitsa Dam water as a source for irrigation showed that total coli-titer (0.01 ml) and E. coli titer (1 -0.1 ml) values did not meet the requirements of Regulation No. 18 (2009) - < 0.1 and < 1.0 ml, respectively. For the other parameter (Salmonella spp.) the water also did not meet the irrigation requirements because intestinal pathogens are not allowed in the water. The reason for this restriction is that these microorganisms remain viable for long periods of time - up to 6 months and can contaminate irrigated soil and plants (ROSEN, They can survive 2000). in aquatic environments by a number of mechanisms, entry viable including into but а nonculturable state and/or residing within free-living protozoa (LIU et al., 2018). The results of our study correspond to the data of different investigations in this area which confirm that the water samples from fish ponds and dams usually contain high concentrations of aerobic mesophilic bacteria, E. coli, coliform bacteria and intestinal pathogens (including Salmonella spp.), which necessitate the need to apply monitoring programs on the microbiological indicators (GULUMBE et al., 2016; VASILE et al., 2017). The standard permits the use of such irrigation water for only after decontamination which is not always possible and economically justified.

*Miscellaneous*. All pH, DO, COD, BOD<sub>5</sub>, unionized NH<sub>3</sub>, NO<sub>3</sub><sup>-</sup> and P-PO<sub>4</sub> values were within the permissible limits for irrigation water (Table 1). Only the water temperature in the June-August (the irrigation period) exceeded the maximum allowed limit of 28 °C, by 1-2 °C in 2016 and with 0.3-3.0 °C in 2017. Notwithstanding this, the elevation of the water temperature above the allowed limit was not great and according to Regulation No. 18 (2009), the water can be used for irrigation when it meets the requirements of the other parameters of this group as in our case.

### Conclusions

two-year study (2016-2017)А of by water 12 Ovcharitsa Dam physicochemical parameters (temperature, transparency, pH, EC, DO, COD, BOD<sub>5</sub>, unionized NH<sub>3</sub>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, total N and P-PO<sub>4</sub>), 1 biological parameter (chlorophyll-a), 9 pesticides and VOC (atrazine, simazine, diuron, 1,2,3-, 1,2,4and 1,3,5trichlorobenzene, tetrachloroethane, trichloromethane, hexachlorobutadiene) and microbiological parameters (aerobic 6 mesophilic microorganism, coliforms, total coli titer, E. coli, E. coli titer, Salmonella spp.), legislation stipulated in Bulgarian concluding that: a) the ecological assessment of the dam water as a natural source determined the water ecological status as "poor" by chlorophyll-a content and as "very poor" by orthophosphates content; b) the pesticides and VOC concentrations did not exceed the environmental quality standards and determined the water as water "in good chemical status"; c) the dam water quality met the requirements for carp fish water by all monitored parameters, with the exception of temperature and unionized NH<sub>3</sub> values, which exceeded the norms in some months; d) by transparency the dam water trophic state was determined as hypereutrophic; e) the dam water did not meet the irrigation requirements as the values of total coli titer and E. coli titer exceeded the norms as well as due to the presence of intestinal pathogens (Salmonella spp.), which are not allowed in the water for irrigation.

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