Bull Environ Contam Toxicol (2008) 80:469–474
DOI 10.1007/s00128-008-9439-0

Investigation of Temporal Trends in Hydrochemical Quality of Surface Water in Western Turkey

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Received: 24 July 2007 / Accepted: 14 April 2008 / Published online: 18 May 2008

Abstract This study comprises application of non-parametric trend analysis (Mann-Kendall test and Sen's Slope estimator techniques) and multidimensional scaling method to water quality data sets. Water samples analyzed (for chloride, nitrate-nitrogen, sodium, sulfate and total dissolved solid parameters) semi-monthly at seven river monitoring stations in Tahtali Basin, Turkey for 6 years were evaluated. The results revealed that agricultural discharges caused spatial differences in terms of water quality in the basin. Moreover, variable concentrations generally decreased or did not change over time. This study showed that, trend detection and data grouping methods help decision makers to judge effectiveness of management programs.

Keywords Mann-Kendall test · Multidimensional scaling · Sen's Slope estimator · Tahtali Basin

In water resources management, the quality of surface waters has recently became as significant as their quantity since the former directly affects the amount of water that can be used for various purposes such as drinking, agricultural, recreational and industrial uses etc. Water quality assessment encompasses monitoring, data evaluation, reporting, and dissemination of the condition of the aquatic environment. Major objectives of water quality assessment are describing water quality at regional or national scales, investigating spatial-temporal trends and determining if the water quality meets previously defined objectives for designated uses etc (World Bank 2003; Ouyang 2005).

Long term ambient water quality monitoring provides historical database that can be used by the institutions at all levels of society to evaluate water quality (Yake 1979). Non-parametric statistical methods including trend analysis and multidimensional scaling are increasing in use to transfer of complex data to information, which is useful to water managers to assess water quality and develop object oriented management plans. Non-parametric tests are applied when the data is incomplete or a significant amount of the data is missing (Naddeo et al. 2007).

This study attempts to evaluate effectiveness of water quality management programs in Tahtali River Basin, Turkey by applying statistical methods to multidimensional data set comprising chemical water quality parameters. In this scope, box plots were plotted to provide a visual impression of the location and shape of the underlying distributions. 'Mann-Kendall' test was used to evaluate whether a significant increase or decrease for each water quality parameter occurred. When a significant trend was found for a specific parameter, a second statistic- 'Sen's Slope estimator' was applied to estimate the slope (unit change per time period) or the magnitude of the trend. Finally, 'multidimensional scaling' was performed to reduce the dimensionality of the data set to a sufficiently small value to allow visual inspection of the set.

Materials and Methods

Tahtali Basin is located in the southern part of the City of Izmir in western part of Turkey and has about 550 km^2

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drainage area. Location of the basin is shown in Fig. 1. Seventy percent of the total basin is covered with forest and another 18% with agricultural land. The climate of the region is typical Mediterranean: hot and dry in summers, and temperate and rainy in winters. The Tahtali Basin has long been subjected to rapid increases in population since 1990s. There are about 30 settlements in the basin where about 60,000 people live in the catchment area as of 2000. Most of these settlements have completed sewage systems and collected wastewaters are discharged out of the basin after being treated at central wastewater treatment plant. On the other hand, the wastewaters of those having incomplete infrastructure system are collected by sewage trucks in charge of local authorities and transferred to the central treatment plant. Therefore, presently domestic discharges in the region are not considered as serious pollution threat (Boyacioglu 2007).

The river water quality in the region has been monitored at seven monitoring sites (see Fig. 1). In the study, statistical analysis techniques were applied to data sets comprising chloride, nitrate-nitrogen, sodium, sulfate and total dissolved parameters observed at these sites semi-monthly along 6 years.

In the scope of statistical analysis firstly box plots of individual variables were examined. Box plots provide a visual impression of the location and shape of the underlying distributions (Vega et al. 1998). Furthermore water quality classes for each variable were identified by comparing characteristic values of data sets with the existing standard-Turkish Water Pollution Control Regulation (WPCR). According to the Turkish legislation, water quality of inland waters is classified into four groups as: high quality waters (Class I), moderate quality waters (Class II), polluted waters (Class III), and highly polluted waters (Class IV). This classification is based on the assessment of about 45 water quality parameters including

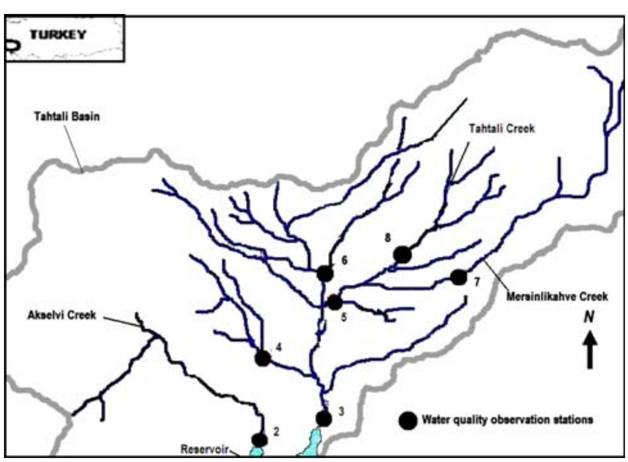

Fig. 1 Tahtali Basin river water quality monitoring stations

but not limited to: total dissolved solids-TDS, sodium-Na^+, chloride Cl^-, sulfate-$SO_4{}^{2-}$ and nitrate-nitrogen-NO_3–N (Official Gazette 2004).

After the general assessment, the main objective of the study was to find an answer to the question of, "whether water quality is getting better or worse over time for the parameters under consideration along 6 years". To answer the question, two statistical tests namely Mann-Kendall test and Sen's Slope estimator were applied using 'Minitab 13' (Minitab Statistical Software 2000). Mann-Kendall test is a signed rank test and assumes no particular distribution for the data. It is based on the difference between the numbers of pairwise differences (number of positive signs minus that are negative). If the difference is a large positive value, then there is evidence of an increasing trend in the data and if it is a large negative value, then there is evidence of a decreasing trend. The null hypothesis or baseline condition for this test is that there is no temporal trend in the data values. The alternative hypothesis is that of either an upward trend or a downward trend. The null hypothesis (there is no trend) is rejected when the computed z value is greater than z_α where α is level of statistical significance. Sen's Slope estimator is an alternative for estimating a slope. This approach involves computing slopes for all the pairs of time points and then using the median of these slopes as an estimate of the overall slope. If there is no underlying trend, there will be an approximately equal number of positive and negative slopes, and thus the median will be near zero (King County 2001).

What is more, multidimensional scaling (MDS) was performed to reduce the dimensionality of the data set to a sufficiently small value to allow visual inspection of the set using 'SPSS 10.0' (Statistical Package for the Social Sciences 2000). MDS describes a family of techniques for the analysis of proximity data on a set of stimuli to reveal the hidden structure underlying the data. The main assumption in the method is that:

- stimuli can be described by values along a set of dimensions that places these stimuli as points in a multidimensional space and
- the similarity between stimuli is inversely related to the distances of the corresponding points in the multidimensional space (Steyvers 2001; USEPA 1998).

Results and Discussion

In the study, firstly in order to define the water quality classes, characteristic values of data sets comprising chloride, nitrate-nitrogen, sodium, sulfate and total dissolved solid parameters analyzed at water samples taken from Tahtali Basin, Turkey for 6 years were compared

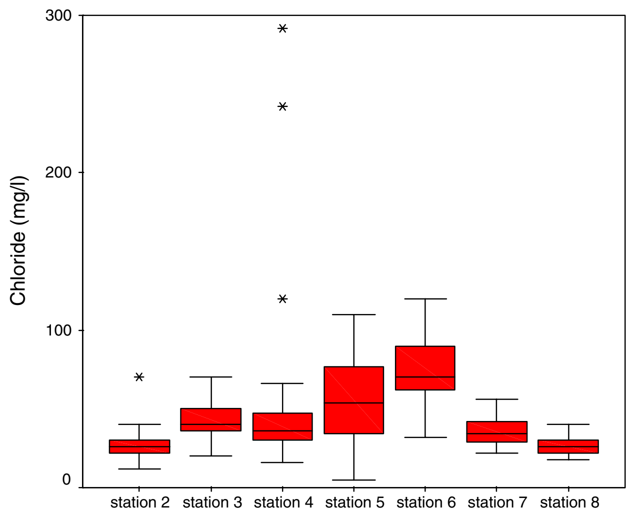

Fig. 2 Box diagram for chloride

with the existing standard-Turkish WPCR. Moreover, trend analysis and multidimensional scaling methods were applied to determine temporal changes of chemical variables. Finally, multidimensional scaling was performed to indicate similarities in data set.

Descriptive statistics (minimum, maximum, mean, 25th percentile, 75th percentile and extreme values) are depicted in box diagrams plotted for each parameter (Figs. 2–6). According to Turkish WPCR, water quality classification study results (based on confidence intervals of the medians at 95% significance level) revealed that surface water of Tahtali Basin mainly belonged to Class I (high quality water) for all the parameters except chloride and nitrate-nitrogen. For both variables, surface water generally felled to moderate (Class II) water quality class in the region (see Table 1). In addition, relatively high concentrations were

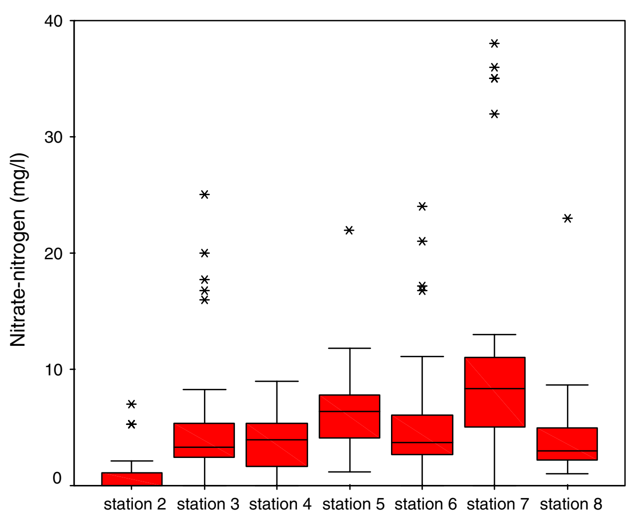

Fig. 3 Box diagram for nitrate-nitrogen

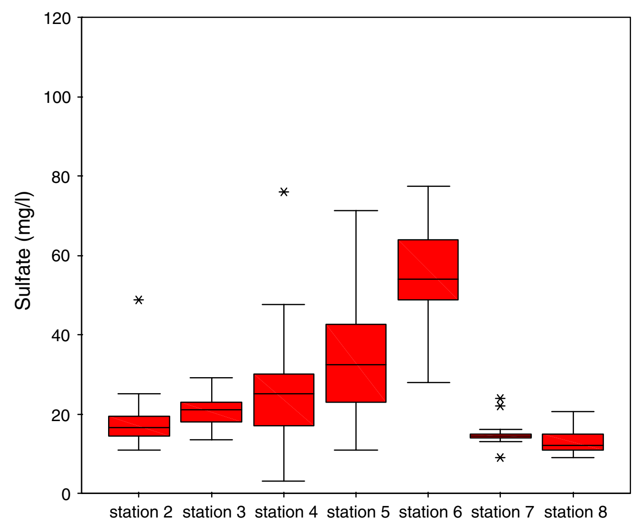

Fig. 5 Box diagram for sulfate

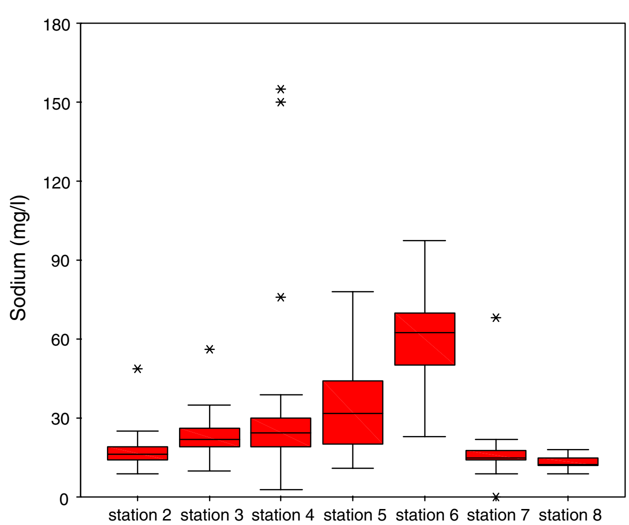

Fig. 4 Box diagram for sodium

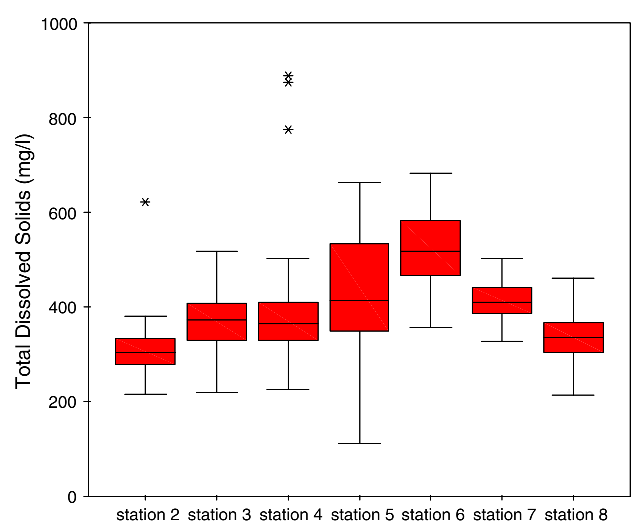

Fig. 6 Box diagram for total dissolved solids

Table 1 Water quality data confidence intervals of the median at 95% significance level

Parameter (unit)	Stations	Confidence Interval	Limit values of the parameters (referred to WPCR)	
			Class I	Class II
Cl^- (mg/L)	2	24.00–28.00	25	200
	3	39.65–46.00		
	4	32.00–40.00		
	5	50.00–66.00		
	6	70.00–80.00		
	7	34.00–38.00		
	8	24.00–28.00		
NO_3–N (mg/L)	2	0.31–1.00	5	10
	3	3.39–4.32		
	4	2.96–4.00		
	5	5.32–7.00		
	6	3.55–4.67		
	7	7.42–9.00		
	8	2.82–3.46		
Na^+ (mg/L)	2	15.00–17.00	125	125
	3	21.00–23.00		
	4	21.00–25.00		
	5	30.00–43.34		
	6	55.88–65.00		
	7	15.00–16.66		
	8	12.00–13.00		
SO_4^{2-} (mg/L)	2	31.00–41.00	200	200
	3	41.70–49.00		
	4	31.00–40.00		
	5	35.00–49.00		
	6	47.35–57.00		
	7	22.21–34.79		
	8	22.00–29.00		
TDS (mg/L)	2	289.00–310.30	500	1500
	3	359.00–398.30		
	4	340.90–372.00		
	5	388.50–471.80		
	6	487.50–522.40		
	7	404.10–432.90		
	8	322.00–350.30		

Table 2 Mann-Kendall test results (Boyacioglu 2007)

Variable	Station	Calculated z score	$z_{0.95}$	Significant trend
Cl^-	2	1.3064	1.645	
	3	1.8122		Yes
	4	0.5538		
	5	2.3214		Yes
	6	0.5992		
	7	1.0012		
	8	0.2846		
NO_3–N	2	2.4528	1.645	Yes
	3	0.1886		
	4	0.8001		
	5	1.4799		
	6	3.0545		Yes
	7	1.4382		
	8	0.0127		
Na^+	2	0.6560	1.645	
	3	1.6773		Yes
	4	0.4367		
	5	2.4855		Yes
	6	3.5446		Yes
	7	1.7601		Yes
	8	1.5852		
SO_4^{2-}	2	0.6003	1.645	
	3	0.6080		
	4	0.7923		
	5	1.4231		
	6	0.1981		
	7	1.5188		
	8	1.9445		Yes
TDS	2	1.7698	1.645	Yes
	3	2.7704		Yes
	4	0.4164		
	5	0.7516		
	6	2.2103		Yes
	7	1.4213		
	8	1.3640		

recorded for the parameters under consideration at the stations located at northern part of the basin (Stations 5, 6 and 7).

Results of Mann-Kendall test applied to determine trends over time are presented in Table 2. Test statistics (z scores) were calculated and critical z value at 5% significance level (1.645) was taken from the standard normal distribution table. Sen's slopes of the parameters showing significant trend (the parameters of which calculated z score is greater then $z_{0.95}$) are given in Table 3. A trend with a negative slope indicates that the concentration is declining. Mann-Kendall test and Sen's Slope estimator results, which is summarized in Table 4 revealed whether water quality generally improved over time or did not change in the basin.

Furthermore, in order to visualize the similarities in data set (Goodness of fit of the configuration to the dissimilarities was measured by Kruskal's stress coefficient). multidimensional scaling was performed. As seen at Euclidean distance model (see Fig. 7), observation stations showed similar characteristics for the parameters total

Table 3 Sen's Slopes of the data sets (Boyacioglu 2007)

Variable	Station	Trend direction	Sen's slope
Cl^-	3	Down	−0.1290
	5	Up	0.1667
NO_3–N	2	Up	0.0050
	6	Down	−0.0190
Na^+	3	Down	−0.0694
	5	Up	0.1515
	6	Down	−0.1962
	7	Down	−0.0313
SO_4^{2-}	8	Up	0.5157
TDS	2	Down	−0.375
	3	Down	−1.1364
	6	Down	−0.8268

Table 4 Water quality trends in Tahtali Basin

Variable	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7	Station 8
Cl^-	0	+	0	−	0	0	0
NO_3–N	−	0	0	0	+	0	0
Na^+	0	+	0	−	+	+	0
SO_4^{2-}	0	0	0	0	0	0	−
TDS	+	+	0	0	+	0	0

+: improving trend, −: deteriorating trend, 0: no change

dissolved solids, sodium and chloride. On the other hand, sulfate and nitrate-nitrogen caused differences in terms of water quality between these sites.

Total dissolved solids represent the amount of inorganic substances (i.e. sodium, chloride, sulfate) that are dissolved in the water (Harley 2002). In surface waters, sodium and chloride are tightly linked. They both originate from natural weathering of rock and from atmospheric transport of oceanic inputs and from a wide variety of anthropogenic sources. On the other hand, the anthropogenic sources of sodium and chloride are so pervasive that concentrations of sodium and chloride have risen by a factor of 10–20 in many rivers in the world (GEMS 2007). Sulfate enters surface waters from groundwater, the oxidation of sulfide minerals during chemical weathering, atmospheric deposition from acid rain, human and animal waste, farming, and industrial processing and manufacturing (Souligny 2001). Common source of nitrate and in water are runoff from fertilizer use, leaching from septic tanks, sewage and erosion of natural deposits etc. (USEPA 2003).

Based on applied statistical analysis tests results, considering the occurrence of these variables in surface water and evaluation of conditions in the region, it was concluded that agricultural discharges caused spatial differences in terms of surface water quality. This statement can be

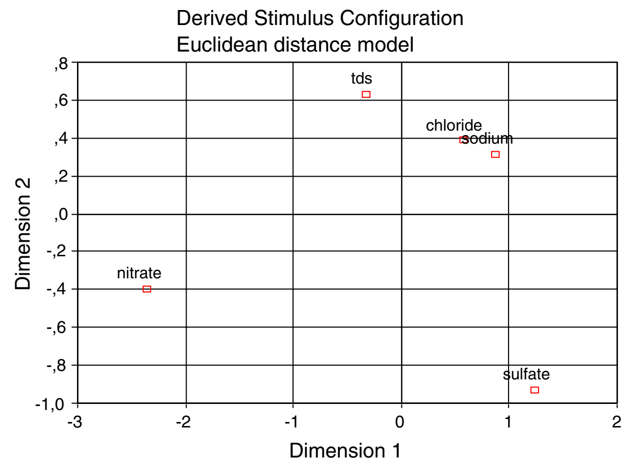

Fig. 7 Euclidean distance model

explained by discrimination of nitrate parameter in two-dimensional scale and belonging of water quality into Class II in northern part, where agricultural activities were intensively practiced.

In summary, Tahtali Basin surface water quality predominantly belonged to high quality water class that supports drinking water supply for the parameters mainly found in the water naturally. Furthermore, primarily agricultural land uses control the surface water quality in the region. This study showed that statistical methods that are performed to investigate the temporal changes and data grouping techniques help decision makers to judge effectiveness of water management programs and allow visual inspection of the data set by reducing the dimensionality.

Acknowledgements The authors express their special thanks to members of the Izmir Water and Sewerage Authority (IZSU) for their assistance in providing necessary data for the study.

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