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TUNDZHA RIVER WATER QUALITY AS A SOURCE FOR IRRIGATION IN AGRICULTURE

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Abstract

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The aim of the study was to investigate the quality of Tundzha River water in the upper stream during the summer of 2010 by 25 physicochemical indices, and assessed their suitability for irrigation in agriculture. For sampling and sample preparation of water, international ISO and BSS references were used. Sample analyses were made by equipment Mrlti 340i/SET, spectrophotometric methods and AAS. It was established that the quality of the surface water corresponded to the standards for irrigation according to 23 indices: temperature, pH, conductivity, total hardness, Ca, Mg, dissolved oxygen, BOD_5, COD, ammonium (NH_4^+), nitrites (NO_2^-), nitrates (NO_3^-), chlorides (Cl^-), sulfates (SO_4^{2-}), phosphates (PO_4^{3-}), K, Fe, Ni, Cu, Zn, Pb, Cd and Cr(VI). Deviations from the regulated standards were established for suspended solids and Mn. The correlation matrix revealed appreciable mutual relationship: between suspended solids-dissolved oxygen, conductivity-BOD, total hardness-BOD and total hardness-conductivity (R^2 0.957 - 0.999), and between Mg-Ca; K-Ca; Mn-Ca; Mn-Mg; Mn-K; Ni-K; Ni-Zn; Cd-Ca; Cd-Mg; Cd-K; Cd-Mn and Cd-Ni (R^2 0.951 - 0.999) in the studied water samples. Data analysis revealed that the anthropogenic impact on Tundzha River water in the investigated area does not affect water quality with a view to its applicability for irrigation purposes. The registered deviations from the quality standard for Mn could be explained by the discharge of industrial and sewage wastewaters from Kazanlak City (46545 inhabitants, large industrial center).

Key words: water quality, indices, assessment, irrigation

Abbreviations used: BOD - Biochemical Oxygen Demand; BSS - Bulgarian State Standards; COD - Chemical Oxygen Demand; MP - Monitoring Point; PCA - Principal Component Analysis, WWTP - Wastewater Treatment Plant

Introduction

The water resources of Bulgaria are of insignificant quantity - estimated as approximately 20.1 billion m^3. Their quantity is determined by the structure and dynamics of the water balance in the river systems. The latter is characterized by relatively limited rainfall (690 mm or 76.5 billion m^3), intense evaporation (514 mm - 57 billion m^3) and low river flow (176 mm - 19 billion m^3). Moreover the water resources are irregularly distributed throughout the territory of the country (RBMP, 2010).

The total water consumption in the country is estimated of over 10 billion m^3 (approximately 50% of the Bulgarian water resources). The major water consumers are agriculture - with annual water consumption for irrigation of 3.44 billion m^3, industry (1.95 billion m^3) and drinking water supply (0.788 billion m^3). The loss of unutilized water in irrigation amounts to 40-50% of the delivered water due to outdated methods of irrigation, moral and physical dinginess of irrigation systems, low efficiency, unsufficient implementation of scientific and technical innovations, etc. (Christov, 2008; 2012; Stoyanova, 2009; Moteva et al., 2010). Besides, there is a steady trend

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of water resources deterioration on global (Jorgensen, 1991; Nielsen, 1991; Randall and Mulla, 2001) and regional scale (Ignatova, 1992; Avakumovic and Stanic, 1998; Diadovski et al., 2004).

The major pollutants of surface water in the country are industrial enterprises, farms and settlements with sewage systems, without built WWTP, and such with acting, but technically outdated and in poor condition WWTP. Agricultural lands used for intensive agriculture and fertilized with nitrogen and phosphate, treated with pesticides, and manure from livestock farms are one of the major sources of diffuse pollution (mainly nitrogen, phosphorus and biodegradable organics) (Simeonov et al., 2004; Kostadinova et al., 2006; 2007; Georgieva, 2011). In this regard Pencheva et al. (2003) outlined that contamination of irrigation water from different sources is a major problem in the country.

With a view of regional climate changes towards overall warming and drought, the role of irrigation will gain importance in the next years. The irrigation regime, irrigation management and the quality of irrigation water in order to protect the lands and agricultural production from pollution will be of key importance in the country (Gadjalska, 2012).

Tundzha River, the second longest river in Bulgaria, is of great importance for the national economy - agriculture, industry, energetics and other human activities (RBMP, 2010). The river is subjected to strong anthropogenic impact as it passes through plenty of settlements, along industrial enterprises, farms and areas with intensive agriculture that discharge their wastewaters into the river creating preconditions for deterioration of the water quality.

In the valley of Tundzha River, some of the most fertile fields of Bulgaria - Kazanlak, Sliven, Karnobat, Yambol and Elhovo, are situated. Arablel land occupy 35.6%, and forests - about 33% of the river basin area. The basic soil types in the river basin are Fluvisols, Chromic Luvisols, Gleic Chromic Luvisols, Eutric Luvisols and Eutric Vertisols (WRBSR, 1998). These soils have high potential for fertility, and irrigation is one of the factors that contribute for that. Irrigation provides increased yields of the crops grown in the river basin (rice, tobacco, corn, tomatoes, peppers, fruit trees - cherries, apples, peaches, grapes) from 20% to 100% (Todorov and Vasilev, 2007).

From June 9, 2009, water used for irrigation in agriculture in the country must meet certain quality requirements regulated by Regulation No 18/2009. Scientific information on this subject is lacking, as previous studies assessed above all the ecological status of waters in the country, including Tundzha River, by physicochemical (Simeonov et al., 2004; Mihaylova et al., 2012; Georgieva, 2012), biological (Mihaylova and Kostadinova, 2012) and other indices (Diadovski et al., 2003). These assessments are significant in terms of ecology, but they do not always coincide with the quality requirements for irrigation water.

The aim of the present study was to investigate and assess the water quality of upper stream of Tundzha River, with a view to their suitability and applicability for irrigation in agriculture.

Material and Methods

Study area

The study was conducted during the period May - August 2010, in the upper stream of Tundzha River within the area between Koprinka Dam (with capacity 140 million m^3) and Zhrebchevo Dam (capacity 400 million m^3) (Figure 1). Tundzha river basin within the country stretches from central Balkan Mountains to the border with Turkey, with a catchment area of 7901 km^2, river length - 350 km and an average altitude of the river bed - 386 m. (Todorov and Vasilev, 2007).

The studied area of Tundzha River basin is a long narrow valley (in places up to 5 - 7 km wide), which occupies the entire Kazanlak field. The water flowrate ranges from 1.0 to 1.5-2.0 $m.s^{-1}$, and the average annual runoff vary from 0.471 $m^3.s^{-1}$ by Kalofer City to 39.8 $m^3.s^{-1}$ at the border with Turkey. The river is deep in the spring due to snow melting in the mountains and shallow in summer, when its water is used mainly for irrigation.

Approximately 301.2 million m^3 from the total river water flow (1265.8 million m^3) are applied for various economic activities. Allocated to sectors, most water is used for irrigation - 204.1 million m^3, followed by drinking households - 24.5 million m^3 and industry - 16.5 million m^3. Irrigation is realized as by the two main reservoirs - Koprinka Dam and Zhrebchevo Dam, so through other irrigation systems fed directly from the river (RBMP, 2010).

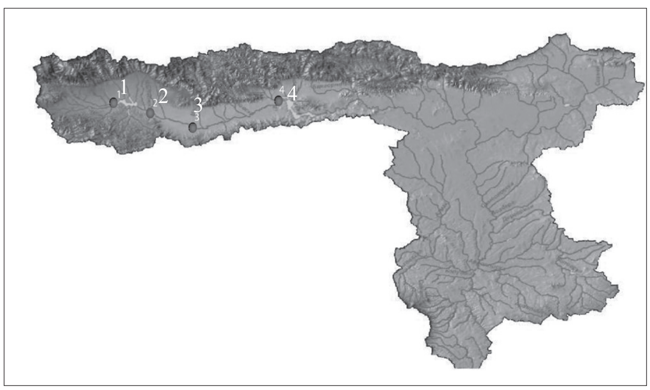

Fig. 1. Tundzha river basin in Bulgaria with monitoring points (1, 2, 3, 4)

Monitoring points

In the study area of Tundzha River four monitoring points were identified in compliance with the requirements of Regulation № 5/2007 and Regulation №18/2009 (Figure 1):

- *Monitoring Point 1 (MP-1)* – Koprinka Dam (N42.41215° E25.18863°);
- *Monitoring Point 2 (MP-2)* – after Buzovgrad Village (N42.34484° E25.24920°);
- *Monitoring Point 3 (MP-3)* – at Yagoda Village (N42.32740° E25.3380°);
- *Monitoring Point 4 (MP-4)* – Zhrebchevo Dam (N42.38333° E25.49350°).

Sampling and sample preparation

During the period May - August 2010, water samples were collected once monthly from each monitoring point (16 samples). For water sampling and sample preparation for analyses, international references (ISO 5667-1 Water Quality – Sampling Part 1: Guidance on the design of sampling programmes; ISO 5667-2 Water Quality – Sampling Part 2: Guidance on the design of sampling programmes; ISO 5667-3 Water Quality – Sampling – Part 3: Guidance on the preservation and handling of samples; ISO 5667-6 Water quality – Sampling – Part 6: Guidance on sampling of rivers and streams) and BSS were used. The samples were collected in dark (to eliminate photo-oxidation processes) glass containers, transported refrigerated (2 - 5ºC) and analyzed immediately after sampling in the laboratories of the Environmental Center at Trakia University - Stara Zagora.

Physical-chemical parameters and methods for analysis

All analyses were performed in triplicate.

In the study, the following 25 physicochemical parameters, characterizing water quality for irrigation according to Regulation No 18/2009, were determined:

- Temperature (ºC), pH, dissolved oxygen ($mgO_2.dm^{-3}$) and conductivity ($\mu S.cm^{-1}$) - *in situ*, with calibrated field equipment Mrlti 340i/SET (with pH – electrode, Cond – electrode and Oxi–electrode with Integral Temperature Sensor);

- Total hardness ($mgeqv.kg^{-1}$), Ca^{2+} and Mg^{2+} concentrations ($mg.dm^{-3}$), nitrates (NO_3^-; NO_3^--N), nitrites (NO_2^-; NO_2^--N), ammonium (NH_4^+; NH_4^+-N), sulfates (SO_4^{2-}), phosphates (PO_4^{3-}; PO_4^{3-}-P), chlorides (Cl^-) and Fe concentrations ($mg.dm^{-3}$) were determined on UV/VIS Spectrophotometer DR 5000 (Hach Lange, Germany) using standard Hach Lange cuvette tests for each individual parameter;

- K, Mn, Ni, Cu, Zn, Pb, Cd and Cr(VI) concentrations ($mg.dm^{-3}$) were determined by atomic absorption spectrometry (AAS) ISO 8288 on AAnalyst 800 (Perkin Elmer) Atomic Absorption Spectrometer;

- Suspended solids ($mg.dm^{-3}$) – by BSS 17.1.04 and BSS EN 872;

- Chemical Oxygen Demand (COD) ($mgO_2.dm^{-3}$) - by Spectrophotometer Checkit Direct COD Vario;

- Biochemical Oxygen Demand (BOD_5) ($mgO_2.dm^{-3}$) - by BOD-System OxiDirect.

Assessment of water quality

The assessment of water quality from the different monitoring points was carried out by comparing the obtained results for the investigated parameters with the regulated limit values in Regulation No 18/2009.

Statistical analyses

The statistical significance of the results was tested based on the standard deviation values calculated by the Student's t-test. Principal component analyses (PCA) were applied to the experimental data to assess relationships between variables and possible distribution patterns. The multivariate statistical analyses were carried out using Microsoft Excel XLSTAT 7.5.2.

Results and Discussion

The results from the analyzed physicochemical parameters for Tundzha River water in the four MPs for the investigated period are summarized in Table 1. The comparative analyses and assessment of water quality, in terms of its use for irrigation in agriculture, in accordance with requirements of Regulation No. 18/2009 revealed the following picture:

Physical parameters

Temperature, pH, conductivity, suspended solids. The determined values of the indices temperature, pH and conductivity during the entire monitoring period in all MPs were within the permissible limits set by Regulation No. 18/2009. Thus, according to these parameters Tundzha River water quality corresponded to the national irrigation standards (Table 1).

The registered average suspended solids contents in the water samples from MP-4 (Zhrebchevo Dam) exceeded the regulated threshold with 1.1 times, while in June the exceeding was 2.25 times above the corresponding limit. In July the suspended solids contents in MP-1 (Koprinka Dam) was 1.2 times, and in MP-2 (Buzovgrad Village) - 1.42 times above the standard (Figure 2). Consequently, the permissible content of suspended solids was exceeded in 21.4% of the analyzed water samples. The latter results point to a systematic control of this indicator due to the fact that suspended solids form suspensions, emulsions or foams in the aquatic compartments. Depending on their density these particles could settle down, float on the surface or remain in suspended state (Vasilev, 2001).

Chemical parameters

Total hardness, Ca, Mg. Total hardness is one of the basic indicators of water quality since it is not only related to the deposition of mineral deposits, but is also reported to affect the toxicity of certain metal ions in aquatic ecosystems (Lerga and O'Sullivan, 2008). In the present study such an effect could not be expected as all measured total hardness values were significantly lower (> 4.7 times) than the permitted level for irrigation water (Table 1). With respect to the values of the index total hardness, the water samples from all MPs could be classified as moderately hard with values within the range of 3.00 - 5.40 $mgeqv.dm^{-3}$ (Ignatova, 1992). The measured Ca and Mg concentrations were also significantly lower than the limit values regulated by Regulation No. 18/2009 (for Ca > 8.8 times, for Mg > 39.4 times). Thus, according to the three parameters the quality of all investigated water samples corresponds to the water irrigation regulations.

Nitrogen-containing compounds - ammonium (NH_4^+; NH_4^+-N), nitrites (NO_2^-; NO_2^--N), nitrates (NO_3^-; NO_3^--N). The nitrogen-containing compounds listed and investigated represent one of the major classes of natural water pollutants. The assessment of water quality in the MPs revealed that according to ammonium and nitrates contents all water samples corresponded to the regulated standards for irrigation. The determined values of both indices were far below the permissible concentrations (> 69.4 times lower for NH_4^+-N and > 13.1 times lower for NO_3^--N) (Table 1).

The results obtained outlined quite wide variability of NO_2^--N concentrations within the range of 0.001 - 0.160 $mg.dm^{-3}$.

Table 1
Mean (C_x), minimum (C_{min}) and maximum (C_{max}) values, standard deviation (SD) and limit values of physicochemical parameters of water of Tundzha river

No	Parameters	Dimension	Cx±SD n=14	C_{min}	C_{max}	Limit values*
1	Temperature	^oC	19.4±2.57	15,2	24,4	28
2	Reaction	pH	7.56±0.55	6,48	8,39	6.0-9.0
3	Conductivity	$\mu S.cm^{-1}$	341.1±133.3	90	459	2000
4	Suspended solids	$mg.dm^{-3}$	40.4±2.2	6,8	112,6	50
5	Total hardness	$mgeqv.dm^{-3}$	2.99±1.17	0,77	4,07	14
6	Ca	$mg.dm^{-3}$	45.6±16.3	14,3	61,5	400
7	Mg	$mg.dm^{-3}$	7.61±4.20	0,03	12	300
8	Ammonium (NH_4^+; NH_4^+-N)	$mg.dm^{-3}$	0.072±0.059	0,01	0,198	5
9	Nitrite-nitrogen (NO_2^--N)	$mg.dm^{-3}$	0.061±0.058	0,001	0,16	0.04**
10	Nitrate-nitrogen (NO_3^--N)	$mg.dm^{-3}$	1.53±0.89	0,27	2,85	20
11	Chlorides (Cl^-)	$mg.dm^{-3}$	12.0±6.03	2,68	20,5	300
12	Sulfates (SO_4^{2-})	$mg.dm^{-3}$	30.9±17.0	6	50	300
13	Phosphates (PO_4^{3-}; PO_4^{3-}-P)	$mg.dm^{-3}$	0.42±0.36	0,15	1,39	3
14	Dissolved oxygen	$mg.dm^{-3}$	6.48±0.83	5,28	7,94	≥2
15	Chemical oxygen demand (COD)	$mg.dm^{-3}$	14.0±15.0	1	39	100
16	Biochemical oxygen demand (BOD_5)	$mg.dm^{-3}$	8.86±3.39	3	16	25
17	K	$mg.dm^{-3}$	2.80±0.99	0,84	4,26	350
18	Fe	$mg.dm^{-3}$	0.09±0.07	0,01	0,27	5
19	Mn	$mg.dm^{-3}$	0.15±0.07	0,03	0,25	0,2
20	Pb	$mg.dm^{-3}$	$0.001\pm2.26x10^{-19}$	<0.001	0,001	0,05
21	Cd	$mg.dm^{-3}$	$0.130x10^{-3}\pm0.096x10^{-3}$	$0.005\ x10^{-3}$	$0.328\ x10^{-3}$	0,01
22	Cu	$mg.dm^{-3}$	0.04±0.01	0,019	0,058	0,2
23	Zn	$mg.dm^{-3}$	0.33±0.50	<0.002	1,307	2
24	Ni	$mg.dm^{-3}$	0.09±0.04	0,004	0,148	0,2
25	Cr(VI)	$mg.dm^{-3}$	0.012±0.015	<0.001	0,039	0,05

* in accordance with Regulation No 18/2009;
** in accordance with Regulation No 7/08.08.1986 on indicators and norms for determining the quality of flowing surface water, because there isn't norm for that indicator in Regulation No 18/2009.

The latter could be explained by the fact that nitrite is the most unstable form among all dissolved inorganic N-containing compounds in natural aquatic systems. The water quality assessment according to this parameter was accomplished in terms of Regulation No.7/1986 for the quality requirements of flowing surface waters, as this index is included in the regulations for irrigation water; however a specific standard value (norm) is not pointed out (Table 1). Data analyses established that only in MP-1 the monthly (0.002-0.017 mg.dm^{-3}) and average (0.010 mg.dm^{-3}) nitrite concentrations for the investigated period corresponded to the requirements. In the rest of the MPs (2, 3 and 4) nitrite contents surpassed the quality standard according to Regulation No. 7/1986 as follows: the average value for the entire period among all samples was 1.52 times higher; the average concentration and July concentration for MP-2 were 1.1 and 2.52 times above the standard, respectively, for MP-3 - 2.35 and 4 times above the limit; and for MP-4 the exceeding was 2.3 and 2.9 times, respectively (Figure 3). The excessive NO_2^- contents in the water samples from MP-3 and MP-4 could be attributed to the larger catchment area of Tundzha River in this zone, characterized by more concentrated agricultural and industrial activities, as well as to the discharge of sewage water from Kazanlak City WWTP. In a study of water pollution with nitrites of Tundzha river Georgieva (2012) expressed similar assumption.

Chlorides (Cl^-) and sulfates (SO_4^{2-}). Chlorides and sulfates are among the basic components found in fresh water. Some of the anthropogenic sources of chlorides in surface water are agricultural activities (organic and mineral fertilizers), sewage, landfill leachate, industrial wastewaters, effluents from WWTPs, etc. Scientific investigations proved that water with chloride concentrations > 150 mg.dm^{-3} are inappropriate for irrigation due to their toxicity to crops (Szynkiewicz et al., 2008). Sulfates distribution in surface and groundwaters is principally controlled by dissolution processes and precipitation of mineral and amorphous solid phases, dissolved oxygen concentration, atmospheric precipitation, biological interactions, point and non-point pollution sources (Souligny and Hollabaugh, 2002; Hudak et al., 2003).

The results obtained with regard to both indices outlined a unidirectional trend of their variation in the studied MPs. The lowest average concentrations were measured in MP-1 (3.25 mg.dm^{-3} Cl^- and 7.00 mg.dm^{-3} SO_4^{2-}), and the highest - in MP-3 (4.67 Cl^- mg.dm^{-3} and 15.4 mg.dm^{-3} SO_4^{2-}). In MP-2 and MP-4 the contents of Cl^- and SO_4^{2-} were within the medium range. The assessment of water quality according to Cl^- and SO_4^{2-} proved its applicability for irrigation purposes as all values (average for the investigated period, minimum and maximum) were significantly lower than the permissible limits (maximum values were 14.6 times lower for Cl^- and 6 times lower for SO_4^{2-}) (Table 1). However, increased attention to these indicators is necessary, because many factors and processes influence their concentrations in water.

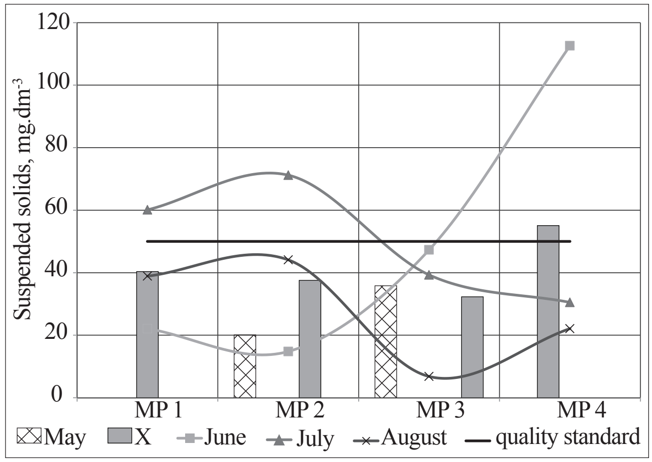

Fig. 2. Spatial distribution of suspended solids content in monitoring points of Tundzha river
*** water samples in May were collected only from MP-2 and MP-3**

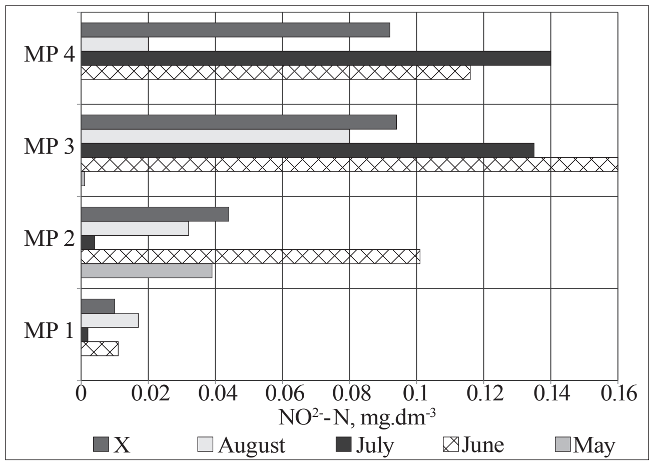

Fig. 3. Monthly and average concentrations of NO^{2-}-N in water of Tundzha river

Phosphates (PO_4^{3-}; PO_4^{3-}-P). The values of this parameter displayed dynamical variations in the samples, thus differentiating the MPs into two groups. The average concentrations throughout the studied period in MP-2 (0.53 mg.dm^{-3}) and MP-3 (0.65 mg.dm^{-3}) were significantly higher than these in MP-1 (0.17 mg.dm^{-3}) and MP-4 (0.21 mg.dm^{-3}). It was assumed that the increased PO_4^{3-} content in the water samples from MP-3 and MP-4 was due to more intensive pollution sources in this part of the river valley - discharge of effluents from the WWTP of Kazanlak City and diffuse pollution with agricultural wastewaters. The latter assumptions were confirmed by the results and observations of other scientists who conducted similar investigations of other water bodies (Stambuk-Giljanovic, 2006; Lin et al., 2010). Besides, the assessment displayed that all measured PO_4^{3-} concentrations (average, minimum and maximum) in all MPs were significantly lower (> 2.15 times with respect to maximum value) than the permissible standard for irrigation water (Table 1).

Dissolved oxygen, COD and BOD_5. The major source of dissolved oxygen in water is the atmosphere in contact with the water surface. Oxygen content in the water bodies is basically dependent on the mass transfer processes through the boundary gas-water layer. Oxygen is significant as for aquatic life, so for the efficiency of the purification processes of contaminated waters (Vasilev, 2001). The results obtained demonstrated that dissolved oxygen concentrations in all MPs were higher than the minimum permissible limit for irrigation water - the average was 3.24, the minimum value - 2.64, and the maximum one -3.97 times above the minimum permitted level (Table 1).

COD is a parameter that indirectly measures the quantity of oxygen necessary to oxidize the organic and inorganic water contaminants (metal ions with variable oxidation state, sulfides, nitrates, hydrogen sulfates, recalcitrant organics, etc.) (Vasilev, 2001). The determined in the present study COD values were significantly lower than the maximum permitted level for irrigation water - 7.1 times lower for the average COD value, 100 times lower for maximum value, and 2.6 times lower for minimum one (Table 1).

BOD_5. Although BOD_5 does not reflect the total mass of organic matter in water (the index can not determine the organic substances used for bacterial growth and those resistant to biochemical degradation), it is the main indicator for characterization of organic water pollution (Vasilev, 2001). The assessment of BOD_5 values determined the quality of analyzed water samples as corresponding to requirements for irrigation as all index values were lower than the permissible limit: the average BOD_5 value was 2.8 times lower, maximum value – 7.4 times lower, and minimum value – 1.6 times lower (Table 1). Consequently, according to the parameters dissolved oxygen, COD and BOD_5, the water samples collected from the studied MPs of Tundzha River meet the quality requirements for irrigation in agriculture and present no risk to crops.

Metal concentrations (K, Fe, Mn, Ni, Cu, Zn, Pb, Cd and Cr(VI). The role and importance of metals in natural water used for irrigation of crops is ambiguous. Some metals (K, Fe, Mn, Ni, Cu, Zn) are essential micronutrients that improve soil fertility and are useful for plants, however, other elements of this group (Cd, Cr, Pb) have the ability to accumulate in them and at sufficiently high concentrations they exhibit strong toxic effect (Rajmohan and Elango, 2005; Kar et al., 2008). The main sources of metal pollution of natural water are: industrial and domestic wastewater, agricultural activities, mining, waste and intermediate products from power plants, factories for the production of non-ferrous metals, sludge from sewage treatment plants for municipal and industrial wastewater, as well as the processes of natural erosion and sedimentation (Aktar et al., 2010).

The results obtained in the present study showed that the contents of the investigated metals in Tundzha River water varied in different degrees among the controlled MPs. The average concentrations for the monitoring period in all MPs were: identical for Pb (0.001 $mg.dm^{-3}$); with insignificant variations for Cu (0.03-0.04 $mg.dm^{-3}$) and Ni (0.08-0.11 $mg.dm^{-3}$), with moderate variations – for K (1.27-3.45 $mg.dm^{-3}$), Fe (0.06-0.14 $mg.dm^{-3}$) and Mn (0.07-0.18 $mg.dm^{-3}$), and with significant fluctuations for Cr(VI) (0.001-0.026 $mg.dm^{-3}$), Zn (0.07-0.67 $mg.dm^{-3}$) and Cd ($0.012x10^{-3}$–$0.328x10^{-3}$ $mg.dm^{-3}$). The observed diversity in the results together with the demonstrated dynamic variations suggests impact of a number of various environmental factors on the pattern of metals distribution in the water. In this regard, Ozmen et al. (2004) reported that the concentration of metal ions strongly depend on the biological processes, redox potential, ionic strength, pH, the activity of organic and inorganic chelators and the purification processes in water.

The assessment of water quality in terms of its use for irrigation, showed that in all MPs the average, minimum and maximum concentrations of K, Fe, Mg, Pb, Cu, Zn, Ni, Cr(VI) and Cd were within the relevant standards postulated by Regulation No. 18/2009 (Table 1). The measured maximum concentrations were from 1.28 times - for Cr(VI) to 2000 times - for Cd, lower than the permissible limits. Only for one element – Mn, concentrations that exceeded the permissible level were established: for MP-2 in May, June and July (0.201-0.252 $mg.dm^{-3}$) and for MP-3 in June and July (0.202-0.205 $mg.dm^{-3}$), i.e. in 35.7% of the analyzed samples. As both MPs (MP-2 and MP-3) are situated along Tundzha River valley after Kazanlak City – a large municipal and industrial center, the probable Mn sources for water pollution could be industrial effluents (from weapon factories) and sewage containing Mn due to the old municipal water network (Georgieva, 2012). Therefore, during the cited months, according to the index Mn, the water from MP-2 and MP-3 was classified as unsuitable for irrigation in agriculture.

Recently, principal component analysis (PCA) proved as a valuable tool for organizing data in environmental monitoring, for simplifying the analysis of complex chemical relationships, and for differentiating between different chemical environments. PCA is a linear analysis technique used to reduce the dimensionality of a dataset while attempting to preserve relationships present in the original data. PCA of the data for water quality of Tundzha River, based on the average concentrations of the indices for the study period, developed three principal components as seen from the eigenvalues presented in Tables 2 and 3, explaining the total variability. The eigenvalues of principal components PC1 and PC2 in both tables were greater than 1 (entity), which accounted for 92.5 % and 93.7 %, respectively, of the total variability.

The correlation matrix presented in Table 2 revealed appreciable mutual relationship between SS - DO, Cond - BOD, TH - BOD and TH - Cond in the studied surface water samples which characterized with the highest values of the Pearson correlation coefficients in the range R^2 0.957 - 0.999.

The correlation matrix presented in Table 3 revealed appreciable mutual relationship between: Mg - Ca; K - Ca; Mn - Ca; Mn - Mg; Mn - K; Ni - K; Ni - Zn; Cd - Ca; Cd - Mg; Cd - K; Cd - Mn and Cd - Ni in the studied surface water samples which characterized with the highest values of the Pearson correlation coefficients in the range R^2 0.951 - 0.999.

The scatter plot based on the case-wise F1 and F2 factor scores regarding metals contents in the investigated sampling points is presented in Figure 4. Obviously, the PCA estab-

Table 2
Correlation matrix, principal components (PC) and eigenvalues of indices: temperature (T), dissolved oxygen (DO), suspended solids (SS), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), pH, conductivity (Cond) and total hardness (TH)

	T	DO	SS	BOD	COD	pH	Cond	TH
T	1							
DO	0.798	1						
SS	0.921	0.957*	1					
BOD	-0.364	0.262	-0.018	1				
COD	-0.253	0.36	0.144	0.9	1			
pH	0.637	0.589	0.731	-0.237	0.165	1		
Cond	0.355	-0.255	0.033	0.993*	-0.844	0.322	1	
TH	0.389	-0.224	0.063	0.995*	-0.854	0.323	0.999*	1

Eigenvalues	PC1	PC2	PC3
Eigenvalue	4.09	3.308	0.602
Variance %	51.124	41.36	7.521
Cumulative %	51.124	92.48	100

*significant values at the level of significance $p \leq 0.05$ (two-tailed test)

Table 3
Correlation matrix, principal components (PC) and eigenvalues of indices: Ca, Mg, Fe, K, Mn, Cu, Zn, Ni, Cr(VI) and Cd

	Ca	Mg	Fe	K	Mn	Cu	Zn	Ni	Cr(VI)	Cd
Ca	1									
Mg	0.998*	1								
Fe	0.405	0.395	1							
K	0.952*	0.936	0.609	1						
Mn	0.995*	0.997*	0.466	0.951*	1					
Cu	0.522	0.56	-0.417	0.236	0.508	1				
Zn	0.723	0.681	0.647	0.888	0.705	-0.178	1			
Ni	-0.894	-0.865	-0.534	0.972*	-0.874	-0.132	0.952*	1		
Cr(VI)	0.623	0.672	0.078	0.406	0.66	0.839	-0.058	-0.213	1	
Cd	0.986*	0.974*	0.474	0.985*	0.976*	0.385	0.828	0.957*	0.487	1

Eigenvalues	PC1	PC2	PC3
Eigenvalue	7.123	2.247	0.631
Variance %	71.226	22.465	6.309
Cumulative %	71.226	93.691	100

*significant values at the level of significance $p \leq 0.050$ (two-tailed test)

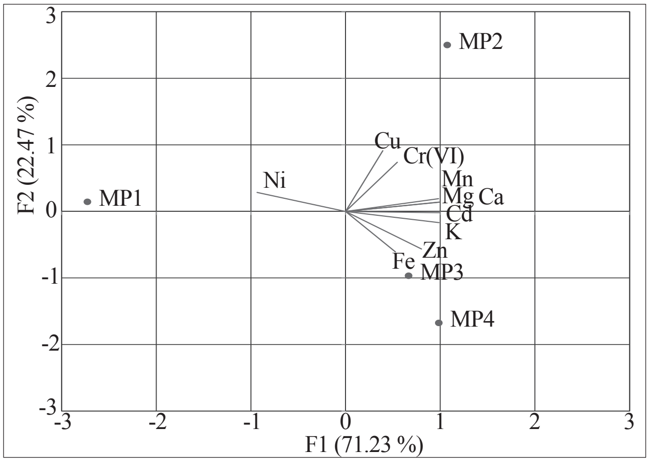

Fig. 4. Scatter plot of the principal component analysis case-wise factor scores for the studied surface water samples from Tundzha river regarding metals contents

lished a general classification of the studied surface water sampling points along Tundzha River downstream, basically distinguishing the extend of individual and complex metal contents in the different parts of the river.

Conclusion

A study of Tundzha River water in four monitoring points (MP-1 Koprinka Dam, MP-2 - after Buzovgrad Village, MP-3 – at Yagoda Village, MP-4 - Zhrebchevo Dam) in upper stream of the river, during the period May-August 2010, by 25 physicochemical indices, and assessment of the water quality for irrigation purposes by means of Regulation No. 18/2009 was conducted. It was established that the water quality for irrigation purposes corresponded to the regulated requirements according to 3 physical (temperature, pH and conductivity) and 20 chemical (total hardness, Ca, Mg dissolved oxygen, COD, BOD_5, ammonium, nitrites and nitrates, chlorides, sulfates, phosphates, K, Fe, Ni, Cu, Zn, Pb, Cd and Cr(VI)) parameters. Deviations from the regulated standards were established for two indices – suspended solids (in 21.4% of the samples analyzed) and Mn (in 35.7% of all water samples). The results provide evidence to suggest that the anthropogenic impact on Tundzha River, in the studied area, does not cause pollution of the water to a degree that makes it unsuitable for irrigation in agriculture. Insignificant anthropogenic pressure on the water quality exists regarding the content of suspended solids and Mn. The over-threshold level of Mn could be defined as a risk indicator. The exceeding of the permissible concentration of this element is probably due to the discharge of industrial effluents (mainly from armories) and Mn-enriched effluents from the old water network of Kazanlak City.

The correlation matrix revealed appreciable mutual relationship: between suspended solids-dissolved oxygen, conductivity-BOD, total hardness-BOD and total hardness-conductivity in the studied surface water samples which characterized with the highest values of the Pearson correlation coefficients (R^2 0.957 - 0.999), and between Mg - Ca; K - Ca; Mn - Ca; Mn - Mg; Mn - K; Ni - K; Ni - Zn; Cd - Ca; Cd - Mg; Cd - K; Cd - Mn and Cd - Ni – featured with the highest values of the Pearson correlation coefficients in the range R^2 0.951 - 0.999.

The whole range of values of the investigated indicators by monitoring points and by months, as well as the established relationships and dependencies between some of them assumes the impact of various environmental factors (pollution sources, quantity of emitted pollutants, climatic conditions, aquatic processes, etc.) on the formation of different pollutant concentrations and the development of diverse spatio-temporal dynamics, with regard to water quality for irrigation in agriculture.

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