



Comparative evaluation of river chemical status based on WFD methodology and CCME water quality index

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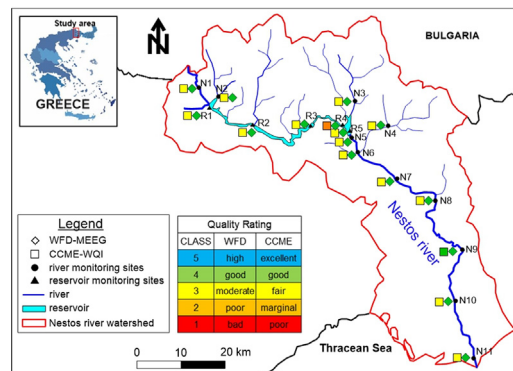
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HIGHLIGHTS

- WFD priority and priority hazardous substances were monitored in a transboundary river.
- Parameters included heavy metals, agrochemicals, PAHs, and nutrients in river and reservoirs.
- The WFD-based methodology was compared to CCME-WQI to classify the water quality.
- The CCME-WQI classification was more conservative than the WFD-based one.
- Pesticide concentrations in the river were lower than AA-EQS and MAC-EQS values.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 April 2020

Received in revised form 13 June 2020

Accepted 8 July 2020

Available online 15 July 2020

Editor: Damia Barcelo

Keywords:

Nestos river

Nutrients

Heavy metals

Priority substances

Water Framework Directive

CCME water quality index

ABSTRACT

The Water Framework Directive (WFD) methodology, proposed by the Ministry of Environment and Energy of Greece (WFD-MEEG), and the Canadian Council of Ministers of Environment Water Quality Index (CCME-WQI) are comparatively applied to evaluate the chemical status of a major transboundary river. Water quality parameters were monitored at 11 sites along the main stream of the river and its main tributaries, and at five sites in the reservoirs, on a monthly frequency, in the period from May 2008 to May 2009. Water temperature (T), dissolved oxygen (DO), pH, and electrical conductivity (EC) were measured in-situ, while water samples were collected for the determination of total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrite-, nitrate- and ammonium-nitrogen, total Kjeldahl nitrogen (TKN), ortho-phosphates (OP), total phosphorus (TP), and chlorophyll-a (Chl-a). The water samples were also analyzed for the determination of seven heavy metals (i.e., Cd, Pb, Hg, Ni, Cr, Cu, Zn) and 33 priority substances, as listed in Annex II of EU Directive 2008/105/EC. The results showed that the physicochemical parameters (i.e., T, DO, pH, EC, inorganic nitrogen, TKN, OP, TP, TSS, and Chl-a) were within the natural range. The mean concentration of the measured heavy metals did not exceed the limits set by WHO (2003, 2017) for drinking water. Regarding the priority substances, some of them (i.e., anthracene, fluorethene, and polyaromatic hydrocarbons) were measured in various stations at higher concentrations than the Annual Average Environmental Quality Standards (AA-EQS). Based on the WFD-MEEG methodology, the river water was in the 'good' quality class, while according to CCME-WQI the river quality ranged from 'marginal' to 'good' category. It seems that CCME-WQI is stricter than WFD-MEEG but could be a WQI appropriate for use.

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1. Introduction

Nowadays, environmental protection and water quality management are risen as important issues in public policies throughout the world. Environmental problems are presently faced through an integrated ecosystem approach, involving the concepts of holistic environmental management and water pollution control (Brack et al., 2018; Giakoumis and Voulvoulis, 2018). The European Council Water Framework Directive (WFD, 2000) has established a framework for community action in the field of water policy and has set the objectives to prevent the deterioration of inland waters (i.e., surface and groundwater), and transitional and coastal waters, aiming to ensure achievement and maintenance of their good ecological status (WFD, 2000; Tsakiris, 2015).

The WFD proposes that the assessment of the ecological status of a river should be based on river basin management plans, including the design of monitoring programs on hydro-morphological, physicochemical and biological elements. Physicochemical elements include supporting parameters for the interpretation of chemical and biological data, priority substances and priority hazardous substances (Decision 2455/2001/EC). Priority substances are those which pose a significant risk to the aquatic environment, including the risks linked to the use of this water as potable. Priority hazardous substances are substances toxic, persistent and prone to bio-accumulation and bio-magnification by organisms, giving rise to an equivalent level of concern. As these substances present a significant risk to the aquatic environment, they should be prioritised according to their hazard (persistence, bio-accumulation and toxicity) and environmental exposure (EU production level, use and partitioning in environmental media), referring ultimately to their Environmental Quality Standards (EQS) (Fliedner et al., 2016; Daginnus et al., 2011). The basic principle in WFD chemical assessment procedure is the 'one out-all out' approach, implying that a good chemical status is assigned when the EQS are met for all pollutants or pollutant groups (Voulvoulis et al., 2017). Therefore, any substance with concentration above the EQS limit results in failure of the whole station to achieve the good chemical status, while if concentrations lie below EQS, this chemical status is apparently met. This approach is based upon the assumption that the worst status of the elements (or priority substances) used in the assessment determines the final status of the ecosystem. However, this rather simplistic approach increases the risk of misclassification, probably based upon only a limited representative element or upon an under-represented variable, thus undermining the potential effectiveness of the WFD to guide management efforts (Borja and Rodríguez, 2010; Prato et al., 2014; Borja et al., 2009). Paucity of a precise definition and lack of specific limits bounding the 'high', 'good', 'moderate', 'poor' or 'bad' chemical status classes appears as a major issue in implementing WFD. For instance, for each priority substance, the WFD gives only one limit. If the average annual concentration of a substance is below this threshold, the water is characterized as having 'good' chemical status; otherwise, it is characterized of 'moderate' status. For this reason, research on the development of common accurate methodologies in assessing the quality status of water systems, as well as common methodologies in integrating results from different physicochemical water parameter matrices should be considered, as some of the most important tasks to be undertaken in the future years (Brack et al., 2018; Giakoumis and Voulvoulis, 2018; Moss, 2008; Baattrup-Pedersen et al., 2019).

Throughout the years, several Water Quality Indices (WQIs) have been developed, aiming to aggregate water quality datasets and produce a single, cumulatively-derived value indicating the level of water quality. This, in turn, is essential for comparing the water quality of different sources and observing the changes in the water quality of a given source as function of time and other influencing factors (Abbasi and Abbasi, 2012; Trikoilidou et al., 2017). Further, such indexing system produces specific, definable and meaningful information for water managers, policy-makers and lay-people, which could be integrated in the WFD process (Abbasi and Abbasi, 2012; Alexakis et al., 2016; Gikas, 2017). However, most WQIs consider only a limited set of physicochemical

variables that assess the impact of nutrients and organic pollution and the associated dissolved oxygen decrease (Zotou et al., 2019; Raju and Singh, 2017). These indices do not specifically address the stresses derived from priority substances, such as mineral and organic micropollutants and pesticides.

In this paper, water quality results are presented on physicochemical and priority substances of Nestos river basin (Northern Greece), covering the surface waters (main route and tributaries) and the two reservoirs developed by dams for hydropower production. Water quality status at the various sites was assessed using *in situ* measured parameters from a water quality monitoring program and: a) the WFD standard procedure; and b) the CCME-WQI (Canadian Water Quality Index; CCME, 2001). The CCME-WQI has been used in many countries and received great assessments because of several merits (Dede et al., 2013). It has been used to evaluate the water quality in rivers (de Almeida and de Oliveira, 2018; Zotou et al., 2019; Gikas, 2017; Tsboula et al., 2019), lakes/reservoirs (Gao et al., 2016; Trikoilidou et al., 2017), surface water (Bilgin, 2018;), ground water (Adimalla et al., 2018; Wagh et al., 2017; Venkatramanan et al., 2016), and drinking water (Bereskie et al., 2017). The CCME-WQI was selected on the basis of its expanded ability to incorporate the highest possible number of physicochemical and priority substances (Finotti et al., 2015), as sampled on a monthly basis according to WFD requirements.

2. Materials and methods

2.1. Site description

Nestos/Mesta river is one of the 71 internationally shared river catchments of Europe, thus providing means for transboundary co-operation, resolving local conflicts and tensions, and promoting administrative, technical and scientific collaboration, leading ultimately towards the need for its effective water management. In terms of the Water Framework Directive 2000/60/EC (Annex XIA), Nestos/Mesta River is located in eco-region 7 (Eastern Balkans). The river drains an area of 5479 km², of which 2703 km² (or 49.34% of the total basin) belong to Bulgaria, while 2776 km² (or 50.66% of the total basin) is located in Greece (Boskidis et al., 2011, 2012). The Bulgarian part, known as Mesta river, has a length of 113 km, while the Greek part, known as Nestos river, has a length of 130 km.

The present research covers only the Greek part of the watershed, from the Greek-Bulgarian borders down to the Nestos river outflow in the Thracian Sea. The relief in this basin is mountainous or semi-mountainous, with limited human activities (i.e., wastewater discharge from riparian settlements, animal farming, crop growing). In the deltaic area, a floodplain is formed covering 440 km², where intense agricultural activities (rice, corn and cotton cultivation) take place (Boskidis et al., 2011, 2012). At the western edge of this floodplain, a series of nine choked, shallow and elongated coastal lagoons are located, four of which are fishery-exploited (Tsihrintzis et al., 2007). These lagoons act as buffer zones for the transfer of agricultural residues from the adjacent plain to the coastal zone (Sylaios and Theocharis, 2002). The coastal zone is shallow with a gradual depth increase, reaching a 50-m depth approximately 20 km southwards of Nestos river mouth.

In the early 1990s, two high dams were constructed in Nestos river course, Thissavros and Platanovrisi hydropower dams (170 m and 95 m in height, respectively), altering the hydrology, hydrochemistry and hydro-morphology of the river (Sylaios et al., 2010). The two reservoirs act as inter-connected lakes, affected by the seasonal stratification-destratification cycle, fueling surface primary production while promoting bottom anoxia (Koutroumanidis et al., 2009).

2.2. Sampling strategy

A sampling network of 16 stations was configured, consisting of 11 sites along the main Nestos river and its tributaries (code N) and 5

sites in the reservoirs (code R) (Fig. 1). Sampling was performed on a monthly basis covering the period May 2008 – May 2009. Water samples were collected by means of a 5-liter Niskin bottle from the surface of each sampling station, except of reservoir stations where surface and bottom samples were taken. Water samples for general analyses were collected in 1-liter plastic bottles. For priority substance analyses, 5-liter samples were collected in dark-glass bottles. All samples were transported to the laboratory and stored at 4 °C, until analysis.

Water temperature (T), dissolved oxygen (DO), pH, and electrical conductivity (EC) were measured in situ, using WTW portable series instruments. Water samples were analyzed in the laboratory to determine the concentrations of total suspended solids (TSS), biochemical oxygen demand (BOD), chemical oxygen demand COD, nitrite-nitrogen (NO₂-N), nitrate-nitrogen (NO₃-N), ammonium-nitrogen (NH₄-N), total Kjeldahl nitrogen (TKN), ortho-phosphates (OP), total phosphorus (TP) and chlorophyll-a (Chl-a) using standard methods for surface waters (APHA, 1998). The water samples were also prepared according to nitric-acid digestion Method 3030E (APHA, 1998), and analyzed for the determination of the following heavy metals: Cd, Pb, Hg, Ni, Cr, Cu and Zn using a Perkin-Elmer AA spectrophotometer. The priority substances and priority hazardous substances determined were all 33 pollutants or group of pollutants, as listed in Annex II of the Directive 2008/105/EC and in Annex I of the Directive 2013/39/EC, and presented in Supplementary material (SM), Table SM1. The extraction of water samples for the determination of pesticides and organohalogenated compounds has been performed according to previously published solid phase extraction procedure (Albanis et al., 1998) and gas chromatography (GC) coupled with different selective detectors such as flame thermionic detector (FTD), electron capture detector (ECD) and mass spectrometry (MS) detection (Albanis et al., 1998; Stamatis et al., 2010; Thomatou et al., 2013). Determination of polycyclic aromatic hydrocarbons and chloroalkanes has been performed according to extraction and analysis (GC-MS) procedures reported elsewhere (Petridis et al., 2014).

2.3. Water quality assessment

The WFD methodology as proposed to be implemented by the Ministry of Environment and Energy of Greece (WFD-MEEG) was used to assess the physicochemical quality of the river and reservoir water. This methodology is based on the Nutrient Classification System (NCS) method (Skoulikidis et al., 2006), which was modified to include the dissolved oxygen parameter (Cardoso et al., 2001). The quality parameters used in this method are presented in Table 1. Furthermore, in the present study, three additional water quality parameters referring to fisheries and aquatic life welfare were included, as follows: pH, BOD and TSS with allowable values from 6.5 to 9.0, <6 mg/L and <25 mg/L, respectively (Directive 2006/44/EC; Gikas, 2017). According to the methodology, during the monitoring period, the monitoring stations are classified into one of five quality classes (i.e., high, good, moderate, poor and bad; Table 1), depending on mean concentrations of nitrate-, nitrite- and ammonium-nitrogen, phosphorus ion and dissolved oxygen, and one of two classes (i.e., good and moderate; Table 1) depending on pH, BOD and TSS mean concentrations. Each quality of the individual parameter is graded according to Skoulikidis (2008), as follows: 4.5, 3.5, 2.5, 1.5 and 0.5 if it is in the high, good, moderate, poor and bad classes, respectively. The mean of values determines the final physicochemical state of the monitoring station, i.e., if the average is between 4 and 5, the final state will be 'high', if the average is between 3 and 4 it will be 'good', if the average is between 2 and 3 it will be 'moderate', etc. The final physicochemical state is taken into account when it is 'high', 'good' or 'moderate' water quality class. If it is 'poor' or 'bad', it will be considered as 'moderate'. The physicochemical state of a surface water system, together with the biological parameters (e.g., phytoplankton, macrophages, invertebrates) and the hydro-morphological elements (e.g., depth, width, flow, etc.) determine the ecological state of the water system.

The water quality of Nestos river was assessed according to the WFD following the EQS established for each priority substance, i.e., the Annual Average (AA) concentration (AA-EQS) and the maximum allowable concentration (MAC; MAC-EQS). Priority substances must at all times comply with the MAC-EQS established, and on the average over a period of one year comply with the AA-EQS. The classification into quality classes of the Nestos river chemical status was performed after checking the compliance of mean concentration of the priority substances and heavy metals that were monitored in the river and reservoir waters with the quality limit values (Tables 4, 5). At each monitoring station and for each parameter (i.e., priority substance and heavy metal), the mean concentration was compared with the value of 'good' chemical status. If the mean concentration value was below the AA-EQS, the water in the station was characterized as having 'good' chemical status; otherwise, it was characterized as 'failing to achieve good' or at 'moderate' status. The final chemical status of the water at each monitoring station was estimated by the same procedure, as was applied to the previously described physicochemical status. In the final classification of the overall situation, the 'one out-all out' rule was applied, according to which the evaluation is based on the lowest value between physicochemical and chemical status. The same procedure was also applied for the reservoir stations.

Further, the water quality at each station and sampling period in Nestos river watershed was assessed based on a widely used water quality index, namely the CCME-WQI (CCME, 2001). The major strength of this index is its capability to allow the inclusion of toxic pollutants (such as heavy metals, hydrocarbons, or pesticides), based on existing environmental quality guidelines and management objectives. Therefore, this index has been selected among a set of several WQIs (e.g., NSF-WQI, Oregon-WQI, Prati's index of pollution, Weighted Arithmetic WQI, as summarised by Zotou et al., 2020) on the basis of its ability to incorporate almost all the measured physicochemical parameters and priority substances monitored in Nestos river.

The CCME-WQI consists of three factors testing the concentration of individual variables against the guideline or the objective applied. Factor 1 (F1) deals with the scope and is the percentage of variables that exceed the objective ('failed variables') at least once during the time period under consideration relative to the total number of variables measured. Factor 2 (F2) deals with the frequency and is the percentage of individual tests that exceed the objectives ('failed tests') relative to the total number of tests. Finally, Factor 3 (F3) deals with the amplitude of deviation by which failed test values do not meet the objectives. Once the three factors have been calculated, the CCME-WQI is calculated as follows:

$$\text{CCME-WQI} = 100 - \left(\frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right) \quad (1)$$

The above formulation produces a value of the index between 0 and 100, and gives a numerical value to the state of water quality. Typically, the water quality is ranked in the following five categories: excellent: 95–100; good: 80–94; fair: 65–79; marginal: 45–64; poor: 0–44.

2.4. Statistical analysis

The Student *t*-test, which compares the mean values of one variable of two groups of cases, was applied in order to check if there is statistically significant difference between the set of values of the parameters measured in the surface water and the respective set of values in the bottom water of Nestos river reservoirs. The Pearson correlation coefficient was used to determine correlations between heavy metal concentrations in reservoirs of Nestos river surface and bottom waters. For statistical analyses, SPSS 19.0 statistical package for windows was used.

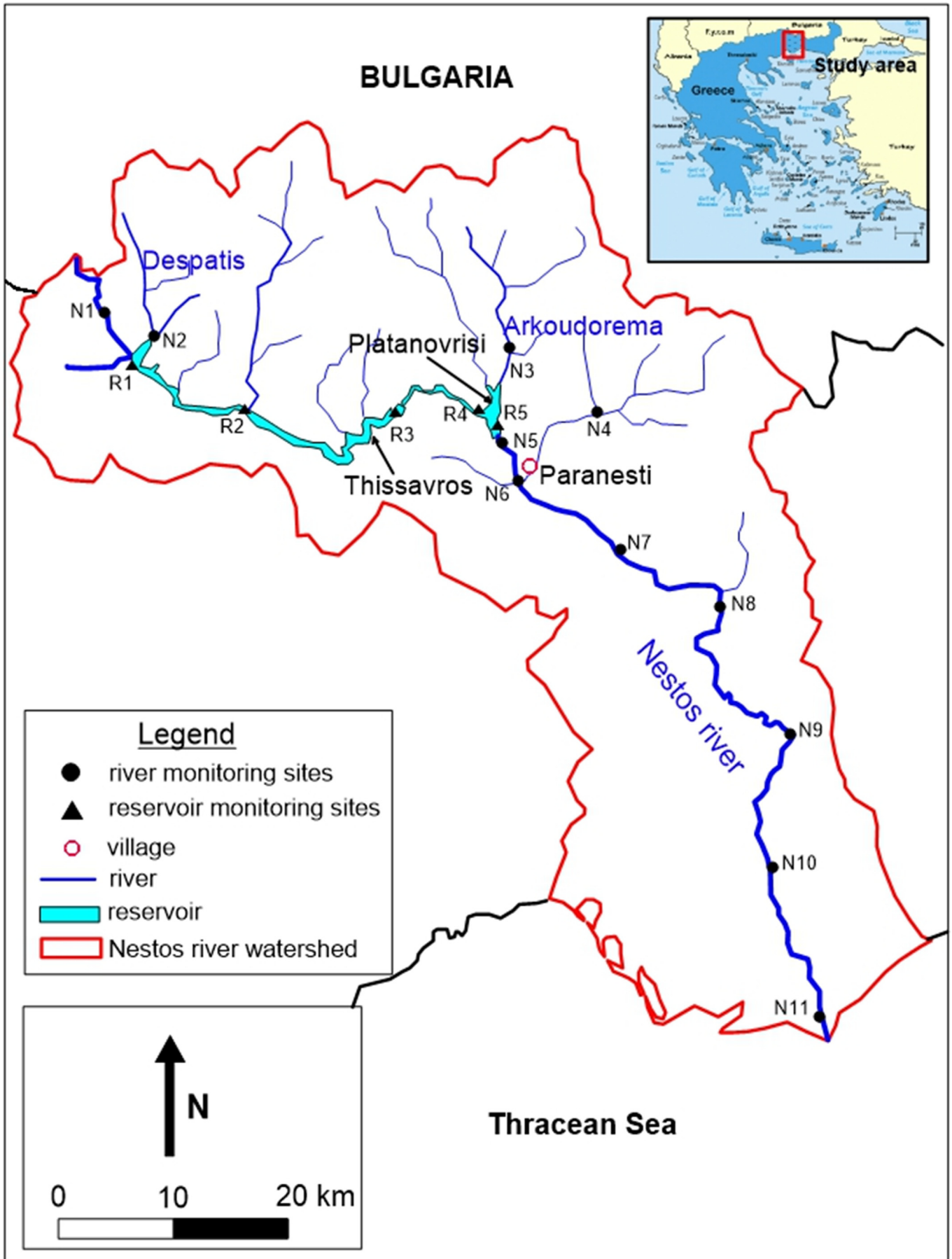


Fig. 1. Nestos river basin (Greek part) with monitoring stations indicated.

Table 1

Classification of quality classes based on nutrient concentrations according to the Nutrient Classification System (NCS), DO, pH, BOD and TSS concentration.

	Quality classes				
	High	Good	Moderate	Poor	Bad
NO ₃ -N (mg/L)	<0.22	0.22–0.60	0.61–1.3	1.31–1.80	>1.80
NH ₄ -N (mg/L)	<0.024	0.024–0.060	0.061–0.2	0.21–0.50	>0.50
NO ₂ -N (µg/L)	<3.0	3.0–8.0	8.1–30	30.1–70.0	>70.0
PO ₄ -P (µg/L)	<70	70–105	106–165	166–340	>340
TP (µg/L)	<125	125–165	166–220	221–405	>405
DO (mg/L)	>9.0	9.0–6.4	6.3–4.0	3.9–2.0	<2.0
pH		6.5–9.0	<6.5, >9.0		
BOD (mg/L)		<6.01	>6.0		
TSS (mg/L)		<25.01	>25.0		

3. Results and discussion

3.1. River water quality data

Physicochemical water quality results for the main part of Nestos river and its tributaries are reported in Table 2. During the monitoring period the mean water temperature along Nestos river varied from 14.4 °C to 22.4 °C. As shown by the mean values, the highest temperature was measured at the mouth of the river and the lowest at stations N5 and N6 located downstream of Platanovrisi dam. These lowest water temperature values at these two stations are due to the operation of Platanovrisi dam, which releases water from the hypolimnion. The mean values of DO in Nestos river ranged from 6.07 mg/L (at N3 station) to 7.63 mg/L at N2 (Table 2) and were inversely related to water temperature. The relatively higher values at N2 station (Despatis tributary) is attributed to the riverbed morphology (cobble, shallow depth). pH showed a spring decrease associated with detritus oxidation, produced through photosynthetic activity; mean pH values at all eleven stations along the Nestos river varied between 7.45 and 8.14 (Table 2). pH values in natural waters vary from 6.0 to 8.5 (Chapman, 1996), therefore, in the case of Nestos river, mean pH values were found within the natural range. Mean EC values in Nestos river water ranged from 176 µS/cm (at N4) to 284 µS/cm (at N11). Relatively higher EC values were observed in Arkoudorema tributary (station N3), due to minerals from the dissolution of karstic rock. According to Chapman (1996), the EC value of most freshwaters varies from 10 to 1000 µS/cm, whereas in polluted water, it may exceed 1000 µS/cm; based on this, the Nestos river water is considered unpolluted by constituents (i.e., salts) which increase the EC.

BOD and COD mean values ranged from 1.89 mg/L to 5.00 mg/L and from 4.27 mg/L to 18.35 mg/L, respectively (Table 2), presenting no major concern. The highest mean values for both BOD and COD were measured at N1 and N2 stations (Fig. 1) showing that there was only minor organic pollution entering the river. The BOD mean concentration at all monitoring stations, with the exception of N3 station, was higher than the limit of 2.0 mg/L for unpolluted water. However, the BOD values at all monitoring stations were lower than the limit set by EU for fisheries and aquatic life (3–6 mg/L; Directive 2006/44/EC). Similarly, at all monitoring stations, the COD mean concentrations were lower than the limit of 20 mg/L for unpolluted water (Chapman, 1996).

Nitrate-nitrogen dominated all inorganic nitrogen forms and ranged from 0.19 mg/L to 0.45 mg/L, showing limited seasonal variation and a gradual increase in the downstream direction (Table 2), due to human activities and the nitrification process. Nitrite-nitrogen and ammonium-nitrogen concentrations were higher at the upstream part (i.e., N1 and N2 stations; Table 2), at the tributaries (i.e., N3 and N4 stations) and in the proximity to the lower dam (N5 station), reducing rapidly along the river course due to the nitrification process. According to Chapman (1996), ammonium-nitrogen concentration in non-polluted waters is usually <100 µg/L and may reach about 2–3 mg/L. The mean

concentration of ammonium-nitrogen in Nestos river varied between 54.29 µg/L and 281.51 µg/L, and was lower than the 100 µg/L threshold at most stations (Table 2). Furthermore, at all eleven stations along Nestos river, mean NH₄-N values were lower than the limit (40–1000 µg NH₄-N) set by EU for fisheries and aquatic life. The TKN mean concentration ranged from 0.83 mg/L to 1.75 mg/L (Table 2). Higher TKN values were detected at the upstream part (N1 and N2 stations) and the lower part (N9, N10 and N11 stations) attributed to minor incoming pollution and anthropogenic activities, respectively. Higher TP concentrations were measured at the upstream stations (N1 and N2) and the lower part (N9, N10 and N11 stations); TP values ranged from 37.35 µg/L to 132.06 µg/L. The concentration of TP in most natural waters varies between 5.0 µg/L and 20.0 µg/L (Chapman, 1996). No important differences of OP and chlorophyll-a values were detected between stations along the river, with relative lower values for OP and Chl-a measured at N5 and N6 stations (Table 2). Mean values of OP ranged from 8.33 µg/L to 19.60 µg/L and did not exceed the UK criterion (100 µg/L) for running freshwaters subject to eutrophication (O'Hare et al., 2018).

Mean concentrations of the measured seven heavy metals along Nestos river and its tributaries are presented in Table 2. Two of the measured heavy metals (i.e., lead and nickel) are included in the priority substances list of WFD, and two others (i.e., cadmium and mercury), in priority hazardous substances list. Mean Pb concentrations ranged from 0.35 µg/L (at N10 station) to 0.99 µg/L (at N3 station) along the river (Table 2), and did not exceed the limit of 10 µg/L for drinking water set by both WHO and EU (WHO, 2017; Directive 1998/83/EC); they were also lower than AA-EQS and MAC-EQS (1.2 µg/L and 14 µg/L, respectively) set by EU. Mean Ni concentrations were at low levels at all monitoring sites and below the MAC-EQS (34.0 µg/L) set by EU, with the exception of station N6, where nickel concentration was measured at 107.00 µg/L. This increased nickel value is attributed to human activities, as at the vicinity of station N6 is Paranesti village. According to Ziolkko et al. (2011), drinking water and household stainless steel products are important sources of Ni, whose concentration in municipal wastewater ranged between 4.0 and 77.0 µg/L (Hargreaves et al., 2018). In Paranesti village, there is no wastewater treatment plant or sewage system, and municipal wastewater is driven to septic tanks. Overflow of septic tanks or/and its leachate may result in wastewater discharge into Nestos river; given that Ni is primarily distributed in the soluble fraction of wastewater (Hargreaves et al., 2018), this results in an increase of Ni concentration in the river water. However, the mean nickel values, at all monitoring stations along the river, were lower than the limit established by WHO (2017; 70 µg/L) for drinking water. Cadmium mean concentration values were >0.15 µg/L at all monitoring stations, with the higher concentration (0.90 µg/L) observed at station N11. These values were higher than AA-EQS (0.15 µg/L) set by EU (Directive 2013/39/EC), while they were lower than the limit of 3.0 µg/L set by WHO (2017) for drinking water. Mercury mean concentrations ranged from 0.13 µg/L to 0.62 µg/L (Table 2); it was higher than the MAC-EQS (0.07 µg/L) set by EU, while it was lower than the limit set by WHO (2017) for drinking water (i.e., 6.0 µg/L for inorganic mercury). Regarding chromium, the mean concentrations ranged from 0.13 µg/L to 24.96 µg/L and were below the limit of drinking water (50 µg/L) set by WHO (2017). The higher mean concentration was observed at station N6, as in case of Ni, probably due to release of untreated municipal wastewater in the river from the nearby Paranesti village. Studies have indicated that the concentration of soluble Cr in raw municipal wastewater ranged from 1.1 mg/L (Kumar and Chopra, 2018) to 1.5 mg/L (Irshad et al., 2015). Copper mean concentrations were below the limit of 2 mg/L for drinking water (WHO, 2017) and ranged from 0.93 µg/L to 35.52 µg/L. Zinc mean concentrations ranged from 31.98 µg/L to 49.97 µg/L and were below the WHO (2003) limits for drinking water (3 mg/L).

Mean concentrations and AA-EQS and MAC-EQS set by EU (Directive 2013/39/EU) of the measured priority and hazardous priority substances along Nestos river and its tributaries are presented in Table 3. Four of the priority substances (i.e., chlorfenvinphos, octylphenols,

Table 2
Physicochemical water quality parameters (mean value \pm standard deviation) along Nestos river main course and its tributaries.

Parameters	Monitoring stations											EQS
	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	N11	
T (°C)	18.86 \pm 4.10	16.11 \pm 3.95	20.17 \pm 4.46	20.41 \pm 4.57	14.39 \pm 3.43	14.66 \pm 1.27	16.70 \pm 1.17	17.21 \pm 1.64	16.71 \pm 1.64	18.03 \pm 2.47	22.37 \pm 4.17	-
DO (mg/L)	6.84 \pm 1.89	7.63 \pm 1.66	6.07 \pm 1.26	7.12 \pm 1.91	6.08 \pm 1.60	7.47 \pm 1.98	7.07 \pm 1.00	7.48 \pm 1.61	7.12 \pm 1.39	7.58 \pm 1.13	7.42 \pm 1.42	4 ^a
DO (%)	75.59 \pm 24.02	83.13 \pm 24.35	68.93 \pm 13.36	75.49 \pm 20.51	62.47 \pm 14.59	74.59 \pm 16.89	75.00 \pm 10.37	81.40 \pm 18.69	75.33 \pm 18.24	77.81 \pm 16.16	74.07 \pm 18.08	-
pH	7.69 \pm 0.42	7.84 \pm 0.39	7.60 \pm 0.79	8.09 \pm 0.42	7.45 \pm 0.54	7.88 \pm 0.61	8.13 \pm 0.40	8.14 \pm 0.42	7.73 \pm 0.25	7.69 \pm 0.34	7.86 \pm 0.29	6-9 ^a
EC (μ S/cm)	251.40 \pm 77.83	232.70 \pm 42.63	282.61 \pm 76.68	176.10 \pm 44.77	205.50 \pm 7.87	188.43 \pm 25.90	196.71 \pm 19.01	198.43 \pm 17.60	252.86 \pm 40.22	257.00 \pm 47.33	284.00 \pm 55.58	-
TSS (mg/L)	6.81 \pm 5.91	2.61 \pm 3.10	2.32 \pm 2.13	1.32 \pm 2.05	2.15 \pm 2.48	0.94 \pm 0.32	0.79 \pm 0.52	0.68 \pm 0.46	4.33 \pm 4.99	7.81 \pm 7.88	15.10 \pm 21.60	25 ^a
COD (mg/L)	18.35 \pm 4.84	14.55 \pm 7.81	6.77 \pm 1.53	8.51 \pm 5.62	10.75 \pm 8.10	9.70 \pm 7.13	5.73 \pm 3.03	6.79 \pm 3.76	6.29 \pm 1.45	5.52 \pm 3.50	4.27 \pm 2.54	-
BOD (mg/L)	4.76 \pm 1.11	5.00 \pm 1.63	1.89 \pm 1.96	2.87 \pm 1.54	3.33 \pm 2.06	3.74 \pm 2.29	2.70 \pm 1.11	3.37 \pm 0.85	2.42 \pm 1.95	2.07 \pm 1.02	3.06 \pm 3.54	3-6 ^a
NO ₂ (mg-N/L)	0.25 \pm 0.10	0.27 \pm 0.11	0.19 \pm 0.06	0.25 \pm 0.13	0.30 \pm 0.32	0.39 \pm 0.17	0.25 \pm 0.10	0.23 \pm 0.11	0.34 \pm 0.19	0.45 \pm 0.25	0.39 \pm 0.15	-
NO ₃ (mg-N/L)	18.01 \pm 10.34	21.83 \pm 22.54	14.32 \pm 9.39	6.07 \pm 2.47	14.50 \pm 6.67	6.80 \pm 2.63	7.30 \pm 5.17	6.59 \pm 2.89	5.97 \pm 3.34	8.53 \pm 7.84	4.43 \pm 2.45	9.1 ^a
NH ₄ ⁺ (mg-N/L)	122.10 \pm 50.10	101.36 \pm 36.04	106.34 \pm 59.03	118.05 \pm 17.51	104.42 \pm 47.05	281.51 \pm 79.95	88.61 \pm 9.59	67.05 \pm 8.40	87.27 \pm 22.38	54.29 \pm 18.07	73.29 \pm 13.08	40-1000 ^a
TKN (mg/L)	1.75 \pm 1.01	1.34 \pm 0.74	1.14 \pm 0.85	1.07 \pm 0.97	0.90 \pm 0.64	1.22 \pm 0.77	0.83 \pm 0.39	0.92 \pm 0.46	1.46 \pm 1.10	1.62 \pm 1.24	1.65 \pm 1.37	-
TP (mg-P/L)	84.94 \pm 48.90	132.06 \pm 47.08	66.58 \pm 19.38	43.92 \pm 17.50	55.33 \pm 8.13	37.35 \pm 7.36	62.36 \pm 10.58	49.99 \pm 9.82	70.52 \pm 22.77	70.83 \pm 17.11	76.31 \pm 17.53	-
OP (mg-P/L)	15.55 \pm 12.11	12.01 \pm 4.67	18.95 \pm 17.75	19.60 \pm 16.36	8.33 \pm 8.45	11.16 \pm 5.43	17.92 \pm 12.47	12.66 \pm 13.40	8.78 \pm 6.23	10.20 \pm 8.29	17.28 \pm 16.40	-
Chl-a (mg/L)	19.14 \pm 3.80	26.41 \pm 6.64	20.89 \pm 1.89	16.04 \pm 10.47	17.08 \pm 3.47	15.29 \pm 8.21	15.94 \pm 8.23	20.49 \pm 6.52	23.68 \pm 5.11	23.22 \pm 3.75	24.98 \pm 4.12	-

Parameters	Monitoring stations											AA ^b	MAC ^c
	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	N11		
Pb (μ g/L)	0.64 \pm 0.24	0.64 \pm 0.24	0.99 \pm 0.99	0.62 \pm 0.22	0.48 \pm 0.15	0.67 \pm 0.19	0.69 \pm 0.16	0.45 \pm 0.20	0.55 \pm 0.16	0.30 \pm 0.27	0.61 \pm 0.53	1.2	
Ni (μ g/L)	3.20 \pm 1.21	3.20 \pm 1.21	2.70 \pm 1.74	16.44 \pm 31.91	2.92 \pm 1.36	22.57 \pm 37.96	7.78 \pm 11.59	6.64 \pm 3.52	7.31 \pm 10.80	3.48 \pm 2.18	3.56 \pm 2.87	4.0	
Cd (μ g/L)	0.17 \pm 0.06	0.15 \pm 0.06	0.87 \pm 1.84	0.21 \pm 0.07	0.43 \pm 0.78	0.20 \pm 0.11	0.33 \pm 0.30	0.27 \pm 0.33	0.18 \pm 0.14	0.29 \pm 0.54	0.77 \pm 1.11	0.15	
Hg (μ g/L)	0.16 \pm 0.21	0.24 \pm 0.44	0.21 \pm 0.19	0.44 \pm 0.93	0.11 \pm 0.10	0.27 \pm 0.50	0.12 \pm 0.10	0.18 \pm 0.21	0.11 \pm 0.12	0.16 \pm 0.19	0.20 \pm 0.22	-	
Cr (μ g/L)	0.83 \pm 0.59	1.48 \pm 1.08	1.82 \pm 1.47	3.71 \pm 5.97	0.70 \pm 0.51	24.96 \pm 48.59	2.01 \pm 0.54	1.73 \pm 1.56	6.69 \pm 11.53	1.25 \pm 0.92	15.00 \pm 18.30	50.0 ^d	
Cu (μ g/L)	1.67 \pm 0.40	1.39 \pm 0.78	35.52 \pm 91.71	2.54 \pm 1.67	0.93 \pm 0.36	3.15 \pm 2.34	2.41 \pm 1.68	1.89 \pm 1.13	2.62 \pm 0.90	2.12 \pm 0.54	2.37 \pm 1.67	2000 ^d	
Zn (μ g/L)	34.36 \pm 26.14	44.39 \pm 8.98	33.29 \pm 23.05	36.42 \pm 13.67	31.98 \pm 22.96	37.90 \pm 17.83	37.34 \pm 19.27	33.28 \pm 22.56	34.85 \pm 17.14	34.09 \pm 22.51	49.97 \pm 22.83	3000 ^d	

Bold values exceed EQS.

^a Values set by Directive 2006/44/EC on the quality of fresh waters needing protection or improvement in order to support fish life.

^b AA = annual average concentration (μ g/L).

^c MAC = maximum allowable concentration (μ g/L); the AA-EQS and MAC-EQS values are set by Directive 2013/39/EC.

^d Value set by WHO (2003, 2017) for drinking water.

Table 3
Priority and hazardous priority substances (mean value ± standard deviation) along Nestos river main course and its tributaries.

Priority and hazardous priority substances (µg/L)	Monitoring stations											EQS	
	N1	N2	N3	N4	N5	N6	N7	N8	N9	N10	N11	AA ^a	MAC ^b
Alachlor	0.004 ± 0.009	0.003 ± 0.009	0.006 ± 0.009	0.001 ± 0.002	0.003 ± 0.003	0.01 ± 0.00	0.003 ± 0.004	0.002 ± 0.003	0.006 ± 0.011	0.005 ± 0.008	0.001 ± 0.002	0.3	0.7
Anthracene	0.028 ± 0.067	nd	0.025 ± 0.004	0.021 ± 0.028	0.014 ± 0.018	0.026 ± 0.034	nd	nd	0.041 ± 0.057	0.030 ± 0.038	0.010 ± 0.027	0.1	0.1
Atrazine	0.015 ± 0.010	0.014 ± 0.011	0.015 ± 0.011	0.016 ± 0.013	0.046 ± 0.067	0.021 ± 0.017	0.035 ± 0.046	0.011 ± 0.007	0.024 ± 0.033	0.036 ± 0.050	0.018 ± 0.026	0.6	2.0
Benzene	nd	nd	0.001 ± 0.001	nd	0.001 ± 0.001	0.001 ± 0.001	nd	nd	0.001 ± 0.001	0.001 ± 0.001	nd	10	50
Brominated diphenylethers	nd	nd	0.002 ± 0.005	nd	nd	0.001 ± 0.004	nd	nd	nd	nd	nd	nd	0.014
C ₁₀₋₁₃ -Chloroalkanes	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.4	1.4
Chlorofeniphos	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.1	0.3
Chlorpyrifos	nd	nd	nd	nd	0.001 ± 0.001	nd	0.001 ± 0.003	nd	nd	0.001 ± 0.002	nd	0.03	0.1
1,2-Dichloroethene	nd	0.001 ± 0.001	0.001 ± 0.001	0.002 ± 0.002	0.002 ± 0.002	0.005 ± 0.006	0.005 ± 0.007	0.002 ± 0.002	0.001 ± 0.001	0.003 ± 0.003	0.004 ± 0.005	10	n/a
Dichloromethane	nd	nd	0.004 ± 0.005	0.001 ± 0.001	0.004 ± 0.005	0.002 ± 0.002	nd	nd	nd	nd	0.001 ± 0.001	20	n/a
Diethylhexylphthalate (DEHP)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.3	n/a
Diuron	nd	nd	nd	nd	nd	nd	<0.001 ± <0.001	nd	nd	<0.001 ± <0.001	<0.001 ± <0.001	0.2	1.8
Endosulfan	nd	nd	nd	nd	<0.001 ± <0.001	<0.001 ± <0.001	<0.001 ± <0.001	nd	nd	<0.001 ± <0.001	nd	0.005	0.01
Fluoranthene	0.629 ± 1.381	0.041 ± 0.066	0.128 ± 0.129	0.126 ± 0.159	0.112 ± 0.148	0.093 ± 0.142	0.189 ± 0.203	0.185 ± 0.206	0.347 ± 0.342	0.301 ± 0.374	0.248 ± 0.318	0.0063	0.12
Hexachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.6	0.6
Hexachlorobutadiene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.02	0.04
Hexachlorocyclohexanes	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.3	1.0
Isoproturon	0.025 ± 0.025	0.032 ± 0.024	0.011 ± 0.011	0.019 ± 0.021	0.023 ± 0.028	0.019 ± 0.028	0.023 ± 0.022	0.016 ± 0.020	0.028 ± 0.016	0.035 ± 0.044	0.012 ± 0.016	2.0	130
Naphthalene	0.402 ± 0.933	0.187 ± 0.246	0.048 ± 0.049	0.108 ± 0.094	0.130 ± 0.249	0.007 ± 0.019	0.022 ± 0.037	0.127 ± 0.248	0.017 ± 0.046	0.10 ± 0.230	0.681 ± 1.740	0.3	2.0
Nonylphenol	nd	nd	nd	nd	<0.001 ± <0.001	<0.001 ± <0.001	nd	nd	nd	<0.001 ± <0.001	nd	0.3	2.0
Octylphenols	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.1	n/a
Pentachlorobenzene	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.007	n/a
Pentachlorophenol	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.4	1.0
Benzo-a-pyrene	0.181 ± 0.233	0.381 ± 0.750	0.114 ± 0.179	0.212 ± 0.162	0.590 ± 0.853	0.270 ± 0.146	0.077 ± 0.075	0.138 ± 0.140	0.050 ± 0.081	0.128 ± 0.197	0.169 ± 0.120	1.7 × 10 ⁻⁴	0.27
Benzo-b-fluoranthene	0.035 ± 0.075	0.056 ± 0.127	0.087 ± 0.151	0.006 ± 0.015	0.062 ± 0.107	0.085 ± 0.188	0.238 ± 0.466	0.061 ± 0.059	0.066 ± 0.093	0.119 ± 0.099	0.080 ± 0.103	0.017	0.017
Benzo-k-fluoranthene	6.564 ± 7.115	12.156 ± 16.966	8.936 ± 10.382	10.115 ± 7.486	12.780 ± 8.031	12.090 ± 7.655	8.187 ± 7.952	7.940 ± 7.142	7.262 ± 6.166	10.981 ± 7.245	11.040 ± 5.085	0.017	8.2 × 10 ⁻³
Benzo-g,h,i-perylene	0.010 ± 0.025	0.058 ± 0.114	0.019 ± 0.035	0.018 ± 0.049	nd	nd	nd	0.008 ± 0.021	0.031 ± 0.083	0.014 ± 0.037	0.040 ± 0.107	0.3	10 ⁻³
Indeno(1,2,3-cd)pyrene	0.188 ± 0.162	0.094 ± 0.163	0.272 ± 0.450	0.228 ± 0.210	0.544 ± 0.502	0.207 ± 0.165	0.153 ± 0.179	0.086 ± 0.141	0.281 ± 0.509	0.185 ± 0.285	0.120 ± 0.234	1.0	4.0
Simazine	nd	nd	<0.001 ± <0.001	nd	nd	<0.001 ± <0.001	nd	nd	<0.001 ± <0.001	0.009 ± 0.024	<0.001 ± <0.001	0.0002	0.0015
Tributyltin compounds	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.4	n/a
Trichlorobenzenes	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	2.5	n/a
Trichloromethane	nd	nd	0.002 ± 0.002	nd	0.003 ± 0.003	0.003 ± 0.003	nd	nd	nd	nd	nd	0.03	n/a
Trifluralin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	n/a

nd = non-detected substances; n/a = not applicable.

^a AA = annual average concentration (µg/L).

^b MAC = maximum allowable concentration (µg/L); both values of AA-EQS and MAC-EQS are set by Directive 2013/39/EC.

^c Benzo(a)pyrene can be considered as a marker for the other PAHs.

pentachlorophenol, trichlorobenzenes) and nine of the priority hazardous substances (i.e., C_{10–13}-chloroalkanes, diethylhexylphthalate, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, nonylphenols, pentachlorobenzene, tributyltin compounds and trifluralin) were not detected in Nestos river water. Eleven of the priority substances (i.e., alachlor, atrazine, benzene, chlorpyrifos, 1,2-dichloroethene, dichloromethane, diuron, isoproturon, naphthalene, simazine and trichloromethane) and two of hazardous priority substances (i.e., brominated diphenylethers, endosulfan) were found to have concentrations below the AA-EQS and MAC-EQS set by EU. In Nestos river and its tributaries, the most frequently detected pesticides were atrazine (95%), alachlor (36%) and isoproturon (64%). The detection frequency of other pesticides was lower than 25% as follows: endosulfan (21%), chlorpyrifos (15%), simazine (7%) and diuron (4%). Finally, the following pesticides were not detected (0% frequency): chlorfenvinphos, hexachlorobenzene, pentachlorophenol and trifluralin. As mentioned above, in the plain area of Nestos river watershed, where the N10 and N11 monitoring stations are located (Fig. 1), intense agricultural activities (rice, corn and cotton cultivation) take place. However, only a few pesticides (i.e., alachlor, atrazine, chlorpyrifos, diuron, endosulfan, isoproturon, simazine,) were detected at station N10 and/or N11 at concentrations below MAC-EQS. For instance, the herbicide diuron, mainly used to control weeds on hard surfaces, was measured at maximum concentrations of 0.11 ng/L and 0.09 ng/L, at N10 and N11 stations, respectively. In another study (Papadakis et al., 2018), diuron was detected at low concentrations in Strymon river water, N. Greece, while it was not detected in Nestos river water. Diuron has also been detected at concentrations exceeding the EQS values in Ebro river, Rioja area, Spain (Herrero-Hernández et al., 2017). The herbicide simazine, which is widely used in agricultural activities and remains active in the soil for 2–7 months after application, was measured at maximum concentrations of 62.8 ng/L and 5.0 ng/L, at N10 and N11 stations, respectively. As in the case of diuron, simazine was detected at a low concentration in Strymon river water, N. Greece, while it was not detected in Nestos river water (Papadakis et al., 2018), probably because its usage was ceased in Greece in 2007. Priority substances were not measured in sediments in this study, but the likelihood of finding these in sediments is small, mainly depending on the physicochemical properties of substances (e.g., molecular weight, octanol/water ratio, etc.) and the size of the riverbed material, which in most reaches of Nestos river is coarse rock and cobble. In a survey conducted by Pose-Juan et al. (2015), pesticides such as atrazine, diuron, metolachlor, chlorpyrifos, simazine etc. were detected in surface and ground waters but none of these was detected in soil samples in vineyard soils from La Rioja Spain. According to Pinto et al. (2016), their tendency to accumulate in sediments is lower. However, chlorpyrifos was detected in the sediment samples from the Pearl river estuary (China) at maximum and mean concentration of 4.5 ng/g dw and 0.2 ng/g dw, respectively (Pintado-Herrera et al., 2017). In addition, it was detected in sediments of the Guadalquivir river basin (Spain) at maximum and mean concentrations of 15.9 and 4.8 ng/g dw, respectively (Masiá et al., 2013). Endosulfan was measured only at station N10 at maximum concentration of 0.67 ng/L (i.e., lower than MAC-EQS of 10 ng/L; Table 3). It is an organochlorine insecticide and acaricide that is being phased out globally due to its acute toxicity and its role as an endocrine disruptor. Lekkas et al. (2004) found concentrations of endosulfan up to 40.0 ng/L in the water of several Greek rivers, while according to Litskas et al. (2012), endosulfan was found to exceed the MAC-EQS in four monitoring stations of Strymon river, N. Greece. Nonylphenol, which acts also as an endocrine disruptor and is used in pesticides, paints, textiles, metal working industries and some personal care products (Sousa et al., 2018; Papaevangelou et al., 2016), was measured at station N10 at maximum concentration of 2.0 ng/L (i.e., lower than MAC-EQS of 2.0 µg/L; Table 3). Nonylphenol has also been measured at concentration of up to 790.0 ng/L in Tagus river, Portugal (Rocha et al., 2015). In the Pearl river estuary, China, nonylphenol poses an

environmental concern, as it was detected in sediments at maximum and mean concentrations of 1907 ng/g dw and 114 ng/g dw, respectively (Pintado-Herrera et al., 2017).

The concentrations of the remaining priority and hazardous priority substances were measured at several stations above the AA-EQS and/or MAC-EQS (Table 3). In particular, mean anthracene concentration was below the AA-EQS at all stations but there was one concentration above the MAC-EQS (i.e., 0.165 µg/L) only at the upper monitoring station in the Greek part of Nestos river (N1); it appears to be a result of human activities, since it is used to make dyes, plastics and pesticides. Anthracene concentrations, higher than the MAC value, have also been measured in Strymon transboundary river, N. Greece (Litskas et al., 2012) and in Aliakmonas and Loudias river basins, N. Greece (Manoli et al., 2000). Anthracene was also measured in the sediments from Pearl river estuary at maximum and mean concentrations of 35 ng/g dw and 5 ng/g dw, respectively (Pintado-Herrera et al., 2017). In this area, the most predominant PAH was fluoranthene whose concentration in sediments ranged from 5.1 to 209 ng/g dw. Fluoranthene mean concentration was above the AA-EQS set by EU (Directive 2013/39/EC) at all monitoring stations along Nestos river. Its presence is an indicator of less efficient or lower-temperature combustion, biomass burning and waste incineration (Lima et al., 2005; Pintado-Herrera et al., 2017). The greater mean value was measured at N1 station and is attributed to incoming pollution to Nestos river. Polyaromatic hydrocarbons (PAHs) are among the most widespread organic pollutants and were measured in rain water and water bodies of Aliakmonas and Loudias river basins (Manoli et al., 2000). PAHs have also been detected at concentrations of up to 1.2 µg/L in Raba river, Hungary (Nagy et al., 2013), and up to 2.16 µg/L in Svatka river, Czech Republic (Jálová et al., 2013). Furthermore, PAHs were measured in estuarine surface sediments from Douro river (Portugal) at concentrations of 36–41 µg/g dw (Rocha et al., 2017), and also, in sediments of the Danube river (Hungarian part) at concentrations ranging between 8.3 and 1202.5 ng/g dw (Nagy et al., 2013). They are found in fossil fuels and are also formed by incomplete carbon combustion. They were measured at all monitoring stations along Nestos river at higher values than AA-EQS, and their presence is mainly attributed to human activities, such as solid waste burning in illicit dumps.

3.2. Reservoir water quality data

The physicochemical data at the surface and the bottom water of Thissavros (R1, R2 and R3 stations; Fig. 1) and Platanovrisi (R4 and R5 stations; Fig. 1) reservoirs are presented in Table 4. Water temperature at R5 station from the surface to the bottom during the monitoring period (i.e., one year) is presented in Fig. SM1. Thermal stratification of water and intense epilimnion-thermocline-hypolimnion creation, lasting from April to mid-November (Julian day 90 to 300; Fig. SM1), were observed, a phenomenon which was more intense during the summer months. Thermal stratification governs the dynamics, and physical and chemical parameters in most similar water systems (Gikas et al., 2009). The surface-to-bottom mean annual temperature difference increased significantly in the downstream flow direction, from 1.7 °C at the entry point (monitoring site R1) in Thissavros to 9.8 °C at the dam crest of Platanovrisi reservoir (monitoring site R5). The mean temperatures of the lake surface and bottom waters for the monitoring period were 23.0 °C and 15.6 °C, respectively. The *t*-test showed statistically significant difference between surface and bottom waters for the mean temperature of the entire monitoring period ($t = 6.7, p < 0.001$). The vertical temperature gradient directly affects dissolved oxygen content, minimizing its presence to hypoxic levels (20–30%), especially in Thissavros reservoir (i.e., monitoring sites R2 and R3; Table 4). For the entire monitoring period, the mean DO concentration of surface water (6.1 mg/L) was higher than the respective value of bottom water (4.1 mg/L), and the *t*-test showed that the difference was statistically significant ($t = 6.1, p < 0.001$).

Table 4Physicochemical water quality parameters (mean value \pm standard deviation) in surface and bottom water of Nestos river reservoirs.

Parameters	Reservoir stations									
	R1		R2		R3		R4		R5	
Surface water	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
T (°C)	22.23 \pm 5.78	20.55 \pm 3.87	24.75 \pm 4.54	10.65 \pm 1.03	23.37 \pm 4.27	19.33 \pm 5.29	22.36 \pm 3.84	15.49 \pm 1.70	22.63 \pm 3.12	12.86 \pm 1.36
DO (mg/L)	6.67 \pm 1.65	5.17 \pm 3.07	5.38 \pm 2.18	2.23 \pm 0.70	5.70 \pm 1.31	5.31 \pm 1.66	5.92 \pm 1.43	4.42 \pm 1.31	6.55 \pm 2.54	3.48 \pm 1.42
DO (%)	74.47 \pm 17.65	56.63 \pm 34.35	69.90 \pm 28.55	19.90 \pm 4.81	67.34 \pm 12.35	61.47 \pm 21.82	71.89 \pm 19.05	45.89 \pm 12.47	77.10 \pm 32.70	31.83 \pm 14.26
pH	8.12 \pm 0.53	7.67 \pm 0.37	7.78 \pm 0.36	7.69 \pm 0.52	7.75 \pm 0.85	7.98 \pm 0.50	7.49 \pm 0.49	7.54 \pm 0.55	7.82 \pm 0.74	7.50 \pm 0.48
EC (μ S/cm)	221.51 \pm 78.65	220.35 \pm 50.62	196.18 \pm 35.42	238.83 \pm 5.71	183.74 \pm 21.47	190.72 \pm 11.53	205.21 \pm 13.84	198.66 \pm 5.55	201.43 \pm 5.93	217.43 \pm 25.04
TSS (mg/L)	6.31 \pm 3.73	6.62 \pm 5.77	2.53 \pm 2.28	2.41 \pm 2.45	3.53 \pm 3.01	1.98 \pm 0.98	2.61 \pm 2.15	8.05 \pm 11.85	2.27 \pm 2.88	1.82 \pm 2.58
COD (mg/L)	17.04 \pm 5.37	–	nd	–	8.88 \pm 2.09	–	6.74 \pm 1.79	–	8.54 \pm 1.32	–
BOD (mg/L)	6.03 \pm 1.90	4.27 \pm 0.81	1.52 \pm 0.70	5.55 \pm 1.86	5.09 \pm 1.17	3.84 \pm 1.96	3.90 \pm 1.35	3.49 \pm 0.84	3.38 \pm 2.18	1.84 \pm 0.67
NO ₃ ⁻ (mg-N/L)	0.57 \pm 0.61	0.41 \pm 0.27	0.25 \pm 0.25	0.21 \pm 0.15	0.26 \pm 0.08	1.37 \pm 2.76	0.18 \pm 0.09	0.23 \pm 0.07	0.21 \pm 0.16	0.33 \pm 0.16
NO ₂ ⁻ (μ g-N/L)	21.13 \pm 11.80	26.08 \pm 8.10	10.98 \pm 6.77	15.52 \pm 9.48	17.41 \pm 8.39	14.54 \pm 5.57	13.91 \pm 7.42	15.94 \pm 10.60	32.86 \pm 17.98	16.68 \pm 14.76
NH ₄ ⁺ (μ g-N/L)	255.56 \pm 83.4	193.68 \pm 104.4	116.05 \pm 49.46	172.75 \pm 85.90	108.07 \pm 75.19	107.51 \pm 42.23	75.90 \pm 44.31	103.01 \pm 51.47	84.54 \pm 38.23	67.98 \pm 21.21
TKN (mg/L)	1.45 \pm 0.93	2.15 \pm 1.50	1.22 \pm 0.92	1.59 \pm 0.56	1.51 \pm 0.97	1.42 \pm 1.32	1.35 \pm 0.87	1.32 \pm 0.42	1.20 \pm 0.79	1.12 \pm 0.73
TP (μ g-P/L)	41.20 \pm 9.32	109.02 \pm 48.45	47.20 \pm 9.19	69.98 \pm 7.22	48.74 \pm 8.74	57.32 \pm 5.10	78.48 \pm 9.46	64.09 \pm 10.41	48.99 \pm 16.04	61.28 \pm 7.33
OP (μ g-P/L)	8.26 \pm 5.30	9.26 \pm 4.43	9.50 \pm 8.76	13.88 \pm 13.63	12.13 \pm 8.75	14.27 \pm 7.13	19.07 \pm 15.36	18.67 \pm 13.49	9.53 \pm 10.12	12.43 \pm 17.24
Chl-a (μ g/L)	19.24 \pm 6.55	22.50 \pm 6.74	25.91 \pm 3.79	22.57 \pm 4.30	23.98 \pm 9.55	20.90 \pm 6.77	25.39 \pm 9.16	23.89 \pm 9.36	19.64 \pm 5.21	21.04 \pm 5.26
Pb (μ g/L)	0.67 \pm 0.38	0.55 \pm 0.39	0.68 \pm 0.21	0.85 \pm 1.11	0.61 \pm 0.24	0.52 \pm 0.09	0.64 \pm 0.35	0.54 \pm 0.30	0.62 \pm 0.37	0.67 \pm 0.37
Ni (μ g/L)	4.22 \pm 2.61	5.47 \pm 4.53	2.15 \pm 0.31	3.50 \pm 1.00	3.29 \pm 2.02	2.80 \pm 1.16	2.03 \pm 1.02	3.72 \pm 2.83	2.91 \pm 1.45	2.67 \pm 0.69
Cd (μ g/L)	0.63 \pm 1.11	0.23 \pm 0.18	0.27 \pm 0.15	0.14 \pm 0.06	0.20 \pm 0.16	0.15 \pm 0.10	0.27 \pm 0.17	0.17 \pm 0.08	0.32 \pm 0.35	0.21 \pm 0.14
Hg (μ g/L)	0.50 \pm 0.61	0.27 \pm 0.35	0.18 \pm 0.10	0.25 \pm 0.18	0.12 \pm 0.11	0.13 \pm 0.12	0.19 \pm 0.12	3.65 \pm 8.51	0.14 \pm 0.06	0.31 \pm 0.27
Cr (μ g/L)	2.26 \pm 1.38	1.05 \pm 0.72	0.87 \pm 0.65	1.10 \pm 0.56	1.01 \pm 0.76	0.77 \pm 0.40	1.15 \pm 0.93	4.46 \pm 4.49	2.58 \pm 2.22	4.05 \pm 4.41
Cu (μ g/L)	2.87 \pm 1.87	2.50 \pm 1.10	1.57 \pm 0.69	2.88 \pm 1.01	2.07 \pm 1.02	3.46 \pm 2.88	1.23 \pm 0.68	2.95 \pm 2.26	2.31 \pm 2.53	1.89 \pm 1.91
Zn (μ g/L)	46.80 \pm 18.86	39.50 \pm 27.30	35.24 \pm 14.84	41.93 \pm 19.48	33.10 \pm 19.86	30.08 \pm 18.85	41.62 \pm 30.73	34.31 \pm 16.49	36.49 \pm 30.28	42.35 \pm 19.16

nd corresponds to non-detected substances.

The highest mean concentration values for BOD and COD were 6.03 mg/L and 17.04 mg/L, respectively, and were measured at the surface water of R1 station (Table 4), showing that the water quality at that location is mostly affected by the human activities in the drainage area, surface runoff and probably in-lake processes. BOD mean concentration at all monitoring stations for both surface and bottom waters were lower than the limit (3–6 mg/L) for fisheries and aquatic life. Furthermore, COD mean concentration at all monitoring stations of surface water was lower than the limit of 20 mg/L for unpolluted water (Chapman, 1996). For the entire monitoring period, the mean concentrations of BOD of surface and bottom waters were 4.05 mg/L and 3.72 mg/L, respectively, and the *t*-test showed that the difference was not statistically significant ($t = 0.68$, $p = 0.49$).

The dominant form of inorganic nitrogen in the reservoirs of Nestos river was the nitrate-nitrogen whose mean concentrations at the surface and bottom waters ranged from 0.18 mg/L to 0.57 mg/L and from 0.21 mg/L to 1.37 mg/L, respectively (Table 4). Nitrite-nitrogen mean concentration in the reservoirs was lower than 33.0 μ g/L for both surface and bottom waters. The mean concentrations of ammonium-nitrogen in the reservoirs in the surface and bottom waters ranged from 75.90 μ g/L to 255.56 μ g/L and from 67.98 μ g/L to 193.68 μ g/L, respectively, and were lower than the limit (40–1000 μ g NH₄-N/L) set by EU for fisheries and aquatic life. The highest concentration was measured at the surface water of R1 station (Table 4). On the other hand, the higher NH₄-N concentrations, compared to the corresponding surface concentration, were measured at the bottom of R2 and R4 stations; this fact could be related to the occurrence of low DO concentrations at the bottom of these stations and the decomposition of organic matter taking place at the bottom sediments (Gikas et al., 2009; Yang et al., 2020). For the entire monitoring period, the mean concentrations of NO₃-N, NO₂-N, NH₄-N and TKN were 0.29 mg/L, 16.30 μ g/L, 128.37 μ g/L and 1.35 mg/L in surface water of the reservoirs, and 0.49 mg/L, 15.16 μ g/L, 126.27 μ g/L and 1.50 mg/L in bottom water, respectively. However, the *t*-test showed that there was no statistically significant

difference between the mean nitrogen concentration in surface and bottom water for all nitrogen forms ($p > 0.352$). These results show that the distribution of nitrogen forms in the water column was not affected by the thermal stratification observed during the monitoring period.

The mean concentration of both TP and OP in the surface water of the reservoirs were lower than that of bottom water for all monitoring stations with the exception of R4 station (Table 4). In lake ecosystems, reduction of DO concentration below 4 mg/L in bottom waters results in the release of phosphorus and other elements from the lake sediments. The most common is the release of phosphorus bound to iron oxide under reducing conditions (Gikas et al., 2006; Markovic et al., 2019; Yang et al., 2020). Phosphorus is released into the water column mainly as OP. In the reservoirs of Nestos river, the mean concentrations of TP, for the entire monitoring period, for the surface and bottom waters were 53.09 μ g/L and 71.73 μ g/L, respectively, and those of OP were 8.65 μ g/L and 11.43 μ g/L for surface and bottom waters, respectively, indicating that the bottom sediments are the main source of phosphorus to these reservoirs. The higher concentration of phosphorus in the bottom water of a lake in comparison to that of surface water, as in the present case, is a common phenomenon and has been documented in various lakes (Yang et al., 2020; Nürnberg and La Zerte, 2016), reservoirs (Gikas et al., 2009) and lagoons (Markou et al., 2006; Gikas et al., 2006). The *t*-test showed that there exists statistically significant difference between the mean phosphorus concentration between surface and bottom waters only for TP ($t = -3.31$, $p = 0.002$). Chl-a mean concentrations at the surface and bottom waters of the reservoirs ranged from 19.24 μ g/L to 25.91 μ g/L and from 20.90 μ g/L to 23.89 μ g/L, respectively. The depth of the reservoirs at R1, R2 and R3 stations is about 70 m while at R4 and R5 stations it is 45 m and 60 m, respectively. The mean turbidity values at R1, R2, R3, R4 and R5 stations during the monitoring period were 16.6, 23.0, 87.4, 67.7 and 130.4 NTU, respectively. Given the low turbidity values, the solar radiation can reach relatively deep in the water, and therefore, the phytoplankton growth is

expected to reach at greater depths. In addition, phytoplankton from the surface layers settles and reaches the reservoirs bottom. Indeed, the mean concentrations of Chl-a, for the entire monitoring period, for surface and bottom waters were 22.74 µg/L and 22.19 µg/L, respectively; the t-test showed that the difference was not statistically significant ($t = 0.38$, $p = 0.75$). However, during the summer (i.e., from mid-June to late August), the Chl-a concentration in the reservoir monitoring stations for surface and bottom water ranged from 22.7 to 29.7 µg/L and from 16.2 to 21.6 µg/L, respectively, due to the increment of phytoplankton growth in surface waters and also thermal stratification during this period (Fig. SM1). During the next period (i.e., from mid-September to late November) when the temperature decreased, the mean Chl-a concentration in surface and bottom water was 21.7 µg/L and 20.1 µg/L, respectively. This similarity is due to the reduction of phytoplankton growth in the surface water as temperature drops and the fall turnover-mixing of the reservoir water.

Mean concentrations of the measured heavy metals in surface and bottom waters of the reservoirs of Nestos river are presented in Table 4. The concentrations of Pb and Ni in surface and bottom water at all monitoring stations (i.e., R1-R5) were below the MAC-EQS (i.e., 14 µg/L and 34.0 µg/L, for Pb and Ni, respectively) set by EU (Directive 2013/39/EC). Regarding Cd and Hg, which are included in the priority hazardous substances list, mean concentration values in surface and bottom water at all monitoring stations were higher than EQS set by EU (i.e., 0.15 µg/L and 0.07 µg/L, for Cd and Hg, respectively; Directive 2013/39/EC), with the exception of Cd mean concentration in bottom waters of R2 and R3 stations which were 0.14 and 0.15 µg/L, respectively. Mean concentration values of the rest of heavy metals (i.e., Cr, Cu and Zn; Table 4) in both surface and bottom waters of all monitoring stations were below the limit set by WHO (2017) for drinking water (i.e., 50 µg/L, 2 mg/L and 3 mg/L for Cr, Cu and Zn, respectively).

Heavy metals measured in the reservoirs of Nestos river were both in dissolved and suspended forms. Increase in pH reduces the solubility of many heavy metals and results in a decrease in the total concentration of many heavy metals in the water column. On the other hand, part of heavy metals, in both suspended and dissolved forms, originates from bottom sediments. The mean concentrations of Pb, Ni, Cd, Hg, Cr, Cu and Zn, for the monitoring period, were 0.64 µg/L, 2.94 µg/L, 0.34 µg/L, 0.17 µg/L, 1.61 µg/L, 2.02 µg/L and 38.75 µg/L at surface waters of the reservoirs, and 0.62 µg/L, 3.60 µg/L, 0.18 µg/L, 0.84 µg/L, 2.44 µg/L, 2.72 µg/L and 37.68 µg/L at the bottom waters, respectively. From these results, it is obvious that the mean concentrations of Pb, Cd and Zn are higher in the surface waters, and for the rest of the heavy metals (i.e., Ni, Hg, Cr, and Cu), they are higher in the bottom waters. However, the t-test showed the absence of statistically significant difference between the mean concentration in surface waters and bottom waters for all measured heavy metals ($p > 0.113$ for all metals). The results of Pearson correlation between metal concentrations in surface and bottom waters are shown in Table SM2. The Pearson correlation values indicated statistically significant positive correlation ($p < 0.01$, 2-tailed) between Ni, Cd and Zn concentrations in surface and bottom waters; for the rest of the measured heavy metals (i.e., Pb, Hg, Cr and Cu), there was no statistically significantly different correlation. These results indicate Ni, Cd and Zn turnover between water and sediments in Nestos river reservoirs, depending on the prevailing conditions (Gikas et al., 2009; Wang et al., 2018).

Mean concentrations and standard deviations of the measured priority and hazardous priority substances in the surface water of Nestos river reservoirs are presented in Table 5. The other priority substances, in addition to heavy metals, were measured at the surface waters of Nestos river reservoirs. Seven of the priority substances (i.e., benzene, chlorfenvinphos, chlorpyrifos, diuron, pentachlorophenol, simazine and trichlorobenzenes) and ten of the priority hazardous substances (i.e., C₁₀₋₁₃-chloroalkanes, diethylhexylphthalate, endosulfan, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, nonylphenol,

pentachlorobenzene, tributyltin compounds and trifluralin) were not detected in surface water of Nestos river reservoirs. Eight of the priority substances (i.e., alachlor, atrazine, 1,2-dichloroethene, dichloromethane, isoproturon, naphthalene, octylphenols, and trichloromethane) and one of priority hazardous substances (i.e., brominated diphenylethers) were found to have concentrations below the AA-EQS and MAC-EQS (Tables 3, 5) set by EU (Directive 2013/39/EU). Anthracene was measured at all monitoring stations of Nestos river reservoirs and its mean concentration was below the AA-EQS (i.e., 0.1 µg/L) at all stations. Finally, fluoranthene and PAHs were measured at concentrations greater than AA-EQS at all stations.

3.3. Evaluation of water quality based on WFD and CCME-WQI

Fig. 2 presents the variation of the quality class for the physicochemical and the overall status in the riverine and reservoir parts of Nestos river, based on the two methodologies, i.e., WFD-MEEG and CCME-WQI. In order to facilitate the comparison of the two methodologies, the same parameters (i.e., physicochemical, heavy metals and priority substances) were used in both of them to evaluate the water quality status. Observing the variation graphs, it becomes clear that the WFD-MEEG values at all monitoring stations of Nestos river and the reservoirs (surface and bottom water) were in the 'good' quality class and showed no fluctuation in both physicochemical and overall status (Fig. 2). On the contrary, the CCME-WQI values present more fluctuation and indicate lower classes than the WFD-MEEG at many monitoring stations. In particular, at the Nestos riverine monitoring stations, the lower quality class of physicochemical status is 3 (fair or moderate) at N6 station and the higher is class 5 (excellent or high) at N10 station (Fig. 2a), whereas, the quality class at the rest of the stations is 4 (good). Regarding the overall status of Nestos river water, the CCME-WQI values indicate quality class 3 (fair or moderate) at all monitoring stations with the exception of station N9 where the quality class is 4 (good). The difference in quality class between physicochemical and overall status (Fig. 2a, b) can be explained by considering that the priority substances and heavy metals, which were detected and measured at several stations (Tables 2, 3) affect the 'overall status' classification. The difference between the lowest value of CCME-WQI and WFD-MEEG in the overall status is equal to one class at all monitoring stations with the exception of station N9 where there is not any difference.

The CCME-WQI class of physicochemical status of the reservoir surface water is 4 (good), as in the case of the WFD-MEEG method, at three of the monitoring stations, i.e., R2, R4 and R5, and it is quality class 3 (fair or moderate) at the rest of the stations (Fig. 2c). Regarding the overall status of the reservoirs surface water, the CCME-WQI class is 3 (fair or moderate) at R1, R2, R3, and R5 monitoring stations and 2 (marginal or poor) at R4 station (Fig. 2d). The lower quality class of reservoir surface water of the 'overall status' in comparison to that of the 'physicochemical status' is attributed, as reported above, to the priority substances and heavy metals (Tables 4, 5). The difference between the lowest value of CCME-WQI and WFD-MEEG of the physicochemical status is observed at R1 and R3 stations and is equal to one class (Fig. 2c), while for overall status it is observed at R4 station and is equal to two classes (Fig. 2d). Finally, the CCME-WQI quality class of the reservoir bottom water for both physicochemical and overall status at R3 and R5 stations is 4, i.e., similar to that of the WFD-MEEG method, and one class lower at the rest of the stations (i.e., R1, R2 and R4; Fig. 2e, f). The variation graphs of water quality classes of the reservoir bottom water (Fig. 2e, f) show that the physicochemical status is equal to the overall status. This is attributed to the fact that the overall status of the reservoir bottom water was evaluated based on the physicochemical parameters and heavy metals measured at the reservoir bottom water, because, as mentioned above, in the bottom water other priority substances were not measured. From the above analysis, it appears that the classification with CCME-WQI is stricter and more sensitive than the classification derived from the WFD-MEEG procedure. Additionally, the

Table 5

Priority and hazardous priority substances (mean value \pm standard deviation) in surface water of Nestos river reservoirs.

Priority and hazardous priority substances ($\mu\text{g/L}$)	Monitoring station				
	R1	R2	R3	R4	R5
Alachlor	0.006 \pm 0.010	0.002 \pm 0.003	0.005 \pm 0.007	0.004 \pm 0.008	0.006 \pm 0.007
Anthracene	0.021 \pm 0.038	0.039 \pm 0.049	0.006 \pm 0.017	0.014 \pm 0.026	0.062 \pm 0.111
Atrazine	0.024 \pm 0.020	0.013 \pm 0.010	0.019 \pm 0.015	0.021 \pm 0.024	0.008 \pm 0.004
Benzene	nd	nd	nd	nd	nd
Brominated diphenylethers	nd	nd	nd	0.003 \pm 0.005	0.002 \pm 0.004
C ₁₀₋₁₃ -chloroalkanes	nd	nd	nd	nd	nd
Chlorfenvinphos	nd	nd	nd	nd	nd
Chlorpyrifos	nd	nd	nd	nd	nd
1,2-Dichloroethene	0.001 \pm 0.001	0.002 \pm 0.002	nd	nd	0.001 \pm 0.002
Dichloromethane	nd	0.007 \pm 0.007	nd	0.001 \pm 0.001	0.002 \pm 0.002
Diethylhexylphthalate	nd	nd	nd	nd	nd
Diuron	nd	nd	nd	nd	nd
Endosulfan	nd	nd	<0.001 \pm <0.001	<0.001 \pm <0.001	nd
Fluoranthene	0.196 \pm 0.230	0.045 \pm 0.084	0.062 \pm 0.104	0.758 \pm 1.882	0.213 \pm 0.310
Hexachlorobenzene	nd	nd	nd	nd	nd
Hexachlorobutadiene	nd	nd	nd	nd	nd
Hexachlorocyclohexanes	nd	nd	nd	nd	nd
Isoproturon	0.015 \pm 0.020	0.023 \pm 0.017	0.009 \pm 0.014	0.011 \pm 0.017	0.011 \pm 0.018
Naphthalene	0.149 \pm 0.221	nd	0.036 \pm 0.046	0.060 \pm 0.058	0.063 \pm 0.032
Nonylphenol	nd	nd	nd	nd	nd
Octylphenols	nd	0.001 \pm 0.000	nd	nd	nd
Pentachlorobenzene	nd	nd	nd	nd	nd
Pentachlorophenol	nd	nd	nd	nd	nd
Benzo-a-pyrene	0.263 \pm 0.397	0.519 \pm 0.818	0.187 \pm 0.178	0.1129 \pm 0.114	0.146 \pm 0.247
Benzo-b-fluoranthene	0.217 \pm 0.364	0.058 \pm 0.116	0.031 \pm 0.053	0.033 \pm 0.057	0.042 \pm 0.112
Benzo-k-fluoranthene	6.346 \pm 5.607	14.941 \pm 23.246	11.335 \pm 14.343	7.850 \pm 7.489	12.705 \pm 11.803
Benzo-g,h,i-perylene	0.314 \pm 0.793	0.160 \pm 0.391	0.006 \pm 0.016	0.011 \pm 0.030	0.030 \pm 0.052
Indeno(1,2,3-cd) pyrene	0.219 \pm 0.418	0.824 \pm 1.917	0.353 \pm 0.685	0.355 \pm 0.627	0.103 \pm 0.063
Simazine	nd	nd	nd	nd	nd
Tributyltin compounds	nd	nd	nd	nd	nd
Trichlorobenzenes	nd	nd	nd	nd	nd
Trichloromethane	nd	0.004 \pm 0.004	nd	0.001 \pm 0.001	nd
Trifluralin	nd	nd	nd	nd	nd

nd corresponds to non-detected substances.

interpretation of the WFD related to the 'one out-all out' principle, in some cases, leads to a misclassification, and therefore, an aquatic system (i.e., river, lake or reservoir) could be classified in 'good' quality class even if it is not (Borja and Rodríguez, 2010; Prato et al., 2014).

Kachroud et al. (2019) conducted a thorough review summarizing current literature of main WQI applications. According to Kachroud et al. (2019), a WQI reflects the combination of many monitored water quality parameters in relation to specific water use objectives. One key factor which affects the final classification of the water body is the number of parameters involved in WQI computation; in the past, this number has ranged from as little as 5 (Said et al., 2004) up to 78 (Dee et al., 1973), and generally, it depends on water use and study objectives, site location, sampling frequency, and limitations in funds, staff and facilities. The number of parameters on one hand should be adequate, and, on the other hand, an excessive number may contain parameters which are not independent (Kachroud et al., 2019). This last issue is not the case with the water quality parameters (physicochemical and priority substances) used in the present CCME-WQI computation, since all these are proposed in monitoring studies by the WFD and are considered independent.

The other two important factors affecting WQI computation is the selection of proper weights for the parameters (i.e., either based on expert opinion or guidelines) and the method used in aggregation (i.e., arithmetic mean, geometric mean, unweighted harmonic square average and logarithmic functions) to compute the final WQI value (Kachroud et al., 2019; Zotou et al., 2019, 2020). All methods have advantages and disadvantages, but the first two have been used most often, while the use of fuzzy logic techniques has also been lately proposed (Icaga, 2007; Kachroud et al., 2019). CCME-WQI uses unweighted harmonic square average and, in the present study, guideline limits were used.

In the literature there is only a small number of studies regarding the comparison involving a significant number of WQIs. Most studies focus predominately on three WQIs, namely the CCME-WQI, NSF-WQI and Oregon-WQI, which are the most commonly applied. Alexakis et al. (2016) applied two water quality indices (i.e., the NSF-WQI and CCME-WQI) in the classification of Polyphytos reservoir-Aliakmon river quality, and compared their class predictions; furthermore, a first attempt was made to also compare the derived classifications to the WFD-ECOFRAME system (Moss et al., 2003). Water quality parameters used included: temperature, DO, EC, pH, Secchi disk depth, BOD₅, COD, TP, Chl-a, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, and TKN. The results showed that the CCME-WQI classification results were, generally, two classes lower than the WFD-ECOFRAME estimates, whereas the NSF-WQI classification results were nearer to those of the WFD-ECOFRAME. These results regarding the CCME-WQI and WFD are similar to those of the present study.

Kachroud et al. (2019) applied the following WQIs in Mejerda watershed, Tunisia: the logarithmic and arithmetic index proposed by Tiwari and Mishra (1985), the arithmetic index proposed by Ramakrishnaiah et al. (2009), the harmonic square average index proposed by CCME-WQI and the fuzzy logic WQI proposed by Icaga (2007). The same water quality parameter dataset was used in all applications, which included 13 monitored parameters (i.e., pH, EC, TDS, DO, COD, calcium, magnesium, sodium, potassium, bicarbonate, sulphate, chloride and nitrate) and application at two locations in the river during three seasons. Discrepancies were detected, but, in the majority of cases, the classes were close to each other. Kachroud et al. (2019) also concluded that more accurate results may be obtained with the application of the fuzzy WQI by Icaga (2007).

Zotou et al. (2019) and Zotou et al. (2020) comparatively tested seven WQIs, including CCME-WQI, respectively in a riverine and a lacustrine water body in Greece. Oregon and CCME-WQI were found to be

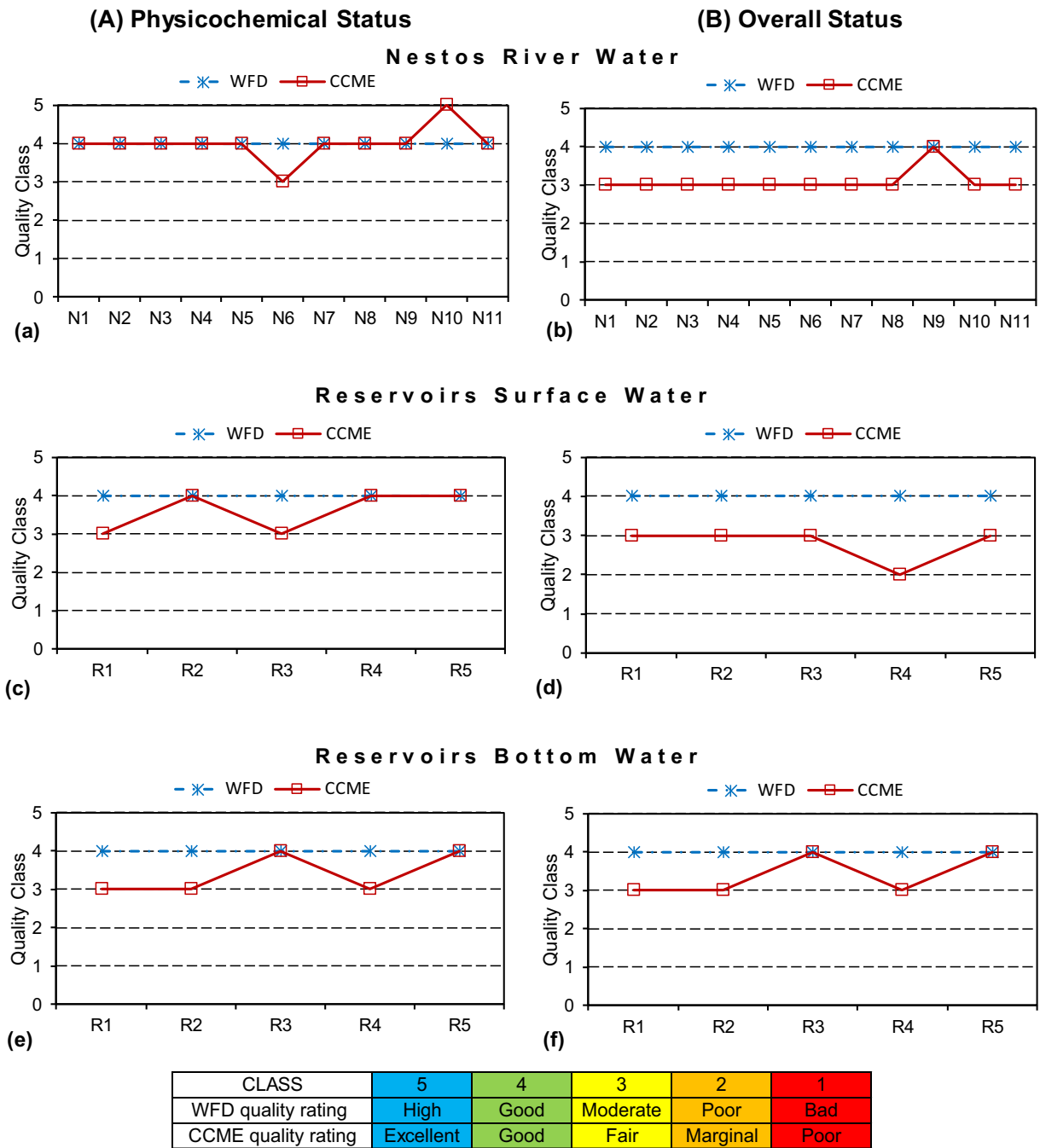


Fig. 2. Variation of WFD and CCME quality classes in the riverine part and the reservoirs of Nestos river for: (A) physicochemical status (a, c and e); and (B) overall status (b, d and f).

comparatively stricter, giving results ranging in the lowest classes of the qualitative ranking. CCME-WQI was suggested as the most appropriate among the examined indices, since it was found both conservative and sensitive to reflect changes in water quality. Similar results regarding the lower classification by CCME-WQI have been reported by Darvishi et al. (2016), Hamlat et al. (2017), Akkoyunlu and Akiner (2012), Hashim et al. (2015), Finotti et al. (2015). It should be mentioned that the studies by Hamlat et al. (2017) and Akkoyunlu and Akiner (2012) refer to water bodies implemented in northern (Algeria) and eastern (Turkey) Mediterranean regions. Finally, Perrie et al. (2012) report the use of two WQIs in assessing quality in various rivers and streams of the Wellington region, New Zealand: the Greater Wellington's WQI and the CCME-WQI. They found the two indices producing comparable

classes, but they regard CCME-WQI as a superior index because it is more complex in accounting the magnitude of guideline exceedances.

To date, comparative evaluations of WQIs encompassing a significant number of them are limited. Most studies have only focused on comparing the most commonly used CCME, NSF and Oregon WQIs to each other. No comparisons also exist between WQIs and WFD methodologies and, the present study, and also that of Alexakis et al. (2016), have attempted to fill this gap. In the present case, a possible reason that the ranking by CCME-WQI is stricter and more sensitive than that obtained by WFD-MEEG methodology may also be due to the fact that the CCME-WQI, as mentioned earlier, uses in the calculation of factors F1, F2 and F3 all the individual values of the parameters which determine the physicochemical and chemical state of the river water. In contrast, in the WFD-MEEG

classification, the average annual value for each parameter is used, resulting in the normalization of the values that ultimately enter into the calculation of the physicochemical and chemical state of the river.

Based on the current and few other recent studies, it seems that the CCME-WQI is appropriate for use as a tool in WFD implementation, particularly because of its capability to allow the inclusion of toxic pollutants; however, in order to finally decide on the use of one particular index, several other studies need to be undertaken in various water bodies of the EU and additional indices should be tested. Furthermore, the performance of other well-established indices should also be tested.

4. Conclusions

In this work, we attempted a comparative approach between the WFD methodology (as it applies to Greece, i.e., WFD-MEEG) and the widely-used CCME-WQI, implemented both on the chemical analysis data from samples collected from a transboundary watershed (main course, tributaries and reservoirs of Nestos river basin, N. Greece). Such approach leads to a deeper understanding of their applicability, their drawbacks as well as their performance and qualitative capacity on expressing the quality of a surface water body. Based on the WFD-MEEG method, the 'overall status' of the river and the reservoirs water quality was in the 'good' quality class, while according to CCME-WQI the 'overall status' of the river water quality ranged from the 'poor or marginal' to 'moderate or fair' category, and of the reservoirs water (surface and bottom) varied from the 'poor or marginal' to 'good' quality class. Therefore, CCME-WQI appears to lead to results stricter than the WFD-MEEG, for the same water body, but it is appropriate for use as a tool in WFD implementation, particularly because of its capability to allow the inclusion of toxic pollutants. Also, several other studies are needed in various water bodies of the EU and additional indices should be tested, in order to decide on the use of the best index.

Focusing on the water quality dataset, it occurs that the mean concentrations of physicochemical parameters (i.e., T, DO, pH, EC, inorganic nitrogen, TKN, OP, TP, TSS, and Chl-a) at monitoring stations along the main Nestos rivercourse and its tributaries and in the reservoirs were in the natural range and below drinking water limits. The highest mean values of BOD, COD, TKN and TP were measured at N1 station showing that there was incoming pollution. Nevertheless, for TP, ammonium-nitrogen and TKN at the lower part of Nestos river, there were concentrations occasionally measured above the water standards, indicating potential pollution from anthropogenic activities.

Mean concentrations of the measured heavy metals did not exceed the limits set by WHO (2017) for drinking water. However, the mean concentrations of Ni, Cd and Hg at various stations, mainly at the lower part of the Nestos river basin, were higher than AA-EQS set by EU. Regarding the priority substances, three of them, i.e., anthracene, fluoranthene, and polyaromatic hydrocarbons, were measured at higher concentrations than AA-EQS both in the upper part of Nestos river (i.e., station N1) and in Nestos river reservoirs, indicating potential incoming pollution. The pesticides diuron, endosulfan and simazine were measured at lower concentrations than AA-EQS and MAC-EQS in the lower part of the Nestos river (i.e., N10 station) indicating that the water quality was not significantly affected by agricultural activities.

CRediT authorship contribution statement

G.D. Gikas: Methodology, Investigation, Formal analysis, Resources, Data curation, Validation, Writing - original draft. **G.K. Sylaios:** Conceptualization, Methodology, Investigation, Validation, Writing - review & editing. **V.A. Tsihrintzis:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing - review & editing. **I.K. Konstantinou:** Methodology, Formal analysis, Resources, Data curation, Validation, Writing - review & editing. **T. Albanis:** Methodology, Formal analysis, Resources, Data

curation, Validation, Writing - review & editing. **I. Boskidis:** Formal analysis, Data curation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.140849>.

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