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Spatial and temporal evaluation of the physicochemical quality of domestic/industrial water in the Kırklareli Reservoir (Turkish Thrace)

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Abstract: The Kırklareli Reservoir, located in the Meriç-Ergene River Basin, is an important drinking/industrial freshwater resource of the Kırklareli Province. In order to ensure the sustainable use of this important reservoir, its current situation should be examined periodically and evaluated by multivariate analyses. For this reason, water samples were taken between the dates April 2018 and February 2019 at monthly intervals from 3 different stations. The data on the environmental and physicochemical variables (water temperature, dissolved oxygen, pH, salinity, conductivity, total dissolved solids, chlorophyll-*a*, light permeability, fluoride, chloride, NO_2-N, NO_3-N, PO_4, SO_4 and essential/potentially toxic elements) were measured and evaluated according to the classes of surface water quality control regulation of Turkey. The parameters exceeding first-class water quality values (chlorophyll-*a*, pH, NO_2-N, chloride, selenium) were mapped in GIS using the spline integration approach. In addition, the sodium absorbtion ratio, Kelly index values and magnesium ratio, were calculated to evaluate the water quality for agricultural irrigation water standards. The water quality of the reservoir was evaluated using multivariance analyses (Bray–Curtis similarity index, correspondence analyses, Pearson correlation index). As a result, it was emphasized that the use of the GIS approach is a potential useful method for monitoring the sustainable water quality of the Kırklareli Reservoir, which was determined to have an oligomesotrophic character.

Keywords: water quality; GIS; environmental variables; multivariate analyses.

INTRODUCTION

Due to the increasing need for freshwater resources because of the increasing human population and the increasing pollution of existing resources, studies on the sustainability of water resources have become increasingly important. Espe-

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cially as water stored in lakes, ponds, dams, and reservoirs is used not only as drinking and industrial water, but also for irrigation of agricultural lands and aquaculture. When considered from this point of view, to determine for what purpose a water resource can be used, first of all, the water quality of the aquatic system should be known.

The physicochemical properties of a water source give important information about the current state of the water. However, considering the temporal and spatial changes of a water resource, monitoring studies are needed for the reliable determination of water quality, which can make interpretation difficult because the data obtained from these studies contain too many variables.[1] Therefore, there is a need for methods that can evaluate multiple factors at the same time and allow the analysis of the whole data set instead of a single one.[2,3] Multivariate statistical techniques can be used for the assessment of water quality.[2–10] Thus, it has become increasingly important to use computer-aided data analysis and visualization tools in the studies of temporal and spatial evaluation of the parameters measured for monitoring water quality, and consequently in the studies carried out for the protection, development, and management of water resources.[11] In addition, it is expected that water quality monitoring studies in aquatic ecosystems, which require time and financial aid, will continue to ensure sustainable use. This means more time and more money spent. However, the monitoring periods of water quality can be determined by the results of appropriate multivariate analysis of the studies, which are carried out periodically for at least one year in a aquatic ecosystem and include sufficient physicochemical data.

In particular, geographic information system (GIS) is one of the most important software in which graphical and objective features of geographic data in different formats are collected and analysed in a common coordinate system in layers. Therefore, in terms of examining the physicochemical changes in water resources, it is valuable software that enables accurate information to be obtained very rapidly.[12,13] By facilitating the use of data sources with the help of these methods, it becomes increasing possible to evaluate water quality parameters and determine appropriate strategies in the management of water resources.[5,14–16] The complexity, which may occur due to the excess of criteria used in the assessment of water quality, has been evaluated using techniques such as GIS and multiple criteria decision making (MCDM) analyses in recent years. Thus, by combining spatial data with other data sources, easy and more reliable results, expressing water quality risks, and estimating spatial distributions, are obtained.[17–19] In Turkey, GIS and remote sensing systems are emphasized in the monitoring of the quality of water resources, and these programs are being used more.[1,11,13,19–22]

The Kırklareli Reservoir, which is an artificial lentic ecosystem, is located in the Meriç-Ergene River Basin at Turkish Thrace and it provides important freshwater supplies to the area. As with many freshwater ecosystems, it is reported that this reservoir is being adversely effected by agricultural and domestic pressure.[23,24] The Kırklareli Reservoir has an area of 6 km^2 and a volume of 112 hm^3. In previous studies, the contents of pesticides and potentially toxic elements were examined during the spring season.[23,24]

In this study, the water quality of the Kırklareli Reservoir was evaluated. For this purpose, the physicochemical properties of the reservoir were evaluated using samples obtained at 3 different stations between the dates April 2018 and February 2019 at monthly intervals. The results on dissolved oxygen, water temperature, pH, salinity, conductivity, total dissolved solids, chlorophyll-*a*, light permeability, nitrite nitrogene, nitrate nitrogene, sulfate, phosphate, calcium, magnesium, chloride and some other essential/potentially toxic element (B, Na, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, As, Cd, Ba, Pb) contents in Kırklareli reservoir were determined and compared with the limit values given in the regulation of surface water resources of Turkey.[25] In addition, sampling stations and sampling periods were compared using the Bray–Curtis similarity index. Some measured parameters of environmental variables were mapped temporary and spatially using the spatial analysis module of the Arc MAP software in the GIS. In this way, it was aimed to identify and visualize areas with high/low water quality by combining the water quality data obtained from Kırklareli Reservoir under a single water quality index, and to determine the temporal and spatial sampling locations and times by grouping periodic analyses.

MATERIALS AND METHODS

Details about the study area are given in Supplementary material to this paper.

A total of 3 sampling stations (St.) which represent the ecological characters of the lake were choosen to take the water samples. The analyses of some parameters (temperature, pH, conductivity, dissolved oxygen, salinity and TDS) in water samples taken from each station at a depth of approximately 2 m with Nansen water samplerer were measured during field studies with Orion Star S/N 610541 model land type multiparameter device. Also, the water samples taken from each sampling stations at monthly intervals by Nansen water samplerer were put into 2 L dark glass bottles and transported to the laboratory for other chemical analyses (fluoride, chloride, NO_2-N, NO_3-N, PO_4, SO_4, B, Na, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Se, As, Cd, Ba, Pb). After the water samples were filtered, the pH levels were lowered by adding HNO_3 and HCl to 10 ml of the sample and were stored for analysis. The ion and metal analyzes of the water taken from each station and in each sampling period were measured in 3 repetitions in Agilent Technologies 7700 XX ICP-MS system device with reference to EPA 200.8 and the average values were obtained.[26] By taking 3 times the standard deviation (Std. deviation/square root (*n*)) of blank sample analysis results studied in the measurement limit (*LOD*) intermediate precision conditions in the device in question; the limit of detection (*LOQ*) was calculated by taking 10 times the standard deviation (Std. deviation/ /square root (*n*)) of the results calculated as a result of intermediate precision studies. In addition, the reproducibility is ensured by 10 independent studies at 2 different concentrations, the reproducibility is ensured by working at 2 different concentrations for 5 days, and the reproducibility and reproducibility values obtained with reference to the validation parameters and criteria were observed in accordance with the HorRatR (it is a normalized performance parameter indicating the acceptability of methods of analysis with respect to among-laboratory precision (reproducibility)) < 2 criteria for each element component. 10 independent studies at 2 different concentrations were used for the recovery where 80–120 % is sought in the measurements and Grubb values (this value detects outliers from normal distributions) from 10 independent studies at 25 ppb were used for accuracy (<2.29).[26] The light permeability at each station in each sampling period was measured by using a Secchi disc and the chlorophyll-*a* values of the water samples were determined by classical spectrophotometric methods.[27] The obtained data were evaluated according to the surface water resources control regulation and water quality class of the lake were determined.[25] In addition, the sodium adsorption rate value (*SAR*), Kelly index (*KI*) and magnesium ratio (*MgR*), the rates giving information about whether the water is suitable for irrigation or not, of the waters were calculated over the meq/L ratios by using the values of Na, Ca, and Mg ions from the obtained chemical analysis results.[28,29]

The similarities of the sampling stations and periods in the distribution of the data were grouped by the Bray–Curtis cluster analysis by the BioDiversity Pro 2.0 program, and the results were also supported by the correspondence analysis.[30] The relationships between physicochemical parameters were evaluated by Pearson correlation coefficient in the Graphpad PRISM software, trial version. The parameters exceeding the second class quality values according to the Water Pollution Control Regulation[25] were mapped by the spatial analysis module using GIS supported in the ArcMap 10.3.1 package program. For this aim, the satellite image of the WGS84-Zone 36 coordinate plane in JPEG format, obtained from Google Earth Pro, connected to the metric coordinate system, was transferred to the ArcMAP, and the stations were digitized and turned into vector data.

RESULTS AND DISCUSSION

Data pertaining to physical and inorganic-chemical parameters (Tables S-I and S-II of the Supplementary material) were evaluated according to the water quality classes included in the surface water resources control regulation.[25]

Accordingly, in terms of physical and inorganic-chemical parameters, it is observed that the averages of the water temperatures of the stations are at seasonal expectations. However, the pH values vary between 8.1 and 9.3, and these values exceed the second class water quality values.[25] The average of the dissolved oxygen values measured at the sampling stations was between 7.4 and 13.7 mg/L and this case indicates that the lake has first class water quality in terms of this parameter, and no significant difference (9.7–9.8 mg/L) was found between the sampling stations (Table S-II). Dissolved oxygen is an important parameter for the sustainability of the self-cleaning capacity of water as well as for aquatic organisms. This parameter, which has a great role in physiological and chemical events, should not exceed first class quality values in aquatic ecosystems for protecting the ecological balance. Although chloride ion values were determined between min. 6.1 mg/L and max. 28.7 mg/L in averages, they were found high at St. 1, especially in summer and autumn seasons. Nevertheless, the chloride ion values did not reach the second class quality (200 mg/L) values in terms of the surface water resources quality values. The sodium values, which did not show a significant difference between the stations and were detected at low rates, vary between 1.2 and 6.6 mg/L on averages and did not exceed the first class water quality value (125 mg/L). Since the total dissolved substance ratio was between 105 and 158 mg/L at average, and it did not exceed 500 mg/L, it was found in first class water quality. Conductivity values measured in the study were well below the 2500 μS/cm limit determined for drinking water and were between the limits compatible with freshwater characters (determined between 213–322 μS/cm in averages and reached the highest values (304 μS/cm) at the St. 1). However, calcium and magnesium are elements that originate from the soil and rock structure where water is located and must be taken for human biology. Ca and Mg values measured in this study did not exceed the limit values in terms of drinking and using water. The chlorophyll-*a* values measured in the study also did not exceed the eutrophication limit values.

When the nutrient salts, which are among inorganic-chemical parameters, were evaluated, it was observed that the sulfate values did not show a significant difference in the stations, varying in range 9.7–10.3 mg/L in averages. They remained at the first class water quality value specified in the regulation on surface water quality.[25] Nitrate nitrogen values were determined as 5 mg/L (min. 0.03, max. 2.1 mg/L in averages), which indicated at first class water quality in the regulation on surface water quality. In terms of phosphate amount, it was observed that the values that should not exceed the limit of 0.1 mg/L increased to 0.7 mg/L only in May, and the station averages did not exceed 0.1 mg/L too much. In terms of nitrite nitrogen, the values generally determined in first and second class water quality decreased to third class water quality at all stations in May. It supports the view that nutrient salts may come from the agricultural or forest areas around the dam lake and they can carry out intensively in May, by runoff.

When looking at the inorganic contamination parameters measured in the study, according to the regulation on surface water quality, the values for Cd (max. 0.1 ppb), Pb (max. 2 ppb), As (max. 1.1 ppb), Cu (max. 2.5 ppb), Cr (max. 11.5 ppb), Co (max. 0.1 ppb), Ni (max. 1.7 ppb), Zn (max. 6.6 ppb), fluoride (max. 120 ppb), Fe (max. 108.6 ppb), Mn (max. 24 ppb), B (max. 57 ppb), Ba (max. 34 ppb) and Al (max 0.1 mg/L) did not exceed the first class water quality values.[25] Selenium values approached the limit value at all stations in November. Although it is one of the elements necessary for the human body, it is reported that high selenium ratios can cause disorders in some organs and systems.[31]

According to the Bray–Curtis similarity analysis, while the degree of similarity of the months according to the physicochemical contents was determined > 80 %. Also, correspondence analysis results grouped the sampling periods in 3 different clusters for the physicochemical similarities (Fig. 1).

Accordingly, while December, January and April were a cluster, the other months (excluding February) constituted the second cluster. Although the stations had some differences especially in terms of parameters exceeding the limit values, it was seen that the similarity rates are over 90 % in terms of their general physicochemical content. The sampling stations St. 1 and St. 2 have found to be the most similar each other (Fig. 2). The reason for this high similarity rate seen in the stations can be explained by the fact that the study area is a small water reservoir, while the fact that the St. 3 is surrounded by agricultural and forest area may have caused it to be small differences from the other stations. Thus, only one station can be used for the monitoring studies which will be performed in this reservoir.

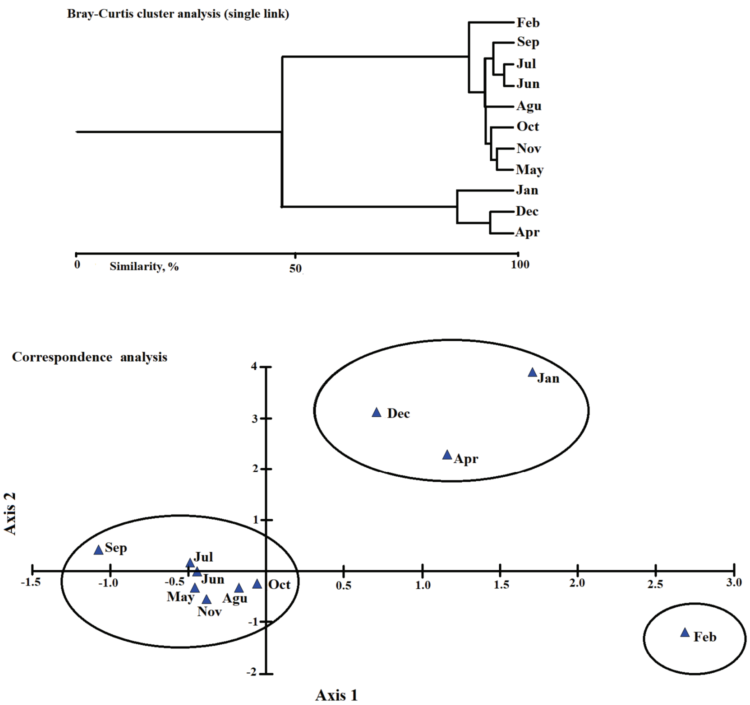

Fig. 1. Monthly similarities according to Bray–Curtis index and cluster analysis.

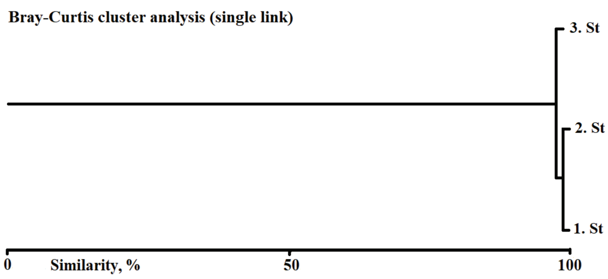

Fig. 2. Similarity of sampling stations according to Bray–Curtis index analysis.

The margin of error is considerably reduced due to GIS using the high-resolution raster data set in water quality monitoring and evaluation studies.[11] Based on this idea, the data of pH, nitrite, chloride, and selenium measured in Kırklareli reservoir lake and found to exceed the first class water quality and the data of chloride value and chlorophyll-*a* distributions of the approaching second class water quality were visualized with the distribution maps created in the spatial analysis results made in the Arc MAP were given in Fig. S-2–S-6 of the Supplementary material.

Accordingly, it was determined that the pH, nitrite nitrogene, selenium, chloride and chlorophyll-*a* values measured at the St. 3 were low, but the chlorophyll-*a* values are low at the St. 1, where the pH was relatively low. Similarly, it was seen that the chlorophyll-*a* values were also high in the St. 3 where the pH value was high. However, at the St. 1, where nitrite nitrogene, chloride and selenium values were high, chlorophyll-*a* values were low. This situation reveals that pH is an important factor in the distribution of algae and supports the view that algae develop faster at high pH values. During periods of algae growth, photosynthesis, respiration, and decay affect the CO_2 level in lakes. This case can cause pH fluctuations. During the periods when photosynthetic microalgae multiply, the pH may rise during the daytime when these organisms fix CO_2.[32] It is suggested that selenium limit ratio in drinking water is 10 ppb specified by Turkish Standards Institute.[33] Selenium is known to be released to the environment by means of sewage effluent, agricultural runoff and industrial waste water.[34] In this study, selenium was measured at above the limit values at some sampling periods (Table S-I).

It is generally known that there is a relationship between Secchi disc depth and chlorophyll-*a*. Secchi depth in the eutrophic reservoir is partially related to the chlorophyll-*a* content. In the mesotrophic reservoir, the Secchi depth cannot be determined only by algae. In the oligotrophic reservoir, the Secchi depth is neither related to chlorophyll-*a* nor to algae in the water. Inorganic turbidity or colour is an important factor in influencing Secchi depth in a mass of water. High rates of inorganic substances also cause turbidity.[35,36] The physicochemical data measured in the Kırklareli reservoir indicate that the lake has an oligomesotrophic character. In this case, a significant relationship between Secchi disk depth and chlorophyll-*a* values cannot be expected.

With respect to the Pearson correlation index relations between the physicochemical variables, the flouride and nitrite showed positive correlation each other ($r = +0.999$, $\rho < 0.05$). Chloride had positive correlations with salinity ($r = +0.999$, $\rho < 0.05$), conductivity ($r = +0.998$, $\rho < 0.05$) and TDS ($r = +0.999$, $\rho > 0.05$). Phosphate and chlorophyll-*a* showed positive correlation ($r = +0.997$, $\rho < 0.05$). TDS had positive correlations with salinity ($r = +0.998$, $\rho < 0.05$), and conductivity ($r = +0.999$, $\rho < 0.05$). Also there was positive correlation between DO and water temperature (r = +1.00, ρ < 0.001). Electrical conductivity (EC) is generally utilized as a salinity indicator and is directly affected by chloride ions. Thus, it is possible to find a correlation between EC, Cl- concentrations, and salinity as found by many studies and this study.[37] It is known that the concentration of chlorophyll-*a* is related to inorganic phosphate concentrations and the Pearson Correlation Index result positive correlation between phosphate and chlorophyll-*a* support it.[38]

The value of Kelly index (*KI*) is less than 1 in all stations and the water is suitable for irrigation (Table S-I). With respect to the sodium adsorption rate (*SAR*), the value is between 0 and 10 in all stations and the results show that the water is excellent for irrigation (Table S-I). The value of magnesium ratio (*MgR*) is 50 in all stations and is suitable for irrigation (Table S-I).

Since the Kırklareli Reservoir is located in the Ergene Basin, which is an important agricultural and industrial area of Turkey, it is inevitable that there is a pollution load in the other drinking water reserves here and around it. When we look at the previous studies in the field, it is seen that there is a pesticide and ion pollution load originating from agricultural and industrial applications both in Kırklareli Reservoir and other drinking water reservoir around it.[23,24,39]

So far, there are similar studies in our country by using GIS methods.[1,11,13,19–22] In these studies, it is aimed to evaluate the potential use of appropriate software tools in water quality determination studies. Thus, it is easier and more understandable to monitor water quality classes with the produced GIS maps. In the study carried out in Lake Gala, it has been summarized more effectively thanks to the GIS that nitrite nitrogen poses the greatest risk in the lake.[22] In the study performed in the Damsa Dam Lake , it was easily observed with GIS that it is not suitable in terms of some ions and toxic substances measured from the lake.[11] For the efficient use of water reservoirs and their ecological continuity, water quality should be continuously monitored by repeating it at certain periods and necessary interventions should be made in case of pollution.

CONCLUSION

As a result of this study, it was determined that the water quality of Kırklareli Reservoir was generally compatible with the first-class water quality in terms of the parameters measured in the study. Considering the similarities of the sampling periods and stations determined in the study, it was concluded that the sampling periods could be selected seasonally in monitoring the water quality of the Kırklareli reservoir lake, and sampling from two sampling stations (St. 1 and St. 3) would be sufficient. In addition, it should be taken into consideration that GIS can be a more effective evaluation system visually in the data monitoring of surface water resources.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/10811, or from the corresponding author on request.

ИЗВОД

ПРОСТОРНА И ВРЕМЕНСКА ПРОЦЕНА ФИЗИЧКО–ХЕМИЈСКОГ КВАЛИТЕТА ВОДЕ У ЗА ПИЋЕ/УПОТРЕБУ У АКУМУЛАЦИЈИ KIRKLARELI (ТУРСКА ТРАКИЈА)

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Резервоар Киркларели, који се налази у сливу реке Meriç-Ergene, важан је извор воде за пиће/коришћење у провинцији Kırklareli. Како би се осигурала одржива употреба овог важног резервоара, његово тренутно стање треба повремено прегледати и оценити мултиваријантним анализама. Из тог разлога, узорци воде узимани су на месечном нивоу, од априла 2018. до фебруара 2019. године, са 3 различите станице. Подаци о еколошким и физичко–хемијским варијаблама (температура воде, растворени кисеоник, pH, салинитет, проводљивост, укупне растворене чврсте материје, хлорофил-*a*, пропустљивост светлости, флуориди, хлориди, NO_2-N, NO_3-N, PO_4, SO_4 и есенцијални/потенцијално токсични елементи) су измерени и оцењени према класама у регулативи контроле квалитета површинских вода Турске. Параметри који премашују вредности квалитета воде прве класе (хлорофил-*a*, pH, NO_2-N, хлорид, селен) мапирани су у географском информационом систему (GIS), уз коришћење Spline интеграције. Такође су израчунати однос апсорпције натријума, вредности Kelly индекса и однос магнезијума да би се проценио квалитет воде за потребе наводњавања у пољопривреди. Квалитет воде у резервоару је оцењиван коришћењем мултиваријантних анализа (Bray–Curtis similarity index, correspondence analyses, Pearson correlation index). Као резултат, закључено је да је коришћење GIS приступа потенцијално корисна метода за праћења одрживог квалитета воде у резервоару Киркларели, за који је утврђено да има олиго-мезотрофни карактер.

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