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Temporal Variation of Boron in Büyük Menderes River, Turkey

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Boron is needed by plants in relatively small amounts. On the other hand, excessive amounts of boron would result in toxicity problems depending on the nature of plants, since some plants are sensitive to boron and some others are not. In some agricultural areas as in Büyük Menderes River basin, ground and surface water which is used for agricultural irrigation would contain appreciable amounts of boron due to geothermal fields. In this study, because of specific importance of boron for agricultural irrigation in Büyük Menderes river basin, temporal variation of boron concentrations observed at 9 water quality monitoring stations along Büyük Menderes River were evaluated using nonparametric Seasonal Kendall tets. Slopes of trends were obtained by using Seasonal Kendall Slope Estimator. The results were discussed on station basis.

Key Words: Temporal Variation, Boron, Büyük Menderes River, Turkey.

INTRODUCTION

Boron toxicity is an important disorder that can limit plant growth on soils of arid and semi-arid environments throughout the world. High concentrations of boron may occur naturally in the soil or in groundwater, or may be added to the soil from mining, fertilizers or irrigation water[1]. Boron is an essential element for plant growth and needed in relatively small amounts, however, if present in amounts appreciably greater than needed, it becomes toxic[2]. Plants need boron in different concentrations as a nutrient. While some plants need much more boron, others are less tolerant to boron[3]. Irrigation water classification[4] regarding to boron rate is given in Table-1.

Boron problems originating from the water are probably more frequent than those originating from the soil. Surface waters rarely contain enough boron at toxic level, but well waters and springs occasionally contain toxic amounts especially near geothermal areas and earthquake faults[2]. The geothermal waters in deep reservoir contain high concentrations of boron which is toxic to the plants. Very small doses are harmful to the plants and higher concentrations have toxic effects on animals as well[5].

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TABLE-1
IRRIGATION WATER CLASSIFICATION REGARDING TO BORON RATE (ppm)

Class of water	Sensitive	Semi-tolerant	Tolerant
Excellent	< 0.33	< 0.67	<1.00
Good	0.33-0.67	0.67-1.00	1.00-2.00
Permissible	0.67-1.00	1.33-2.00	2.00-3.00
Doubtful	1.00-1.25	2.00-2.50	3.00-3.75
Unsuitable	> 1.25	> 2.50	> 3.75

Concentrations of boron in surface waters depend on such factors as the geothermal nature of the drainage area, proximity to marine coastal regions and inputs from industrial and municipal effluent discharges. Concentrations of boron in surface waters range widely from 0.001 to as much as 360 mg/L. However, mean boron concentrations for water of Europe, Pakistan, Russia and Turkey are typically well below 0.6 mg/L. Concentrations of boron in waters of Japan, South Africa and South America are generally below 0.3 mg/L. Typical boron concentrations in North American waters are below 0.1 mg/L, with about 90 % at or below 0.4 mg/L[6].

Büyük Menderes river basin is located in the south-western part of Turkey with great agricultural potential. Its wide spectrum of agricultural products varying from field crops to horticultural fresh consumed goods meets most of the requirements of the inhabitants of western Turkey. On the other hand, the region is an outstanding geothermal area. The geothermal fields of western Turkey provide a unique setting of extremely high enthalpy combined with a large variation in the chemical composition. The distribution of the thermal systems follows the tectonic patterns of Turkey[7]. The utilization of geothermal water resources for different purposes cause Büyük Menderes river to be polluted and contaminated by boron which is naturally found in the geothermal systems. Since Büyük Menderes river is the main irrigation water resource of the basin, the potential hazards of excessive boron found in irrigation water either to the plants or the animals should be well-known.

The Büyük Menderes graben hosts the geothermal fields and Büyük Menderes river. The contribution of thermal waters and river to cold-water aquifers causes contamination to groundwater resources of the basin. Especially uncontrolled water abstraction from cold water aquifers causes thermal water intrusion into groundwater wells[4]. Some irrigation water resources, especially those in areas where geothermal wastewater is discharged have higher boron concentrations. Some of the tributaries of Büyük Menderes river contain great amounts of boron up to 21.1 mg/L. Since boron is considerably less mobile in soil, boron accumulation occurs in the soil profile and inproductivity becomes inevitable[3].

Since Aydin province has abundant geothermal water resources and these resources contain high concentrations of boron, great amounts of boron containing waters flow into the Büyük Menderes River, especially from geothermal power plants. Moreover boron pollution in domestically used waters which originates from underground water supplies or from industrial effluents are threatening for both human and animal health[3].

According to the research results obtained by Aydin and Seferoglu[3] in Büyük Menderes basin, it was determined that boron concentrations fluctuate throughout the year. Samples taken in September had higher boron concentrations than those taken in June. Boron concentrations of irrigation waters from June to September were higher than those of other months in a year. Koç[1] has determined that boron content of Büyük Menderes River was high particularly in the upper basin and boron has been accumulated more than plants needed. Boron concentration in the Büyük Menderes River was to decrease from upstream to downstream. Another finding of the study was the relative decrease in boron content of the river in rainy months and irrigation season compared to the dry season.

In this study, due to specific importance of boron for agriculture in Büyük Menderes river basin, temporal variation of boron concentrations observed at 9 water quality monitoring stations along Büyük Menderes river were evaluated using non-parametric Seasonal Kendall Test. Slopes of trends were obtained by using Seasonal Kendall Slope Estimator.

EXPERIMENTAL

Study area: Büyük Menderes river is located in the western part of Turkey and an important resource of water especially for irrigation in Büyük Menderes basin. It has a length of 584 km and drains an area of about 24873 km^2, parts of 5 provinces, namely Aydin, Mugla, Denizli, Usak and Afyon, which corresponds 3.2 % area of Turkey. The river 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, Çürüksu, Dandalaz, Akçay and Çine streams. Major cities in the basin are Usak, Denizli, Sarayköy, Nazilli, Aydin and Söke.

Data: Boron data were obtained from the State Hydraulic Works of Turkey (DSI). Boron monitoring stations are Yenice, Sarayköy, Çubukdag, Feslek, Nazilli, Yenipazar, Aydin, Koçarli and Söke.

Water samples were analyzed for boron by Colorimetric Carmine Method at DSI's Quality Control and Laboratory Department in Aydin. Prior to boron analysis, suspended solids were removed by membrane filtration followed by acidification to 1 % HNO_3 level. Carmine method involves combination with carmine or carminic acid in sulphuric acid followed by photometric measurement. Plastic containers and equipment (filtration unit) were used in order to eliminate possible contamination from glassware[1].

Boron data were compiled in bimontly basis throughout the year, 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[8].

Seasonal Kendall test: Non-parametric Seasonal Kendall test was used to determine significance of boron trends. Early studies on trend assessment in water quality have used parametric methods that require any underlying statistical distribution[9]. 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[8,10]. Then, non-parametric teschniques 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[11].

Seasonal Kendall test is a generalization of the Mann-Kendall test and can be applied as follows[12,13]: First Mann-Kendall test statictic, S_i, are computed for each season seperately:

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

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

$$\left.\begin{aligned} \operatorname{sgn}\left(x_{il} - x_{ik}\right) &= 1 \qquad \text{if } x_{il} - x_{ik} > 0 \\ &= 0 \qquad \text{if } x_{il} - x_{ik} = 0 \\ &= -1 \quad\; \text{if } x_{il} - x_{ik} < 0 \end{aligned}\right\} \tag{2}$$

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

$$\left.\begin{aligned} VAR(S_i) = \frac{1}{18}\Bigg[& n_i\left(n_i-1\right)\left(2n_i+5\right) - \sum_{p=1}^{g_i} t_{ip}\left(t_{ip}-1\right)\left(2t_{ip}+5\right) \\ & - \sum_{q=1}^{h_i} u_{iq}\left(u_{iq}-1\right)\left(2u_{iq}+5\right)\Bigg] \\ & + \frac{\sum_{p=1}^{g_i} t_{ip}\left(t_{ip}-1\right)\left(t_{ip}-2\right) \sum_{q=1}^{h_i} u_{iq}\left(u_{iq}-1\right)\left(u_{iq}-2\right)}{9n_i\left(n_i-1\right)\left(n_i-2\right)} \\ & + \frac{\sum_{p=1}^{g_i} t_{ip}\left(t_{ip}-1\right) \sum_{q=1}^{h_i} u_{iq}\left(u_{iq}-1\right)}{2n_i\left(n_i-1\right)} \end{aligned}\right\} \tag{3}$$

where, g_i = the number of groups of tied (equal-valued) data in season i, t_{ip} = the number of tied data in the p^{th} 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 q^{th} 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:

$$\begin{aligned} Z &= \frac{(S'-1)}{\left[VAR(S')\right]^{1/2}} \quad \text{if } S' > 0 \\ Z &= 0 \quad \text{if } S' = 0 \\ Z &= \frac{(S'+1)}{\left[VAR(S')\right]^{1/2}} \quad \text{if } S' < 0 \end{aligned} \tag{6}$$

The null hypothesis, H_0, of no trend *vs.* 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[13]. First, 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 i^{th} season of the l^{th} year, x_{ik} = the datum for the i^{th} season of the k^{th} year, where $l > k$. The Seasonal Kendall slope is the median of all individual slopes. Above given statistical tests was done by using WQStat Plus software package.

RESULTS AND DISCUSSION

In present study, the trends of boron concentrations observed at, from upstream to downstream, Yenice, Sarayköy, Çubukdag, Feslek, Nazilli, Yenipazar, Aydin and Söke water quality monitoring stations were examined using Seasonal Kendall test. Slopes of trends were quantified using Seasonal Kendall Slope Estimator. For the sake of simplicity, these stations were grouped into three categories, upper basin stations (namely, Yenice, Sarayköy, Çubukdag and Feslek), middle basin stations (namely, Nazilli and Yenipazar) and lower basin stations (namely, Aydin, Koçarli and Söke).

Descriptive statistics: Descriptive statistics of boron concentrations at the monitoring stations Yenice, Sarayköy, Çubukdag, Feslek, Nazilli, Yenipazar, Aydin, Koçarli and Söke are given in Table-2. It includes period of data record, number of data, maximum, minimum, mean, median and standard deviation of boron data at each monitoring station. Number of data ranges from 44 at Yenice to 88 at Sarayköy, Feslek, Nazilli and Aydin stations, depending on period of record. Minimum boron concentrations are all zero except Çubukdag station which is 0.2 mg/L. Lowest maximum boron concentration occured as 0.3 mg/L at Yenice, whereas highest one occured as 2.1 mg/L at Feslek. Mean boron concentrations are 0.0432, 0.1955, 0.6753 and 0.7080 mg/L at upper basin stations of Yenice, Sarayköy, Çubukdag and Feslek, respectively, 0.3841 and 0.2549 mg/L at middle basin stations of Nazilli and Yenipazar, respectively and 0.2, 0.1461 and 0.1152 mg/L at lower basin stations of Aydin, Koçarli and Söke. Median value of boron data at the monitoring stations are zero at uppermost station, Yenice and downmost stations, Koçarli and Söke. Other stations have a median value of 0.2, 0.6, 0.8, 0.35, 0.2 and 0.2 mg/L, from upstream to downstream, at Sarayköy, Çubukdag, Feslek, Nazilli, Yenipazar and Aydin, respectively. Standard deviation statistic is highest at Feslek being 0.3815 and lowest at Yenice being 0.0950.

Temporal variation of boron: Temporal variation of boron concentrations at the water quality monitoring stations in Büyük Menderes river is evaluated on station basis, from upstream to downstream.

TABLE-2
DESCRIPTIVE STATISTICS OF BORON IN BÜYÜK MENDERES RIVER

Station	Period of record	Number of data	Maximum	Minimum	Mean	Median	Standard deviation
Yenice	1995-2006	44	0.3	0.0	0.0432	0.00	0.0950
Sarayköy	1992-2006	88	0.6	0.0	0.1955	0.20	0.1646
Çubukdag	1992-2005	77	1.8	0.2	0.6753	0.60	0.3167
Feslek	1992-2006	88	2.1	0.0	0.7080	0.80	0.3815
Nazilli	1992-2006	88	0.9	0.0	0.3841	0.35	0.2191
Yenipazar	1992-2005	82	0.9	0.0	0.2549	0.20	0.2086
Aydin	1992-2006	88	0.6	0.0	0.2000	0.20	0.1647
Koçarli	1994-2006	76	0.6	0.0	0.1461	0.00	0.1701
Söke	1996-2006	66	0.6	0.0	0.1152	0.00	0.1591

Yenice is the uppermost water quality monitoring station contained in present study. It is situated in the vicinity of Yenice Thermal Springs. Boron data of this station were recorded for the period 1995-2006 with 44 data values. These data belongs to April, June, August and October seasons. Seasonal Kendall test statistic were estimated as -0.1115. This indicates that boron concentrations were decreased in the course of data record. But, it is not statistically significant at 0.2 level and also the slope of the trend was found to be zero (Fig. 1).

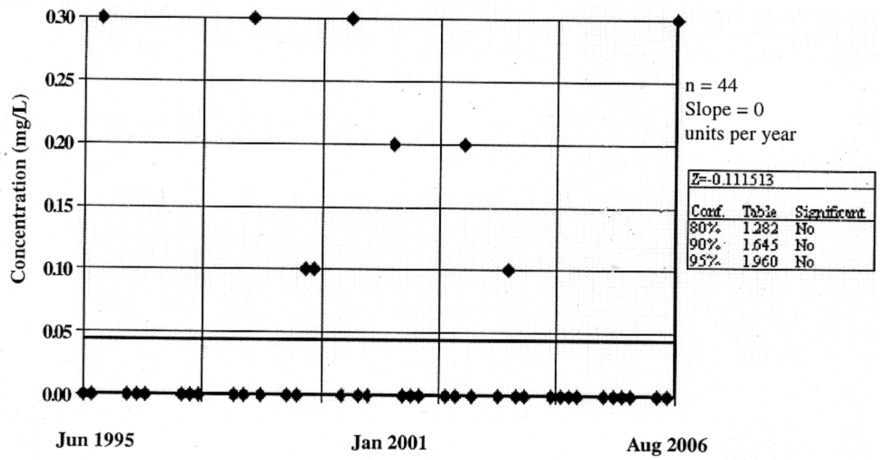

Fig. 1. Temporal variation of boron at Yenice

Second station, Sarayköy, is *ca.* 17.5 km downstream of Yenice station in stream distance. Boron data of this station is for the period 1992-2006 with 88 data values. Boron data were recorded in February, April, June, July, August, October and December seasons. An increasing trend in boron concentrations of Sarayköy station was detected with Seasonal Kendall statistic of 1.3328, which is statistically significant at 0.2 level. Besides, slope of the trend was estimated as zero using Seasonal Kendall Slope Estimator (Fig. 2).

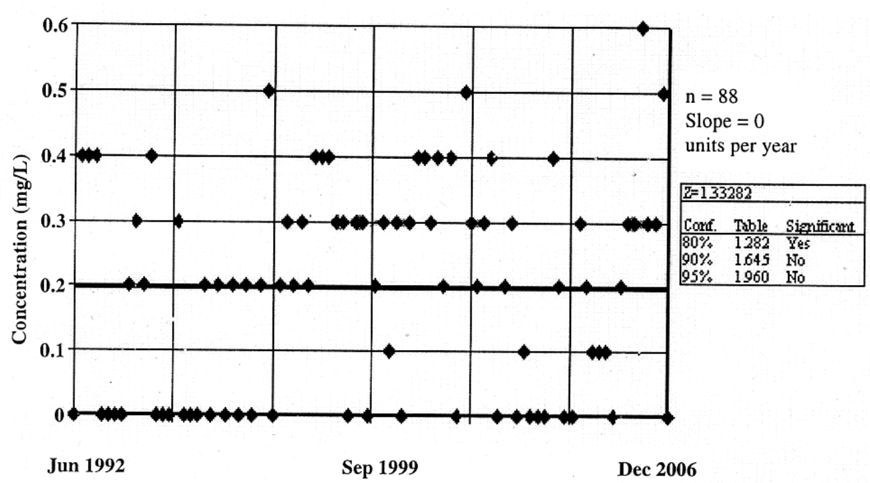

Fig. 2. Temporal variation of boron at Sarayköy

Çubukdag is the third station and 21.7 km away from Sarayköy station and situated just after Kizildere Geothermal Power Plant and Tekke Thermal Spring. Boron data in this station covers the period 1992-2005 with 77 data values. As in most of other monitoring stations, boron data in Çubukdag were gathered bimonthly, *i.e.*, in February, April, June, July, August, October and December. In this stations, the results suggested that boron level showed a highly significant decreasing trend with Seasonal Kendall test statistic of -3.6395, at 0.05 level. The slope was found to be *ca.* -0.027 mg/l/year (Fig. 3).

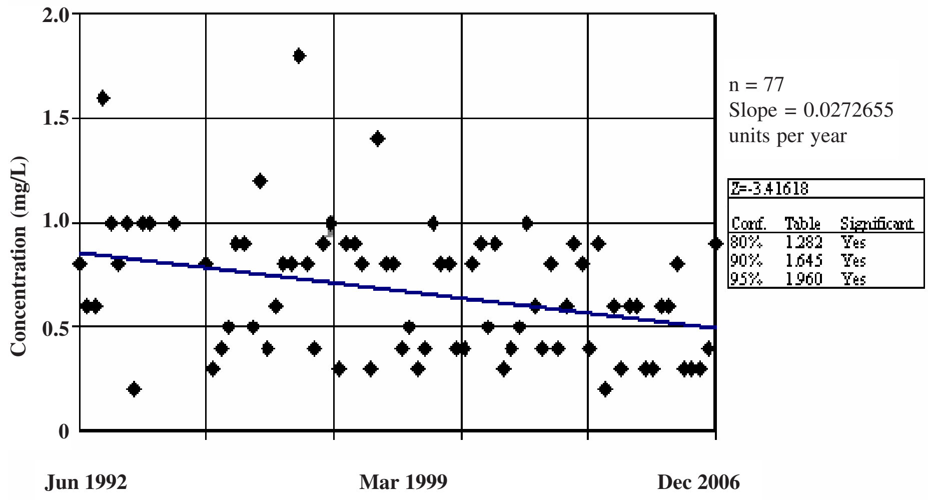

Fig. 3. Temporal variation of boron at Çubukdag

Feslek is the downmost one of upper basin stations. It is 3.5 km downstream of Çubukdag station. February, April, June, July, August, October and December are the sampling seasons. Data record period is between 1992 and 2006 with 88 data values. As in Çubukdag station, boron level showed a highly significant decreasing trend. Seasonal Kendall test statitics was estimated as -2.4522 which is significant at 0.05 level. The slope of the trend was also estimated as -0.0166 mg/L/year (Fig. 4).

For middle middle basin stations, Nazilli and Yenipazar, the period of data recorded for 1992-2006 and 1992-2005, respectively. The data were recorded February, April, June, July, August, October and December in both stations. Sample sizes contain 88 data value for Nazilli and 82 for Yenipazar. A slight decrease was observed in Nazilli station where Seasonal Kendall test statistic was estimated as -0.4984 (Fig. 5), whereas a slight increase was detected in Yenipazar with Seasonal Kendall test statistic of 0.9487 (Fig. 6). However, all are not statistically significant at 0.2 level. Similarly, slopes of trends were found to be zero at two stations.

In last, lower basin stations are Aydin, Koçarli and Söke. Temporal variation of boron concentration at these lower basin stations are evaluated for each station as given below.

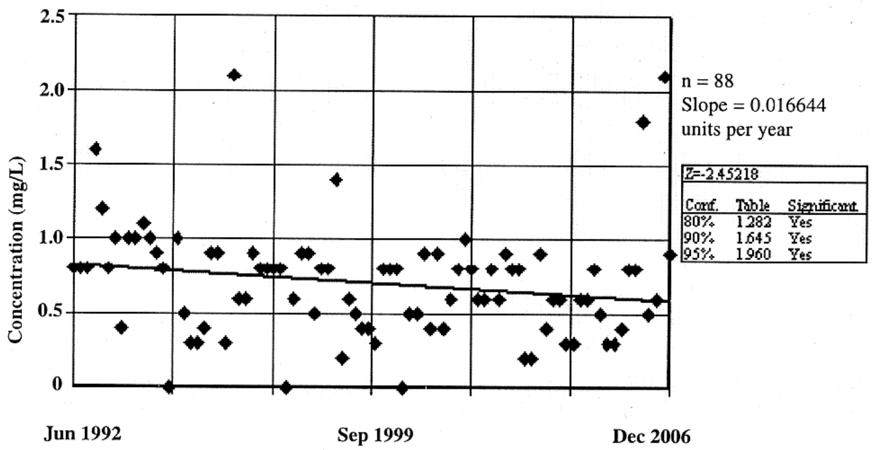

Fig. 4. Temporal variation of boron at Feslek

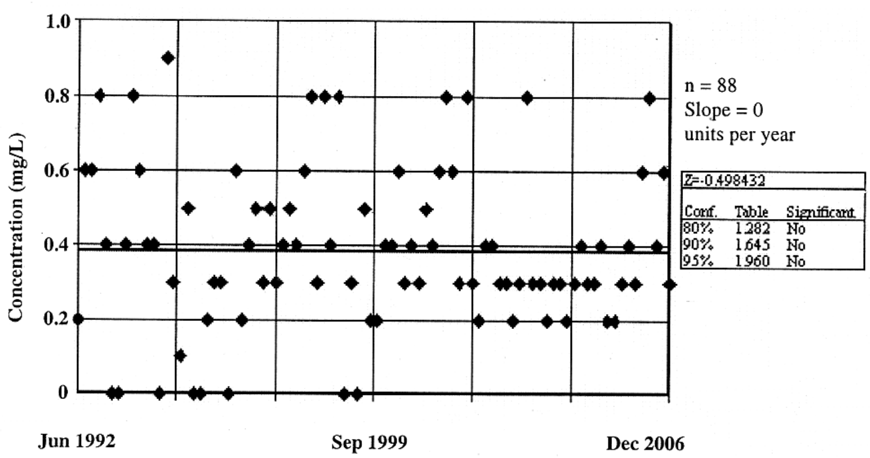

Fig. 5. Temporal variation of boron at Nazilli

The monitoring station Aydin is situated *ca.* 52 km downstream of Yenipazar station. Data of this station which covers the period 1992-2006 were collected in February, April, June, July, August, October and December seasons and sample size contains 88 data value. Boron concentrations in this station showed moderately strong increase during the period of record, with the Seasonal Kendall test statistic Z = 1.7132 which is statistically significant at 0.1 level (Fig. 7). On the other hand, Seasonal Kendall Slope Estimator yields an exactly zero slope.

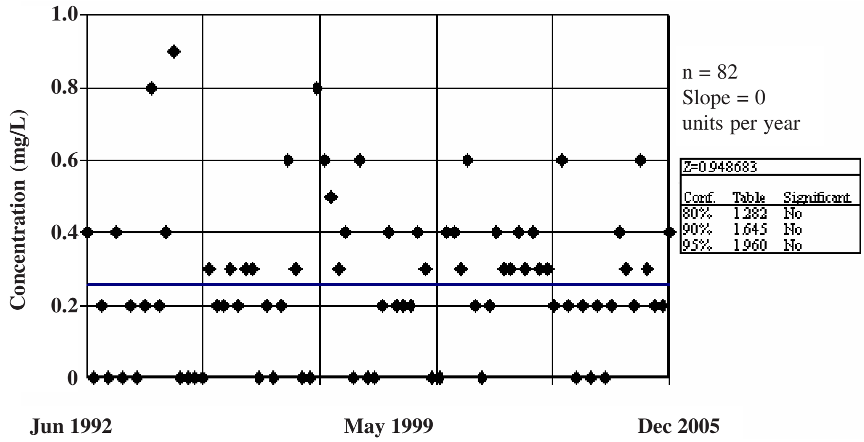

Fig. 6. Temporal variation of boron at Yenipazar

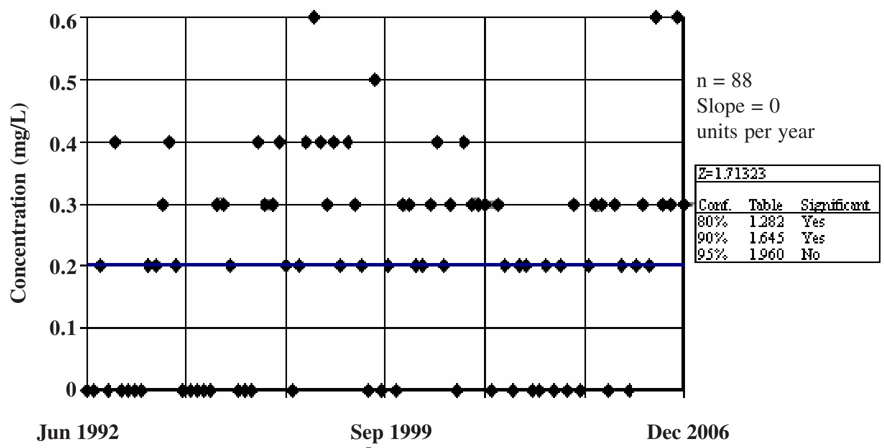

Fig. 7. Temporal variation of boron at Aydin

There also exists streamflow discharge data in Aydin station. Temporal variation of annual mean discharge and monthly variation of long term monthly mean discharge recorded at this station is shown is Figs. 8 and 9, respectively. There has been a steady increase in annual mean discharge with exception 2000 through 2002. As seen in Fig. 9 where monthly variation of long term monthly mean discharge are shown, monthly mean flow tends to increase in October, beginning of water year. Montly mean flow rate reaches a peak in February (59.12 m^3/s), then starts to decrease until May or June, which is the beginning of dry season. But, mean monthly discharge is higher in July and August than May and June, because more water in July and August are released from reservoirs to meet irrigation water demand in the basin. This practice not only meet irrigation water demand in dry season but also result in dilution of boron concentration in river water, especially important in irrigation season.

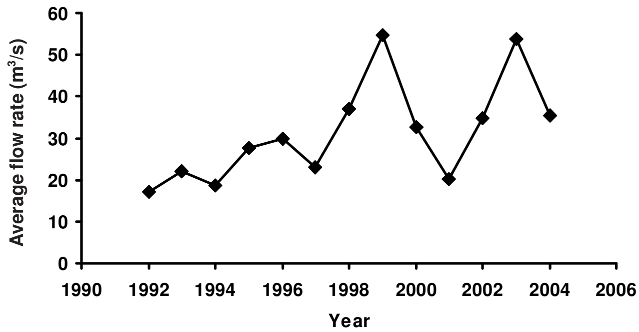

Fig. 8. Long term variation of annual mean discharge at Aydin Station

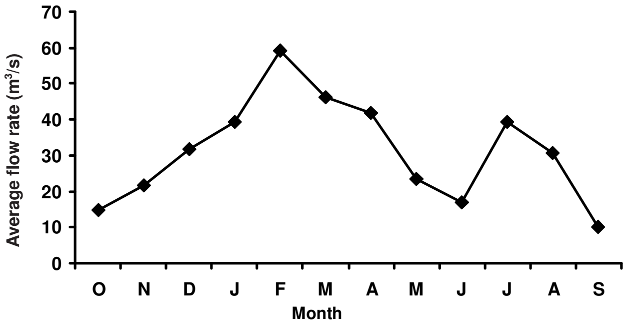

Fig. 9. Monthly variation of monthly mean discharge at Aydin station

Koçarli station is located 26 km downstream of Aydin station. Boron data belonging to this station are in between the years 1994 and 2006. Sample size used in this study is 76 which were compiled in February, April, June, July, August, October and December seasons. A statistically insignificant decrease in boron concentrations of Koçarli station was observed in the course of period of record (Seasonal Kendall test statistic, Z = -1.1361), together with zero trend slope (Fig. 10).

Söke is the last station which is *ca.* 49 km downstream of Koçarli station. This station has a sample size of 66 which were recorded between 1996 and 2006 in the February, April, June, July, August, October and December seasons. Seasonal Kendall trend test yielded a slight decrease in boron concentrations with the test statistic -0.4785, which is not significant 0.2 significance level (Fig. 11). Slope of trend was estimated as zero.

Apart from temporal variation boron concentration at individual stations, a valuable insight can be gained into spatial distribution of boron along the river from Table-2, where the descriptive statistics are tabulated. Although minimum boron concentrations are zero at all stations except in Çubukdag with 0.2 mg/L, the statistics mean, median and maximum tend to increase from uppermost station Yenice through downstream stations, reaching a peak in Feslek (maximum = 2.1 m/L, mean =0.7080 m/L and median = 0.80 mg/L), then tending to decrease along

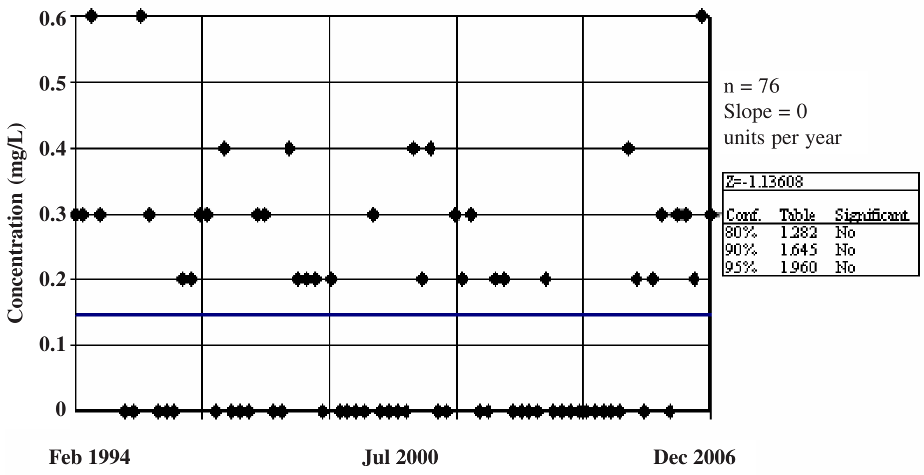

Fig. 10. Temporal variation of boron at Koçarli

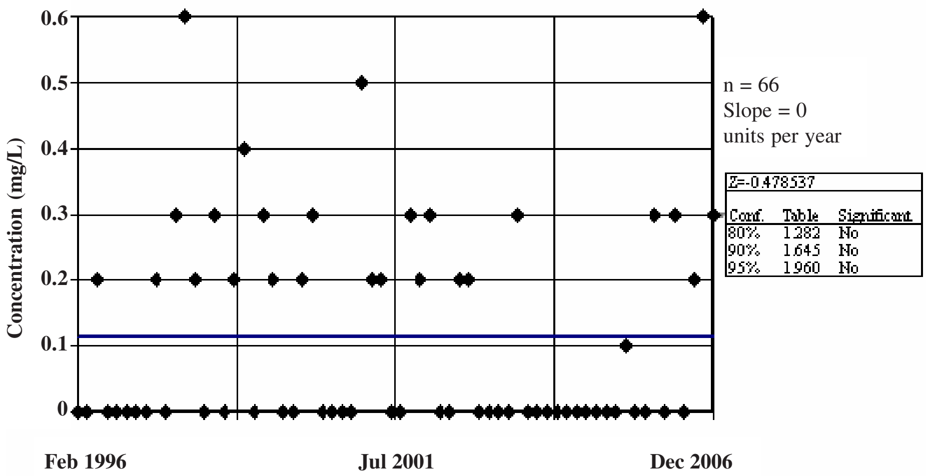

Fig. 11. Temporal variation of boron at Söke

downstream stations till downmost station Söke. This spatial pattern could be easily attributed to relatively fresh water contribution from tributaries such as Dandalas, Akçay and Çine Creeks and other small tributaries.

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