

## ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

# STATISTICAL ANALYSIS OF WATER QUALITY TRENDS: AN APPLICATION TO THE PORSUK STREAM

Erdem ALBEK<sup>1</sup>

### **ABSTRACT**

In this study, nonparametric statistical trend analysis is conducted to assess trends in water quality time series. For the analysis, the Seasonal Kendall Trend Test is used, together with other auxiliary statistical tests. The methodology is applied to water quality time series from the Beşdeğirmen monitoring station situated on the Porsuk stream, the largest tributary of the Sakarya River. Together with flow, seven water quality parameters are investigated and their trends from 1983 to 2000 are determined. It is found that the stream water quality has improved for suspended solids and the nitrogen species but become worse in terms of other water quality variables, indicating that the pollution of this important water course is continuing.

**Key Words:** Water quality, Streams, Nonparametric trend analysis, Time series.

## SU KALİTESİ EĞİMLERİNİN İSTATİSTİKSEL ANALİZİ: PORSUK ÇAYI İÇİN BİR UYARLAMA

### **ÖZ**

Bu çalışmada, su kalitesi zaman serilerinde eğilimlerin saptanması için parametrik olmayan eğilim analizi uygulanmıştır. Analizler için, diğer istatistiksel testlerin yanısıra, Mevsimsel Kendall Eğilim Testi kullanılmıştır. Yöntem Sakarya nehrinin en büyük kolu olan Porsuk çayı üzerinde bulunan Beşdeğirmen gözlem istasyonundan elde edilen su kalitesi zaman serilerine uygulanmıştır. Akım ile birlikte yedi su kalitesi parametresi incelenmiş ve 1983-2000 yılları arasındaki eğilimler saptanmıştır. Akarsuyun kalitesinin askıda katı maddeler ve azot türleri için daha iyiye gittiği, diğer parametreler için bozulduğu bulunmuştur. Bu da, bu önemli akarsuyun kirlenmesinin devam ettiğini göstermektedir.

**Anahtar Kelimeler:** Su kalitesi, Akarsular, Parametrik olmayan eğilim analizi, Zaman serileri.

## 1. INTRODUCTION

Today, the water quality of streams is largely determined by human activities occurring along the stream and within its watershed. Discharge of domestic and industrial wastewaters into the stream, agricultural and mining operations affect the stream water quality, most of the time adversely. Natural processes usually lag in effect behind anthropogenic (man-made) influences, especially for streams draining urbanized and industrialized watersheds and areas where intensive agriculture is practised.

The deterioration of the stream water quality has pronounced effects on the various uses of the water. Streams are intensively used as sources of irrigation and potable water supplies. Water quality deterioration will render the stream water useless, especially if the water to be abstracted has to meet high quality standards. Pollution of streams by various anthropogenic activities has in this way led to serious problems in many countries of the world, often necessitating costly water treatment as the lack of other water supplies prohibits the abandonment of the polluted stream supply.

<sup>1</sup> Anadolu Üniversitesi, Mühendislik-Mimarlık Fakültesi, Çevre Mühendisliği Bölümü, İki Eylül Kampüsü, 26470, Eskişehir.

E-mail: ealbek@anadolu.edu.tr

Received: 06 February 2002; Revised: 14 June 2002; Accepted: 17 June 2002.

The anthropogenic influences are usually highly dynamic. Whereas natural processes (weathering of rocks, leaching of solutes, among others) are fairly stationary (they change in magnitude over geologic time scales), anthropogenic activities change relatively rapidly, generally on the increasing side. As urbanization increases, so do the effects on the stream water quality. New industrial wastewater sources are added to the already existing inventory. Forest clearing and expansion of agricultural lands, exploitation of new mining grounds increase the burden on the water sources. On the positive side, as concerns about the environment are increasing, new and effective measures are sometimes taken by polluting sources, thereby decreasing the negative impacts on stream water quality.

In the twentieth century, many of the world's important streams (important in the sense that they are used intensively by humans) have shown dramatic deterioration in water quality. Only in the last quarter of the century have effective stream pollution control measures stopped, and in some cases reversed the trends in stream water quality changes. Most trend reversals have taken place in developed countries of Europe and the United States. In other parts of the world, especially in developing countries where environmental concerns generally lag behind economic ones, stream quality deterioration continues largely unabated. Only in rare cases have water quality enhancements been recorded in such countries (Gleick, 2000; UNEP, 1995).

The detection of temporal trends in stream water quality (i.e. changes in pollutant concentrations and/or loads over time) is important for two purposes. First, the determination of whether a stream's water quality gets better or worse will aid in making decisions about the use of the stream and about the measures to be taken to abate the pollution which could make it difficult to achieve the designated uses. Second, trend determination will help in determining whether a measure has been successful in abating water pollution. Trend detection may be done qualitatively, by examining scatterplots of the parameters of interest against time. However, visual examination will only reveal very obvious trends, and outliers (extreme values) and plot areas with a high number of observations (crowded areas) will hide trends or produce fake ones. Quantitative and dependable results are only obtained by statistical trend analysis.

Today, statistical trend detection techniques are employed widely for streams. To name two examples, the United States Geologic Survey uses trend detection to assess the state of national waters (Smith et al, 1987). Statistical trend detection techniques are used, especially in northern Europe, to track the recovery of water

sources from acidification in areas previously affected by acid rains (Kahl, 1993).

In Turkey, statistical trend detection in water quality time series has not been widely adopted till now. Trend analysis is mostly applied to meteorological time series to detect climatic changes. Albek (2000) has applied trend analysis to various Turkish streams to detect trends in chloride concentrations.

## 2. STATISTICAL TREND ANALYSIS

Trend analysis of water quality time series can be done either parametrically or nonparametrically. Parametric trend analysis employs linear regression, time being the predictor variable and the water quality parameter of interest the criterion variable. By a t-test it is investigated if the slope coefficient is significantly different from zero. The application of parametric methods, however, is burdened by two difficulties. First, the regression residuals need to be normally distributed and have constant variance. When dealing with water quality time series with skewed distributions, achieving normality and homoscedasticity of the residuals might be difficult. Second, outliers in the data set may cause misleading interpretations if not taken care of.

Nonparametric methods (also called distribution-free methods) circumvent these problems and are very widely used in trend analysis of environmental time series which usually are skewed and possess outliers data (Hirsch et al., 1982). As these methods do not take into account the numerical values of the observations but their ranks relative to each other, outliers do not distort the results. Moreover, normality of the residuals is not a necessary condition. In nonparametric trend analysis, gaps in data are tolerated and the data need not be collected based on a strict time schedule. In this study, nonparametric methods have been employed for trend analysis and for auxiliary statistical tests (such as testing for serial dependence).

### 2.1. The Seasonal Kendall Test

The Seasonal Kendall Test is used for the nonparametric trend analysis of seasonal data (Hirsch et al., 1982). It is a modified form of the original Kendall Trend Test, taking into account the seasonality of environmental time series. It is a hypothesis test in which the null hypothesis states that the data (disaggregated into seasonal subsamples) are independently and identically distributed. The alternative hypothesis is that the data are not identically distributed. The test statistic  $S_i$  for a given season  $i$  is given as

$$S_i = \sum_{k=1}^{n_i-1} \sum_{j=k+1}^{n_i} \text{sgn}(X_{ij} - X_{ik}) \quad (1)$$

where  $n_i$  is the number of observations for season  $i$  and the  $x$ 's stand for the observations. The function  $\text{sgn}$  is +1 if the observation  $x_{ij}$  is greater than  $x_{ik}$ , a former observation in time. It is -1 otherwise, and zero if the observations are equal to each other (a tie). If later observations are for the most part larger than former ones (which means that the value of the water quality parameter is increasing in time, indicating an upward trend), a positive  $S_i$  is obtained. Likewise, if later observations are smaller than former ones (which means that the water quality parameter is decreasing in time, indicating a downward trend), a negative  $S_i$  is obtained. If  $S_i$  is close to zero, the time series is trendfree. There are however cases, when there are opposing trends in different parts of a time series which also may give an  $S_i$  value close to zero as will be shown for the Porsuk time series. Such cases need special attention.

Summing the  $S_i$  values of all seasons gives an overall  $S$  value. The expected values of both the  $S_i$ 's and  $S$  (which are random variables themselves) are equal to zero for trendfree data. The variance of  $S_i$  is

$$\text{Var}[S_i] = \frac{n_i(n_i - 1)(2n_i + 5) - \sum t_i(t_i - 1)(2t_i + 5)}{18} \quad (2)$$

where  $t_i$  is the extent of a given tie in season  $i$ . The variance of  $S$ , the statistics expressing the overall trend, is defined as

$$\text{Var}[S] = \sum_{i=1}^{ns} \text{Var}[S_i] + \sum_{i=1}^{ns} \sum_{l=1}^{ns} \text{cov}(S_i, S_l) \quad i \neq l \quad (3)$$

where  $ns$  is the number of seasonal subgroups. The second term in Eq. 3. is equal to zero when the data are not serially correlated. In this term,  $S_i$  and  $S_l$  are the  $S$  values for different seasons. In this case, the variances for each season are just summed up to give the total variance. If the data are serially correlated, the second term needs to be calculated. An estimation for this term is provided in Hirsch and Slack (1984) as

$$\text{cov}(S_i, S_l) = \frac{\left[ K_{il} + 4 \sum_{j=1}^n R_{ij} R_{lj} - n(n_i + 1)(n_l + 1) \right]}{3} \quad (4)$$

where  $R_{ij}$  and  $R_{lj}$  are the ranks of the data for the respective seasons  $i$  and  $l$ . In this equation,  $K_{ij}$  is given below as

$$K_{ij} = \bullet \text{sgn}[(x_{ji} - x_{ij})(x_{jl} - x_{lj})] \quad (5)$$

$i < j$

Once the  $S$  values and the variances are calculated, a standard normal variate  $Z$  can be computed as

$$Z = \begin{cases} \frac{S - 1}{(\text{Var}(S))^{1/2}} & \text{if } S > 0 \\ 0 & \text{if } S = 0 \\ \frac{S + 1}{(\text{Var}(S))^{1/2}} & \text{if } S < 0 \end{cases} \quad (6)$$

In this equation, the -1 and +1 are added to  $S$  for continuity correction. The standard normal variate can be computed based on a particular  $S_i$  value or for the overall test statistic  $S$ . The  $Z$  score obtained is then compared to critical  $Z$  values corresponding to a preselected significance level. Moreover,  $p$ -values (attained significance values) can be computed to check the believability of the null hypothesis (Helsel and Hirsch, 1992). The null hypothesis is rejected (indicating that there is a trend) if the computed  $Z$  score is larger than the critical  $Z$  score or the  $p$ -value is smaller than the significance level.

The Seasonal Kendall Test can be used to detect trends for a given season or for the whole data set. Seasons may exhibit significant trends in different directions and give rise to no overall trend. Heterogeneity of trend can be checked by a Chi-Square Test (Helsel and Hirsch, 1992; Peters et al., 1997). The trend magnitude, which can be expressed as a slope (change in concentration per unit time), is also of interest in trend analysis studies. The Seasonal Kendall-Theil Slope Estimator used in this study is computed as follows (Hirsch et al., 1982). For every data pair in a given season the slope is computed, by taking the difference between the two data points and dividing this value by the corresponding distance. The median of all the pairwise slopes gives the slope estimator for the season. The median of all the pairwise slopes for all seasons gives the overall slope estimator.

## 2.2. Other Statistical Tests

The Seasonal Kendall Test is the main statistical test used in this study. Besides this test, four other statistical tests have been utilized. A Chi-Square Test is utilized to check for trend heterogeneity (Helsel and Hirsch, 1992). The Spearman's Rho Test is used to determine if there is serial correlation in a data set (McCuen, 1992). The Kendall Tau Test, being the nonparametric equivalent of the correlation coefficient calculates the strength of the monotonic relationship between two variables. The Friedman Test is utilized to detect differences among seasonal observations (Helsel and Hirsch, 1992).

### 2.3. Scatterplot Smoothing

In this study, a period covering 18 years is used. To see trends more clearly among the high number of data points, smoothing of data is required. For this purpose, a technique called LOWESS (LOcally WEighted Scatterplot Smoothing) is utilized (Cleveland, 1979). LOWESS curves or smooths make visual examination of data easier and prevent misinterpretations caused by data overcrowding. They are created by first selecting a window size. The window size determines the upper and lower limits of local regression and consequently the degree of smoothing. The greater the window size the smoother is the curve. For every data point in time, a locally weighted polynomial regression is performed. The weights used decrease as the distance to the center of the window increases. A tricube function is usually used in the weighting procedure. The residuals from the regression are computed. A new regression is performed by assigning new weights to the data points which are functions of residuals. Larger residuals are assigned smaller weights. This procedure gives the method its robustness by minimizing the effects of outliers.

The above-mentioned procedures require a lot of computational effort. All computations have been performed by utilizing FORTRAN computer programs written by the author.

### 3. APPLICATION OF TREND ANALYSIS TO THE PORSUK STREAM

In this study, the time series whose trend patterns have been analyzed, belong to a station situated on the Porsuk Stream. The Porsuk Stream (Figure 1) is a tributary of the Sakarya River. It arises in the Murat Mountain to the south of the city of Kütahya. After taking up various creeks, it flows past Kütahya and enters the reservoir named after itself. Leaving the reservoir, the stream passes through the city of Eskişehir. It then flows through a wide valley named again after itself before joining the Sakarya River, being its most important tributary. Over its course, the Porsuk Stream travels a distance of 460 km. Its watershed area is 11325 km<sup>2</sup> (DSİ, 1995).

The stream is very important for its surroundings as it provides the two cities mentioned with potable water. The agricultural areas in the watershed, especially along the valley after Eskişehir are irrigated with its water. The stream, however, is grossly polluted. Domestic wastewater and wastewater from various industries (textile, food processing, earth-based industries, fertilizer production, among others) have been discharged into the stream for years without any treatment. The Porsuk Reservoir, part of the system, is a hypertrophic lake (DSİ, 1995). Today, a number of wastewater sources treat their wastewater, though mostly inefficiently. Diffuse pollution sources are not controlled at all and the stream still is a heavily burdened watercourse.

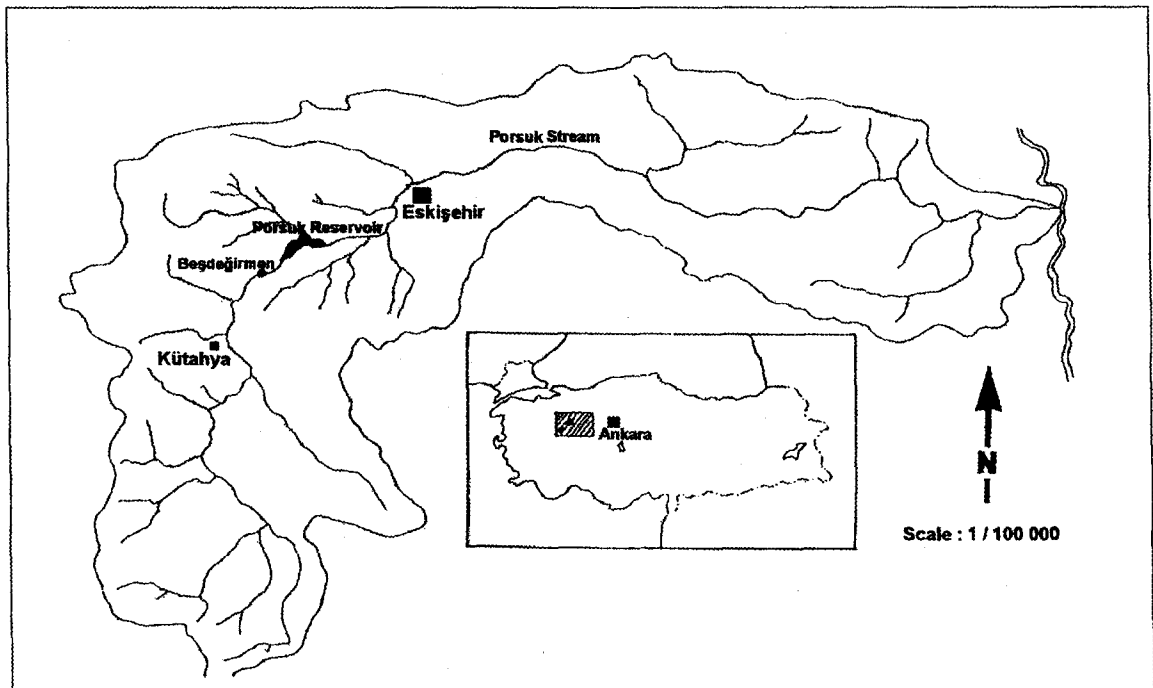


Figure 1. Map of the Porsuk Stream Watershed and the Location of the Beşdeğirmen Station (adapted from DSİ, 1995).

There are a number of stream gauging stations along the Porsuk stream, operated by two distinct state agencies, namely: Devlet Su İşleri (State Hydraulic Works) and Elektrik İşleri Etüd İdaresi (Electrical Power Resources Survey and Development Administration). On some of these stations, water quality is also monitored. Also, DSİ has conducted special programmes to monitor the water quality of the stream (DSİ, 1995).

In this study, water quality time series from one of these stations is examined and trend analysis is conducted based on a number of water quality parameters measured in this station. The station is named Beşdeğirmen and is situated 17 km after the city of Kütahya, before the stream enters the reservoir. EİE operates at this point a flow-gauging station and daily flows are available from this agency. Moreover, EİE also monitors the water quality here for a limited number of parameters (temperature, pH, electrical conductivity, sediment, calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulfate, organic matter and boron). The monitoring frequency is usually once per month. DSİ also monitors water quality at this station. The samples are taken usually every second month, sometimes even less. However, the number of parameters analyzed is higher, encompassing important water quality parameters like BOD<sub>5</sub>, nitrogen species and phosphate.

In this study, seven water quality parameters from the Beşdeğirmen station, together with streamflow, will be examined for trend. The study period is from 1983 to 2000, thus 18 years are covered. The parameters examined are Dissolved Solids (DS), chloride (Cl<sup>-</sup>), ammonia (NH<sub>3</sub>), nitrate (NO<sub>3</sub><sup>-</sup>), 5-day Biochemical Oxygen Demand (BOD<sub>5</sub>), phosphate (PO<sub>4</sub><sup>3-</sup>) and Suspended Solids (SS). These parameters, as mentioned above, are water quality parameters of primary importance.

Table 1 gives some statistical measures regarding these parameters. As seen from the table, there are around 80 observations for all parameters in the 18 years

studied. Compared to a once per month sampling frequency, around 63% are missing. In 1984 and 1985, almost every month has been sampled. There are two missing years. For 1990 and 1994, there are no data. In the remaining years, bimonthly or trimonthly sampling has been conducted.

The IQR (Interquartile Range) given in the table is the nonparametric equivalent of the standard deviation. The COV (Coefficient of Variation) value is the standard deviation normalized with respect to the average. The COV value provides a measure of the spread of the data and allows for comparisons between different parameters. As evident from the table all parameters except DS and chloride show wide spread.

Table 2 displays the correlation of the parameters with flow. The correlations have been performed non-parametrically. As the data are nonnormal, skewed and there are outliers, parametric correlation can lead to misleading interpretations. Also, the Pearson correlation coefficient measures the extent of linear dependence between two variables. Kendall's Tau which measures the extent of monotonic dependence is a more robust measure, being also resistant against the effect of outliers. As evident from the table, all the dissolved substances, show a negative Tau value, indicating an inverse relationship with flow. This inverse relationship is universally observed for substances carried in dissolved form in water when significant natural sources are absent (Behrendt, 1993), indicating that they are added to the stream by anthropogenic sources. However, the relationship between nitrate and flow is not significant. Suspended solids are typically directly related to flow. The inverse relationship observed between phosphate and flow indicates that the majority of phosphate originates from point sources because of the dilution process of the point source contribution by the streamflow (Drever, 1982).

Figure 2 and Figure 3 display the change of these parameters with time. The plots also include the LO-WESS smooths to reveal better the time evolution of

Table 1. Some Statistical Measures for the Water Quality Parameters Studied.

	Flow (m <sup>3</sup> /s)	DS (mg/L)	Cl <sup>-</sup> (mg/L)	NH <sub>3</sub> (mg/L N)	NO <sub>3</sub> <sup>-</sup> (mg/L N)	BOD <sub>5</sub> (mg/L)	PO <sub>4</sub> <sup>3-</sup> (mg/L P)	SS (mg/L)
Observations	81	82	82	82	82	77	82	82
Average	7.8	440.8	14.2	10.6	4.7	9.9	1.2	215.8
Standard Deviation	8.8	79.1	5.7	11.5	4.3	7.4	1.2	409.5
Median	4.9	432.0	12.4	6.1	3.5	7.3	0.7	92.0
Interquartile Range	3.6	413.0	10.5	4.5	2.7	6.0	0.4	59.3
Minimum	1.0	295.0	6.5	0.7	0.1	0.4	0.0	11.0
Maximum	52.0	954.0	31.1	67.5	22.5	40.0	4.9	3198.0
COV	112.1	17.9	39.8	107.8	91.8	74.9	101.5	189.8

Table 2. Nonparametric Correlation of the Parameters with Flow.

	Kendall's Tau	p-value
Dissolved Solids	-0.491	<0.001
Chloride	-0.557	<0.001
Ammonia	-0.474	<0.001
Nitrate	-0.124	0.093
BOD <sub>5</sub>	-0.342	<0.001
Phosphate	-0.563	<0.001
Suspended Solids	0.407	<0.001

these parameters. As seen in the plots, there are time trends in the observations and there are opposing trends in different parts of the study period.

To apply the Seasonal Kendall Test, a season needs to be defined. If the data were collected monthly, a month would naturally be chosen. However, the sampling is done bi- or trimonthly. Therefore three months are represented by at least one value for each year. Based on this and on the monthly flow distribution, four seasons can be distinguished. The Winter Season inclu-

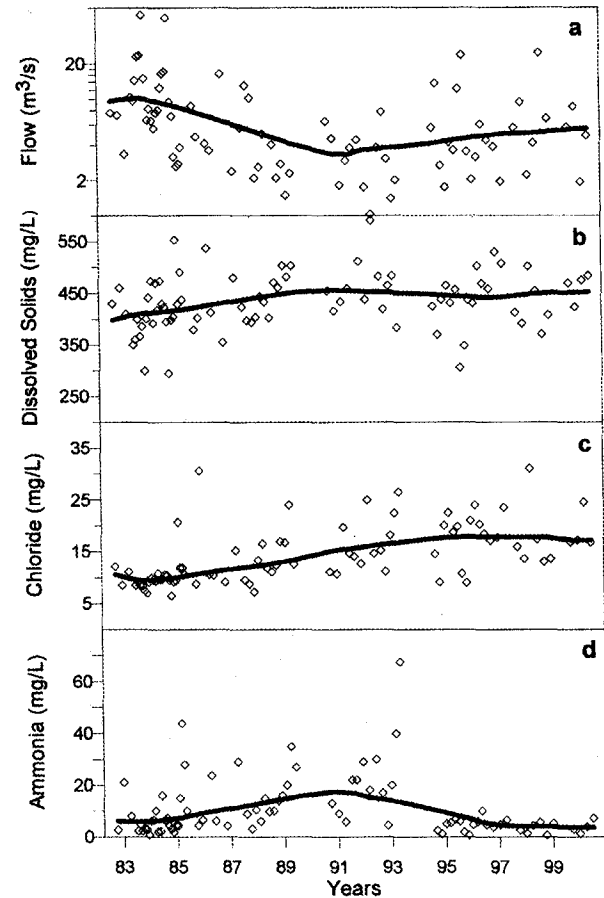


Figure 2. Plots of the Water Quality Parameter Concentrations Against Time and the LOWESS Curves (a=Flow, b=Dissolved Solids, c=Chloride, d=Ammonia).

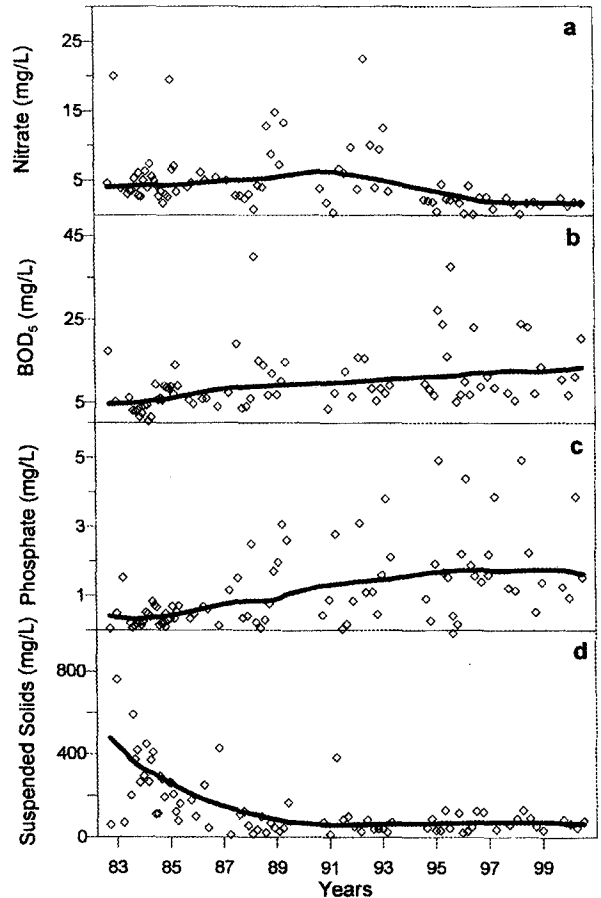


Figure 3. Plots of the Water Quality Parameter Concentrations Against Time and the LOWESS Curves (a=Nitrate, b=BOD, c=Phosphate, d=Suspended Solids).

des the months January, February and March, the Spring Season the months April, May and June, the Summer Season July, August and September and the Fall Season October, November and December. Here, it must be stated that the determination of seasons is more or less based on the judgement of the researcher. The Friedman Test applied to this data has revealed that the medians are distinct from each other, indicating that the seasons represent different patterns of flow.

Once the extent of the seasons are determined, the next step is to find out one aggregate value for each season. For this purpose, the median has been chosen. It is preferred over the mean as it is a nonparametric measure of location and is robust against outliers and non-normality. Based on the intent, other data reduction measures may be chosen, the minimum or maximum, as an example.

The Seasonal Kendall Test is applied to the seasonal data thus obtained. Based on the data, Seasonal and Overall Kendall-Theil Slope Estimators are computed.

#### 4. RESULTS AND DISCUSSION

Table 3 gives the results of the application of the Seasonal Kendall Test to the Porsuk time series. For each parameter except BOD and phosphate, there are three results. One is for the whole period from 1983 to 2000. As mentioned before, there are opposing trends in the time series. To determine the significance of these opposing trends, the time series have been split into two periods. The first period includes the years between 1983 and 1991, the second period the remaining years. For chloride, the first period is two years longer, extending to 1993.

In Table 3, the Z values and the p-values are shown. The p-values tell about the significance of the trend, the smaller the value the more likely the trend (e.g. the more likely the rejection of the null hypothesis). If, for example, it is desired that the trends are cap-

tured at a confidence level of 95 % (which pertains to a significance level of 0.05), the p-value needs to be smaller than 0.05. The Z values, when compared to critical Z values from a normal distribution, tell the same thing, however they contain the additional information, namely the direction of the trend by being positive or negative.

Table 4 displays the results of the application of the Kendall-Theil Slope Estimator. For each season there are three values for every period. The median slope estimator and the upper and lower confidence limits (for a confidence level of 95 %). As the intervals are nonparametric ones, they are not symmetrical.

Below, the results for individual parameters are discussed.

Table 3. Results of the Kendall Test (Trends that are significant at a significance level of 0.05 have Z and p-values printed in bold and italic. The critical Z value at a significance level of 0.05 is 1.96).

Parameter	Winter		Spring		Summer		Fall		Total	
	Z	p	Z	p	Z	p	Z	p	Z	p
<b>FLOW</b>										
Whole period	-0.531	0.5954	-0.492	0.6224	-1.943	0.0520	-0.417	0.6769	-1.746	0.0809
83 - 91	-0.626	0.5316	-0.938	0.3481	<b>-2.097</b>	<b>0.0360</b>	-1.460	0.1444	<b>-2.714</b>	<b>0.0066</b>
92 - 00	1.581	0.1138	0.730	0.4655	1.284	0.1991	1.251	0.2109	<b>2.578</b>	<b>0.0099</b>
<b>DS</b>										
Whole period	0.530	0.5959	0.682	0.4951	0.606	0.5445	0.795	0.4264	1.364	0.1726
83 - 91	0.834	0.4042	0.313	0.7545	0.313	0.7545	0.626	0.5316	1.199	0.2305
92 - 00	-0.938	0.3481	-0.521	0.6022	0.417	0.6767	0.000	1.0000	-0.469	0.6390
<b>Cl</b>										
Whole period	<b>2.197</b>	<b>0.0280</b>	1.819	0.0688	<b>2.954</b>	<b>0.0031</b>	<b>2.123</b>	<b>0.0338</b>	<b>4.604</b>	<b>0.0000</b>
83 - 93	1.323	0.1857	1.090	0.2758	<b>2.491</b>	<b>0.0127</b>	<b>2.499</b>	<b>0.0125</b>	<b>3.818</b>	<b>0.0001</b>
94 - 00	0.376	0.7071	0.000	1.0000	0.939	0.3476	-0.564	0.5730	0.377	0.7059
<b>NH<sub>3</sub></b>										
Whole period	-0.493	0.6222	-1.137	0.2555	-1.478	0.1393	0.379	0.7047	-1.384	0.1665
83 - 91	1.877	0.0606	0.521	0.6022	0.000	1.0000	1.251	0.2109	1.929	0.0538
92 - 00	-1.147	0.2515	-1.468	0.1422	-1.251	0.2109	-0.626	0.5316	<b>-2.401</b>	<b>0.0163</b>
<b>NO<sub>3</sub><sup>-</sup></b>										
Whole period	-1.517	0.1292	<b>-2.198</b>	<b>0.0279</b>	-1.402	0.1608	-0.871	0.3837	<b>-2.156</b>	<b>0.0311</b>
83 - 91	0.000	1.0000	-0.730	0.4655	-0.210	0.8339	1.043	0.2971	0.000	1.0000
92 - 00	-0.949	0.3428	<b>-2.189</b>	<b>0.0286</b>	-0.417	0.6767	-1.460	0.1444	<b>-2.666</b>	<b>0.0077</b>
<b>BOD<sub>5</sub></b>										
Whole period	0.114	0.9095	1.477	0.1396	1.288	0.1978	1.629	0.1034	<b>2.311</b>	<b>0.0208</b>
<b>PO<sub>4</sub><sup>3-</sup></b>										
Whole period	<b>2.197</b>	<b>0.0280</b>	<b>2.386</b>	<b>0.0170</b>	<b>3.106</b>	<b>0.0019</b>	1.061	0.2885	<b>4.432</b>	<b>0.0000</b>
<b>SS</b>										
Whole period	-0.909	0.3633	-1.174	0.2403	-0.152	0.8796	-0.947	0.3437	-1.648	0.0994
83 - 91	-0.834	0.4042	<b>-2.189</b>	<b>0.0286</b>	0.000	1.0000	-0.626	0.5316	-1.929	0.0538
92 - 00	0.104	0.9170	0.521	0.6022	1.460	0.1444	0.417	0.6767	1.407	0.1593

Table 4. Kendall-Theil Slope Estimator (LL=95% Lower Limit, M=Median, UL=95% Upper Limit).

Parameter	Winter			Spring			Summer			Fall			Total		
	LL	M	UL	LL	M	UL	LL	M	UL	LL	M	UL	LL	M	UL
<b>FLOW</b>															
Whole period	-0.5	-0.2	0.3	-0.6	-0.1	0.3	-0.2	-0.1	0.0	-0.4	-0.1	0.1	-0.4	-0.3	-0.2
83 - 91	-2.0	-1.0	0.3	-3.5	-0.9	0.5	-0.7	-0.2	-0.2	-2.0	-0.7	-0.2	-0.9	-0.5	-0.2
92 - 00	0.0	0.3	2.7	-0.4	0.4	1.4	0.0	0.1	0.2	0.2	0.5	0.9	0.3	0.5	0.9
<b>DS</b>															
Whole period	-3.7	2.1	6.5	-1.8	1.2	5.0	-1.5	1.9	4.7	-1.1	3.5	8.7	2.1	3.6	6.5
83 - 91	-3.5	6.5	15	-13	2.3	12	-12	2.9	18	-1.7	9.2	21	0.2	4.8	14
92 - 00	-61	-16	9.0	-19	-4.9	5.0	-6.0	4.8	12	-23	3.7	15	-29	-18	-11
<b>Cl</b>															
Whole period	0.2	0.4	0.6	0.2	0.5	0.7	0.8	1.1	1.4	0.5	0.7	0.8	0.5	0.6	0.7
83 - 93	0.1	0.5	0.9	-0.1	0.5	1.3	1.1	1.5	1.9	0.7	0.7	1.0	0.3	0.6	0.7
94 - 00	-1.2	0.5	1.5	-0.5	0.0	1.6	-0.4	0.5	3.5	-1.0	-0.6	0.1	-0.3	0.4	0.5
<b>NH<sub>3</sub></b>															
Whole period	-0.3	-0.1	0.5	-0.9	-0.3	0.1	-1.8	-0.5	-0.1	-0.2	0.1	2.2	0.2	0.6	1.0
83 - 91	0.6	1.3	1.7	-1.5	0.8	2.0	-3.6	0.2	5.2	1.2	2.5	4.1	0.6	1.0	1.5
92 - 00	-3.2	-1.7	0.0	-3.5	-1.4	-0.3	-4.2	-1.8	-0.3	-8.6	-2.9	0.1	-5.7	-4.7	-3.6
<b>NO<sub>3</sub><sup>-</sup></b>															
Whole period	-0.2	-0.1	0.0	-0.5	-0.2	-0.1	-0.5	-0.3	0.0	-0.3	-0.2	0.0	-0.2	-0.1	-0.1
83 - 91	-0.2	-0.1	0.6	-2.3	-0.1	0.9	-1.1	-0.4	1.1	0.2	0.5	1.7	-0.3	-0.1	0.3
92 - 00	-1.0	-0.2	0.0	-1.2	-0.7	-0.1	-1.1	-0.3	0.3	-3.5	-0.4	-0.2	-1.9	-1.2	-0.9
<b>BOD<sub>5</sub></b>															
Whole period	-0.4	0.1	0.4	0.0	0.2	0.5	0.1	0.4	1.0	0.5	0.9	1.3	0.3	0.4	0.9
<b>PO<sub>4</sub><sup>3-</sup></b>															
Whole period	0.0	0.1	0.1	0.0	0.1	0.1	0.2	0.3	0.4	0.0	0.1	0.2	0.1	0.1	0.1
<b>SS</b>															
Whole period	-15	-5.3	1.5	-21	-10	0.7	-10	-0.9	2.2	-7.2	-3.3	0.1	-15	-7.9	-4.0
83 - 91	-70	-35	1.5	-119	-57	-18	-60	-1.8	39	-21	-5.8	8.2	-60	-20	-5.8
92 - 00	-18	2.1	8.0	-7.1	3.6	10	2.0	3.0	7.0	-1.7	1.3	2.5	1.3	2.0	3.5

#### 4.1. Flow

The flow in the Porsuk stream at the Beşdeğirmen station shows opposing trends in the two time periods. In the first period, a total downward trend is observed and this trend is significant (p-value = 0.0066). In the second period, a total significant upward trend is observed (p-value = 0.0099). Over the whole period, these trends cancel each others influence and an overall trend cannot be inferred from the data at a significance

level of 0.05 (p-value = 0.0809). If a significance level of 0.1 is chosen, a downward trend is predicted. On a seasonal basis, there is only one season with a significant trend, namely the fall season for the first period. In the trend analysis of seasonal time series, this is a widely encountered case. No season might show a trend, but an overall or total trend might be found. The trend slopes are almost equal to each other in magnitude, though in opposite directions.



This fluctuation in flow, with a period of roughly ten years, is also observed in other streams in Turkey (Albek, 1999a, 2000). It is related to climatic patterns. This fluctuation in flow reflects itself also in the other parameters as most of them are closely related to flow.

#### 4.2. Dissolved Solids

Dissolved Solids is an important water quality parameter, especially if the water is to be used for irrigation purposes. For dissolved solids, no trend is observed, not even at a significance level of 0.1. From the plots (Figure 2), a visual upward trend is observed for the first period, however, it is not significant. Dissolved solids concentrations are inversely related to flow. Therefore, the nonsignificant upward trend in the first period is explained by the corresponding downward trend in flow. As flow increases in the second period, a corresponding downward trend in the dissolved solids should be apparent. This, however, is not the case. In the second period, the concentrations level off. This might be caused by new inputs to the stream, indicating that the sources of dissolved solids in the watershed might be increasing.

#### 4.3. Chloride

Chlorides can reveal human influences to streams as they enter streams mainly through wastewaters and after road deicing. In some regions, there may be predominant natural sources, originating from evaporite deposits in the watershed. As evident from Figure 2, chloride shows a similar pattern to dissolved solids. However, the upward trend in the first years is longer (it extends till 1993) and, the overall trend in this first period is significant and chlorides increase with a rate of 0.6 mg/L per year. In this first period, trends in summer and fall seasons are significant. Chlorides in the stream are increasing when flows are at their lowest levels. Albek (1999b) has found out that in the Porsuk stream for the Beşdeğirmen station, natural sources dominate over anthropogenic sources around 90% of the time. It can then be concluded that there is an increase in natural sources in these months. This increase might be caused by increased chlorides in the irrigation return flows (the first period is characterized by decreasing flows so irrigation needs have increased over the years).

For the second period, the pattern is the same as in the dissolved solids. No trend is observed. Overall for the whole period, there is a significant trend, mostly induced by the trend in the first period.

#### 4.4. Ammonia

Ammonia can lead to serious water quality problems when elevated concentrations are encountered. Ammonia toxicity can lead to fish deaths in streams. Moreover, oxidation of ammonia depletes oxygen, leading to anaerobic conditions. Ammonia is also important in eutrophication control of reservoirs and lakes, being a plant nutrient. Ammonia shows two opposing trends over the period investigated. As a dissolved substance, it is inversely related to flow and where flow increases, ammonia decreases and vice versa. Though there are no significant seasonal trends for the three periods studied, the second period shows a significant downward trend. As evident from Figure 2, this period is characterized by lower ammonia concentrations (though these concentrations are extremely high for a stream) and most remarkably, by the little spread in these concentrations. The two different concentration patterns reflect a change in the sources. The principal nitrogen source to the Porsuk stream has been the Kütahya Nitrogen Plant (TÜGSAŞ, Kütahya Azot Fabrikası). Beginning in 1994, efforts have been intensified to prevent leaks and a new treatment system has been installed for ammonia removal from the plants wastewater (DSI, 1995). These improvements have certainly led towards reduced ammonia discharges to the stream, reflecting itself in the reduced concentrations. Moreover, rising flows will also have contributed to the lower concentrations. From 1992 till 2000, the concentrations in the stream have fallen by around 4.7 mg/L a year as computed by the Kendall-Theil Slope Estimator.

#### 4.5. Nitrate

Nitrate, like ammonia, is important in eutrophication control. Also the presence in drinking water above certain concentrations is undesirable because of health concerns. Nitrate shows similarly two opposing trends. However, the first period trend is not significant. In the second period, a highly significant downward trend is observed (1.2 mg/L per year). This reduction is attributable to the improvements in TÜGSAŞ. The overall trend is influenced by the trend in the second period and the whole period shows a significant downward trend.

#### 4.6. Biochemical Oxygen Demand

For BOD<sub>5</sub>, opposing trends are not observed. Over the whole period, BOD<sub>5</sub> shows a monotonic upward trend. Statistically, no seasonal trends are significant. However, the total trend is significant with a p-value of 0.0208. BOD<sub>5</sub> has increased over the 18 years by 0.4 mg/L per year. In this period, there have been efforts to

reduce the discharge of organic matter into the stream by building wastewater treatment plants (the domestic wastewater plant of Kütahya being an example). However, the sources of organic matter to the stream are numerous and it seems that the sources have increased both in number and in magnitude in such a way as to offset the effects of wastewater treatment.

#### 4.7. Phosphate

Phosphate shows a similar pattern to BOD<sub>5</sub>. For the whole period, an upward trend is observed, and this trend is again highly significant (p-value<0.0001). However, in the years following 1995, a leveling-off is observed. Phosphate enters the stream predominantly from anthropogenic sources (domestic wastewaters among others) and these sources have increased as exemplified in the case of BOD<sub>5</sub>. Moreover, conventional wastewater treatment which is practised in the region, will not remove phosphorus from the wastewater to a significant extent. The increase in phosphate in the stream (at the rate of 0.1 mg/L P per year) is important from the point of view of eutrophication control of the Porsuk reservoir.

#### 4.8. Suspended Solids

Suspended solids behave similarly to flow. They reach streams by surface runoff from rural areas and by urban runoff and hence are associated with high flows in streams, usually after precipitation events (diffuse sources). Some point anthropogenic sources of suspended solids (domestic and industrial wastewaters) are more steady and these sources will increase the concentration in the stream at low flows. However, as suspended solids in the Porsuk stream are directly related to flow (Kendall Tau value is 0.407 with a p-value of less than 0.001), most sources are diffuse.

In the first period, suspended solids show a downward trend. The p-value is 0.0538, slightly higher than 0.05. So, one should be careful in rejecting a trend. In this period of 9 years, suspended solids concentrations have fallen by almost 200 mg/L. In the second period, the pattern levels off. The decrease in the first period may be attributed to downward trends in flow and to improved water pollution control measures. In the second period, as flows increase, suspended solid levels show no trend. This pattern also points towards the improved control measures.

## 5. CONCLUSIONS

Trend analysis of water quality time series is important for the proper management of water supplies (streams, lakes, etc.) which are vital for the welfare of society. Correct decisions can only be reached if the quality of a water source is precisely known. Whether a water supply deteriorates in quality or recovers from a badly polluted state, can be assessed by statistical trend analysis.

For the case of the Porsuk stream, it can be concluded that the stream water quality is better in terms of nitrogen species and suspended solids compared to that 18 years ago. This is attributable to improvements in pollution control practised in the sources. For the other water quality parameters, the stream shows no significant enhancement in quality. Indeed chlorides, BOD and phosphates show positive trends.

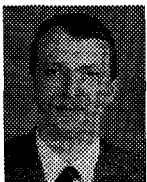
## REFERENCES

- Albek, E. (1999a). Seasonal and Long-term Trends in Sediment Transport of Turkish Streams, *The Fourth International Conference on the Mediterranean Coastal Environment, The Fourth International Conference on Environmental Management of Enclosed Coastal Seas (MEDCOAST-EMECS)*, Antalya, Türkiye. pp.49-60.
- Albek, E. (1999b). Identification of the Different Sources of Chlorides in Streams by Regression Analysis Using Chloride-Discharge Relationships. *Water Environment Research* 71(7), 1310-1319.
- Albek, E. (2000). Türkiye Akarsularında Klorür Derişimlerinin Mevsimsel Bazda Yıllar Boyu Değişimleri, *1. Ulusal Çevre Kirliliği Kontrolü Sempozyumu*, Orta Doğu Teknik Üniversitesi, Ankara, Türkiye. pp.133-140.
- Behrendt, H., (1993). Separation of Point and Diffuse Loads of Pollutants Using Monitoring Data of Rivers. *Wat. Sci. Tech.* 28(3-5), 165-175.
- Cleveland, W.S. (1979). Robust Locally Weighted Regression and Smoothing Scatterplots. *J. Am. Stat. Assoc.* 74, 829-836.
- DSİ (1995). *Porsuk Havzasında 1994 Yılı Su Kalite Değerlendirmeleri*, Teknik Araştırma ve Kalite Kontrol Şube Müdürlüğü.
- Drever, J.I. (1982). *The Geochemistry of Natural Waters*, Prentice-Hall, Inc., London.
- Helsel, D.R. and Hirsch, R.M. (1992). *Statistical Methods in Water Resources*, Elsevier, The Netherlands.

- Hirsch, R.M., Slack, J.R. and Smith, R.A. (1982). Techniques of Trend Analysis for Monthly Water Quality Data. *Water Resources Research* 18(1), 107-121.
- Hirsch, R.M. and Slack, J.R. (1984). A Nonparametric Trend Test for Seasonal Data with Serial Dependence. *Water Resources Research* 20(6), 727-732.
- Kahl, J.S., Haines, T.A., Norton, S.A., and Davis, R.B. (1993). Recent Trends in the Acid-Base Status of Surface Waters in Maine, USA. *Water, Air and Soil Pollution* 67, 281-300.
- McCuen, R.H., (1992). Microcomputer Applications. *Statistical Hydrology*. Prentice Hall, New Jersey.
- Peters, N.E., Bricker, O.P. and Kennedy, M.M. (Eds) (1997). *Water Quality Trends and Geochemical Mass Balance*, Wiley, England.
- Smith, R.A., Alexander, R.B. and Wolman, M.G. (1987). *Analysis and Interpretation of water Quality Trends in Major US Rivers, 1974-81.*, United States Geologic Survey Water Supply Paper 2307.
- Gleick, Peter H. (2000). *The World's Water, 2000-2001: The Biennial Report on Freshwater Resources*, Island Press, Washington, D.C.
- United Nations Environment Programme (1995). *Water Quality of World River Basins*, Collaborating Centre for Freshwater Quality Monitoring and Assessment, Nairobi

## ACKNOWLEDGEMENTS

The author acknowledges the efforts of the staff of Devlet Su İşleri and Elektrik İşleri Etüt İdaresi, who collect and analyze countless water samples from the waters of Turkey and make the results available to investigators.



**Erdem Albek**, was born in İstanbul in 1961. He graduated from Boğaziçi University in 1984. He completed his MSc. and Ph.D. studies at the Institute of Environmental Sciences, Boğaziçi University. He is currently belonging to the staff of the Department of Environmental Engineering, Anadolu University as an Assistant Professor.