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Water Quality Parameters of Buyuk Menderes River, Turkey

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In this study, some water quality parameters at 8 sampling stations in Buyuk Menderes river were investigated. These water quality parameters are chemical oxygen demand (COD), electical conductivity (EC), sulphate, chloride, bicarbonate, sodium, potassium, calcium and magnesium. Significance of trends were tested using nonparametric Seasonal Kendall test and trend slopes were quantified using Seasonal Kendall slope estimator. Significant increasing trends at six stations suggested that water quality of Buyuk Menderes river has been deteriorated. It is expected that the results of this study not only will provide public with the recent change in water quality of Buyuk Menderes river quantitatively but also will help establish future management strategies.

Key Words: Turkey, Buyuk Menderes river, Water quality, Trend analysis.

INTRODUCTION

Buyuk Menderes river, located in the western part of Turkey, is an important source of water especially for irrigation in Buyuk Menderes Basin. After 1980's, rapid urban and industrial development in the Buyuk Menderes river basin have lead to deterioration of river water quality and the status and decline of water quality of Buyuk Menderes river have become an important public concern.

Buyuk Menderes river, with a length of 584 km, drains an area of about 24,873 km^2, parts of 5 provinces, namely Aydin, Mugla, Denizli, Usak and Afyon, which corresponds 3.2 % of Turkey. It raises near Dinar county of Afyon province and discharges into Agean Sea within the boundaries of Aydin province. Its major tributaries are Kufi, Banaz, Dokuzsele, Curuksu, Dandalaz, Akcay and Cine streams. Major cities in the basin are Usak, Denizli, Saraykoy, Nazilli, Aydin and Soke.

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Buyuk Menderes river and its tributaries have long been considered as receiving water body for disposal of industrial and municipal wastewaters. Until recently this did not pose a serious problem. But, especially within last one or two decades, due to population increase and industrial development, the water quality of the river has been deteriorated. Major industries creating pollution in Buyuk Menderes river, with their wastewaters either partially treated or untreated, are leather processing industries, sugar and textile mills. Geothermal sources in Kizildere and Saraykoy should also be counted. In addition to industrial and geothermal effluents, municipal wastewaters is the other source of pollution in surface waters in the basin. Especially in 1980s considerable investments had been made on construction of sewarage systems in residential areas in the basin, as in other parts of Turkey. Municipal wastewaters which had been previously disposed through septic tanks, then, have been collected by a sewerage system and disposed as a point source to a nearby receiving water body, namely to Buyuk Menderes river or its tributaries, creating more serious problems in surface waters in the basin compared to septic tank disposal, because wastewater treatment plants were not constructed and operated simultaneously[1].

Since the status and deterioration in water quality of Buyuk Menderes river has been an important public concern in the basin, the objective of this study was to quantify the temporal changes of some water quality parameters in Buyuk Menderes river using the seasonal Kendall test.

EXPERIMENTAL

Water quality monitoring in the Buyuk Menderes river are carried out by the State Hydraulic Works of Turkey (DSI) and the monitoring stations whose data were used in this study. Starting year of monitoring data differs among stations in spite of common end year. In the stations Saraykoy, Cubukdag, Feslek, Nazilli, Yenipazar and Aydin monitoring data starts in 1992 and ends in 2003. On the other hand, it is between 1995-2003 in Kocarli and 1996-2003 in Soke stations.

Laboratoary analysis for water samples were conducted at DSI's Quality Control and Laboratory Department in Aydin. Nine water quality parameters used in this study are chemical oxygen demand (COD), electrical conductivity (EC), sulphate, chloride, bicarbonate, sodium, potassium, calcium and magnesium. Analytical methods are given in DSI's Quality Control and Laboratory Manual[2]. Data quality was checked by ion-balance calculations. The analysis with an ion-balance error greater than 10 % were excluded from the study.

Water samples were collected primarily bimonthly, namely in February, April, June, August, October and December. On the other hand, in early 1 or 2 years of data period of some stations samplings were done in other months and these data were excluded from the study in order to ensure sampling frequency consistent in all years and all stations which is necessary to conduct Seasonal Kendall test[3].

Seasonal Kendall test: Nonparametric Seasonal Kendall test was used to determine significance of trend of water quality parameters. Early studies on trend assessment in water quality have used parametric methods that require any underlying statistical distribution[4]. But, some characteristics of water quality data make the application of parametric methods problematic. Some of them are non-normality, outliers, cycles, gaps and/or missing values, censored data, serial correlation[3,5]. Then, non-parametric techniques for the detection of trends in such water quality data sets have received considerable attention because fewer assumptions must be satisfied than with parametric methods[6].

Seasonal Kendall test is a generalization of the Mann-Kendall test and can be applied as follows[7,8]: Firstly Mann-Kendall test statictic, S_i, are computed for each season seperately:

$$S_i = \sum_{k=1}^{n_i=1} \sum_{l=k+1}^{n_i} \mathrm{sgn}(x_{il} - x_{ik}) \tag{1}$$

where, l > k and n_i is the number of data in season i and

$$\begin{aligned} \mathrm{sgn}(x_{il} - x_{ik}) &= 1 && \text{if } x_{il} - x_{ik} > 0 \\ &= 0 && \text{if } x_{il} - x_{ik} = 0 \\ &= -1 && \text{if } x_{il} - x_{ik} < 0 \end{aligned} \tag{2}$$

Then, the variance, $Var(S_i)$, is computed:

$$\begin{aligned} VAR(S_i) = \frac{1}{8}\Bigg(& n_i(n_i - 1(2n_i + 5) - \sum_{p=1}^{g_i} t_{ip}(t_{ip} - 1)(2t_{ip} + 5) \\ & - \sum_{q=1}^{h_i} u_{iq}(u_{iq} - 1)(2u_{iq} + 5)\Bigg) \\ & + \frac{\sum_{p=1}^{g_i} t_{ip}(t_{ip} - 1)(t_{ip} - 2) \sum_{q=1}^{h_i} u_{iq}(u_{iq} - 1)(u_{iq} - 2)}{9n_i(n_i - 1)(n_i - 2)} \\ & + \frac{\sum_{p=1}^{g_i} t_{ip}(t_{ip} - 1) \sum_{q=1}^{h_i} u_{iq}(u_{iq} - 1)}{2n_i(n_i - 1)} \end{aligned} \tag{3}$$

where,

g_i = the number of groups of tied (equal-valued) data in season i,
t_{ip} = the number of tied data in the pth group for season i,
h_i = the number of sampling times in season i that contain multiple data,
u_{iq} = the number of multiple data in the qth time period in season i.

After the S_i and Var(S_i) are computed, overall statistics are obtained by summing across K seasons:

$$S' = \sum_{i=1}^{K} S_i \tag{4}$$

and
$$VAR(S') = \sum_{i=1}^{K} VAR(S_i) \tag{5}$$

Next, seasonal Kendall test statistics, Z, is computed:

$$\begin{aligned} Z &= \frac{(S'-1)}{[VAR(S')]^{½}} && \text{if } S'>0 \\ Z &= 0 && \text{if } S'=0 \\ Z &= \frac{(S'+1)}{[VAR(S')]^{½}} && \text{if } S'<0 \end{aligned} \tag{6}$$

The null hypothesis, H_0, of no trend *versus* the alternative hypothesis, H_A, of either and increasing or decreasing trend is rejected at significance level α if the absolute value of Z is greater than Z_{crit} where Z_{crit} is the value of the standard normal distribution with a probability of exceedance of $\alpha/2$.

Seasonal Kendall slope estimator: Magnitude of trend was estimated through the seasonal Kendall slope estimator[8]. Firstly, for the each season individual slopes are computed:

$$d_{ilk} = \frac{x_{il} - x_{ik}}{l - k} \tag{7}$$

where, x_{il} = the datum for the ith season of the lth year, x_{ik} = the datum for the ith season of the kth year, where $l > k$.

The seasonal Kendall slope is the median of all individual slopes.

Effect of streamflow: Streamflow is one of the most important variables, other than time trend, influencing on the concentration of a water quality parameter. By removing the variation in the concentration cuased by streamflow, the background variability or 'noise' is reduced so that any trend 'signal' present can be seen[3]. On the other hand, removal of the effect of streamflow (flow-adjustment) depends on objective. If the purpose is only to look at concentrations as they ocur without considering the cause of trend, a trend test without flow-adjustment could be used. However, if the cause of trend is important, a flow-adjustment is needed. Since the objective of this study was to quantify the temporal changes of some water quality parameters in Buyuk Menderes river, focusing on concentrations as they occur without considering the cause of the trend, no attempt was made to remove the effect of flow.

RESULTS AND DISCUSSION

The results of trend analysis for each water quality parameter are given in Tables 1-3. In the tables, magnitude of the trend, *i.e.* Seasonal Kendall slope estimator (SKSE) and Seasonal Kendall test statistic are presented. Significant trends at the significance level of 10 % are shown in bold. Negative sign in front of both trend magnitudes and Seasonal Kendall test statistics indicates that the trend is decreasing.

TABLE-1
TREND RESULTS FOR CHEMICAL OXYGEN DEMAND, ELECTRICAL CONDUCTIVITY AND SULPHATE AT THE STATIONS IN BUYUK MENDERES RIVER
(Bold figures indicate significance at 0.1 level)

Station	Chemical oxygen demand		Electrical conductivity		Sulphate	
	A	B	C	B	A	B
Saraykoy	7.994	**6.094**	12.350	0.699	-7.720	**-2.001**
Cubukdag	3.995	**3.895**	-13.320	-0.597	-13.610	**-2.228**
Feslek	3.997	**4.154**	-15.970	-0.906	-21.640	**-3.469**
Nazilli	2.221	**3.172**	-19.360	**-2.073**	-13.790	**-3.309**
Yenipazar	0.999	**1.925**	-6.665	-1.021	-13.700	**-3.291**
Aydin	1.599	**2.619**	-9.992	-1.490	-14.520	**-2.983**
Kocarli	0	-0.652	0	-0.216	-15.470	**-2.124**
Soke	0	-0.309	3.664	0.305	-12.810	-1.411

A = Seasonal Kendall slope (mg/L/year); B = Seasonal Kendall test statistics (Z); C = Seasonal Kendall slope (µS/cm/year)

Chemical oxygen demand (COD): Significant increasing trends in COD were detected at the stations Saraykoy, Cubukdag, Feslek, Nazilli, Yenipazar and Aydin, with the SKSE being in the range 7.994 mg/L/year at Saraykoy to 0.999 mg/L/year at Yenipazar (Table-1). The increases at these stations represent deterioration in water quality. On the other hand, decreasing trends were observed at the stations Kocarli and Soke which were not significant, with SKSE being zero. Increases represent deterioration in water quality. One interesting result is that magnitude of trends tended to be weaker from upstream stations to downstream stations and stabilized to zero at two downmost stations. Chemical oxygen demand test allows mesurement of a waste in terms of the total quantity of oxygen required for oxidation to carbon dioxide and water[9]. In this context, COD analysis in surface waters can give the indication of the degree of pollution from municipal or industrial wastewaters. Increasing trends in COD at most of the stations indicate that more wastewaters, treated, untreated or partially treated, have been discharged to Buyuk Menderes river or its tributaries due to population increase and industrial development in the basin.

Electrical conductivity (EC): Decreasing trends in EC were observed at Cubukdag, Feslek, Nazilli, Yenipazar, Aydin and Kocarli stations (Table-1). Among these, the trend at Nazilli station was significant, with the SKSE being -19.360 µS/cm/year. On the other hand, the trends at Saraköy and Soke are increasing, but not significant, with the SKSE being 12.350 µS/cm/year and 3.664 µS/cm/year, respectively. Increases represent deterioration but decreases represent improvement in water quality. In terms of EC which is a measure of salinity, water quality of Buyuk Menderes river has improved for the period of data record at most of stations, but this improvement is said to be not statistically significant except Nazilli station.

Sulphate: Significant decreasing trends in sulphate concentrations were observed at all stations except Soke station, with the SKSE being in the range -21.640 mg/L/year at Feslek station to -7.720 mg/L/year at Saraykoy station (Table-1). Decreases represent improvements in water quality. Sulphate arises from atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds from sedimentary rocks and industrial discharges and atmospheric precipitation can also add significant amounts of sulphate to surface waters[10].

Chloride: Increasing trends in chloride concentrations were detected at all stations, with the SKSE being in the range 5.053 mg/L/year at Saraykoy to 0.591 mg/L/year at Kocarli (Table-2). Increasing trends are significant at stations Saraykoy, Cubukdag, Feslek, Nazilli, Yenipazar and Aydin, but not at Kocarli and Soke. Increases represent deterioration in water quality. Chloride enters surface waters with atmospheric deposition of oceanic aerosols, with the weathering of some sedimentary rocks and from industrial and municipal effluents and agricultural and road run-off. As chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible faecal contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies[10].

Bicarbonate: Bicarbonate trends at all station were in increasing direction (Table-2). But, they are statistically significant at the stations Saraykoy, Cubukdag, Kocarli and Soke, with the SKSE being 8.161, 8.537, 8.780 and 20.000 mg/L/year, respectively. Increases represent deterioration. The alkalinity of a water is a measure of its capacity to neutralize acids. The alkalinity of natural waters is due primarily to the salts of weak acids, although weak or strong bases may also contribute. Bicarbonates represent the major form of alkalinity. In polluted or anaerobic waters, salts of weak acids such as acetic acid, propionic acid and hydrosulfuric acid may be produced and would also contribute to alkalinity[9].

Sodium: For sodium concentrations, increasing trends were observed at the stations Saraykoy and Nazilli, with the SKSE being 4.083 mg/L/year and 0.666 mg/L/year, respectively (Table-2). On the other hand, decreasing trends were detected at Cubukdag, Feslek, Yenipazar, Aydin, Kocarli and Soke, with the SKSE being in the range -0.144 mg/L/year at Cubukdag to -1.447 mg/L/year at Aydin. Among them, only significant trend was at Saraykoy in increasing direction. Increases represent deterioration in water quality, whereas decreases represent improvement in water quality. All natural waters contain some sodium since sodium salts are highly water soluble and it is one of the most abundant elements on earth. Increased concentrations in surface waters may arise from sewage and industrial effluents and from the use of salts on roads to control snow and ice[10].

TABLE-2
TREND RESULTS FOR CHLORIDE, BICARBONATE AND SODIUM AT THE STATIONS IN BUYUK MENDERES RIVER
(Bold figures indicate significance at 0.1 level)

Station	Chloride		Bicarbonate		Sodium	
	A	B	A	B	A	B
Saraykoy	5.053	**3.729**	8.161	**2.418**	4.083	**3.172**
Cubukdag	3.547	**2.241**	8.537	**2.653**	-0.144	-0.070
Feslek	3.540	**3.393**	4.997	1.313	-0.998	-0.582
Nazilli	2.364	**2.195**	1.665	0.566	0.666	0.714
Yenipazar	1.419	**1.773**	3.997	1.041	-0.650	-0.565
Aydin	2.047	**1.990**	3.540	1.464	-1.447	-1.336
Kocarli	0.591	0.656	8.780	**2.599**	-0.635	-0.598
Soke	2.367	1.416	20.000	**4.133**	-1.174	-0.312

A = Seasonal Kendall slope (mg/L/year); B = Seasonal Kendall test statistics (Z)

Potassium: For potassium concentrations an increasing trend was observed at Saraykoy station with SKSE being 0.086 mg/L/year, whereas decreasing trends were detected at all other stations, with the SKSE being in the range -0.053 mg/L/year at Aydin to -0.128 mg/L/year at Feslek (Table-3). But, none of trends were significant. Potassium is found in low concentrations in natural waters since rocks which contain potassium are relatively resistant to weathering. However, potassium salts are widely used in industry and in fertilizers for agriculture and enter freshwaters with industrial discharge and run-off from agricultural land[10].

TABLE-3
TREND RESULTS FOR POTASSIUM, CALCIUM AND MAGNESIUM AT THE STATIONS IN BUYUK MENDERES RIVER
(Bold figures indicate significance at 0.1 level)

Station	Potassium		Calcium		Magnesium	
	A	B	A	B	A	B
Saraykoy	0.086	0.903	-0.666	-0.350	-1.633	-1.340
Cubukdag	-0.066	-0.626	0.472	0.914	-1.561	-1.359
Feslek	-0.128	-1.255	0.666	0.555	-2.271	**-2.308**
Nazilli	-0.117	-1.074	-1.666	**-2.188**	-1.459	**-1.667**
Yenipazar	-0.083	-0.456	0	-0.179	-1.216	**-1.968**
Aydin	-0.053	-0.426	0	-0.215	-0.793	-1.342
Kocarli	-0.106	-0.831	0	-0.046	-2.003	**-2.033**
Soke	-0.086	-0.522	0.999	0.786	-0.300	-0.156

A = Seasonal Kendall slope (mg/L/year); B = Seasonal Kendall test statistics (Z)

Calcium: Increasing trends in calcium concentrations were observed at the stations Cubukdag, Feslek and Soke, SKSE being 0.472, 0.666 and 0.999 mg/L/year, respectively (Table-3). On the other hand, decreasing trends were detected at other stations, namely Saraykoy, Nazilli, Yenipazar, Aydin and Kocarli. Magnitudes of trends were -0.666 and -1.666 at Saraykoy and Nazilli, respectively, but zero at Yenipazar, Aydin and Kocarli which all have decreasing trends. Among all stations, the only significant trend was at Nazilli station in decreasing direction. Calcium is present in all waters as Ca^{2+} and is readily dissolved from rocks rich in calcium minerals, particularly as carbonates and sulphates, especially limestone and gypsum. The cation is abundant in surface and groundwaters. Industrial, as well as water and wastewater treatment, processes also contribute calcium to surface waters[10].

Magnesium: Decreasing trends in magnesium concentrations were observed at all stations but significant at Feslek, Nazilli, Yenipazar and Kocarli. Magnitudes of trends were highest at Feslek being -2.271 mg/L/year and lowest at Soke being -0.300 mg/L/year (Table-3). Magnesium is common in natural waters as Mg^{2+} and along with calcium is a main contributor to hardness. Magnesium arises principally from the weathering of rocks containing ferromagnesium minerals and from some carbonate rocks. Although magnesium is used in many industrial processes, these contribute relatively little to the total magnesium in surface waters[10].

Conclusion

In this study, temporal changes of some water quality parameters in Buyuk Menderes river were detected using observed values of concentrations of water quality parameters, focussing on concentrations as they occur without considering the cause of the trend. The trends could be evaluated for each parameter and for each station. Significant increasing trends in COD values at most of the stations suggest that water quality of Buyuk Menderes river has been deteriorated in terms of organic pollution from industries and from residential areas in the period during which data were obtained. The results of this study will be expected not only to provide public with the recent changes quantitatively in water quality of Buyuk Menderes river but also to help establish future surface water quality management strategies in the basin.

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