SPATIAL DIFFERENTIATION OF WATER QUALITY BETWEEN RESERVOIRS UNDER ANTHROPOGENIC AND NATURAL FACTORS BASED ON STATISTICAL APPROACH

HÜLYA BOYACIOGLU

Dokuz Eylül University, Department of Environmental Engineering, Tinaztepe Campus Buca, 35160 Izmir, Turkey
Corresponding authors e-mail: hulya.boyacioglu@deu.edu.tr

Keywords: Discriminant analysis, source identification, surface water quality, trend analysis.

Abstract: This study illustrates the benefits of statistical techniques to analyze spatial and temporal variations in water quality. In this scope water quality differentiation caused by anthropogenic and natural factors in the Tahtali and Balçova reservoirs in western Turkey was investigated using discriminant analysis-DA, Mann Whitney U techniques. Effectiveness of pollution prevention measures was analyzed by Mann Kendall and Sen’s Slope estimator methods. The water quality variables were divided into three groups as physical-inorganic, organic and inorganic pollution parameters for the study. Results showed that water quality between reservoirs was differentiated for “physical-inorganic” and “organic pollution” parameters. Degree of influence of water quality by urbanization was higher in the Tahtali reservoir and in general, no trend detection at pollution indicators explained by effective management practices at both sites.

INTRODUCTION

Discharges originating from domestic, industrial and agricultural activities degrade surface water quality and impair their use [21]. Rivers are water bodies most vulnerable to pollution due to their role in transporting point and non-point discharges in their vast drainage basins. Accordingly, reservoirs constructed across the rivers are vulnerable to pollution [12, 15, 27].

There are several studies focusing on a relationship between water quality and urban development in the literature [6, 7, 10, 11, 13, 22, 24 and 25]. Ren et al. (2003) revealed that rapid urbanization corresponded with rapid degradation of water quality. Urban land uses were positively correlated with the decline in water quality. Similarly, Quang et al. (2006) found out that there was a positive correlation between the rapidity of urbanization and the pollution levels of urban river water. Compared to the rural river water, urban river water was polluted more seriously.

Due to spatial and temporal variations of surface water quality caused by natural and anthropogenic factors, a monitoring program providing a representative and reliable
estimation is necessary. Various methods can be applied to characterize and evaluate freshwater sources by interpreting complex water quality data sets created by long-term monitoring programs [27].

Since the state of an ecosystem is dependent simultaneously on many factors and parameters, these systems are multivariate in nature [16]. Therefore the interpretation of the monitoring data sets has to be performed by use of the multivariate statistical methods rather than univariate.

In recent years, a wider use of multivariate statistical methods has been made in the analysis of environmental data. These methods were proved as useful tools to extract the meaningful information from data sets [12, 15, 18, 27, 28 and 29]. The goal of the environmetric interpretation is a) to identify similarity-dissimilarity between data sets, b) to detect hidden factors responsible for the data structure c) to reveal discriminating parameters etc.

In the present study, water quality data sets obtained from two reservoirs in Izmir, Turkey on a semimonthly/monthly basis for three years were subject to examination by statistical techniques. The objective was to a) investigate dissimilarities between reservoirs b) determine parameters discriminating water quality c) analyze water quality trends d) detect actual or potential water quality problems; if such problems exist. Overall aim of the study was investigation of water quality differentiation caused by anthropogenic factors and examination of effectiveness of management practices using statistical tools.

STUDY AREA

Tahtali and Balcova reservoirs are used to supply drinking water to Izmir, the third largest metropolitan area with over 3 million population in western Turkey (Fig. 1). Balcova reservoir is located on Ilıca Creek with 41.6 km² catchment area. Reservoir capacity at normal water surface elevation is 8 million m³. Land use in the region is dominated by forests. Furthermore, Tahtali Reservoir is fed by the Tahtali Creek having about 550 km² drainage area and has the capacity to generate 175 million m³ water. 42.1% of the basin is covered by forest, 31.8% of the area is composed of agricultural land, 0.2% of the area is industrial area and 1.8% of the basin is residential area. The climate of the region is typically Mediterranean: hot and dry in summers and temperate and rainy in winters [9, 5 and 19]. Balcova and Tahtali Reservoirs are operated by Izmir Water and Sewerage Authority (IZSU) and all the activities in these basins are controlled by the same agency to protect water quality.

METHODOLOGY

In the study, water quality samples obtained from Tahtali and Balcova reservoirs on a semimonthly/monthly basis for three years were subject to examination by dicriminant analysis-DA, Mann Whitney U test, Mann Kendall test and Sen’s Slope estimator techniques. Sampling was repeated from abstraction structures and water quality samples were analyzed for physical-inorganic (Cl, NO₃-N, pH, DO, color, SO₄ and TDS), organic (BOD and COD) and inorganic pollution (Al, Fe, Mn, Cu, Ba, B and Zn) parameters at the laboratory using standard methods [2].
Discriminant analysis and Mann Whitney U test

DA is a statistical method used to determine the variables discriminating between two or more naturally occurring groups. It operates on raw data and the technique constructs a discriminant function (DF). In forward stepwise mode DA, variables are included step-by-step beginning with the more significant until no significant changes are obtained, whereas, in backward stepwise mode DA, variables are removed step-by-step beginning with the less significant until no significant changes are obtained [17]. The objectives of the method can be summarized as:

- **description of group separation:** linear functions of the several variables (discriminant functions-DFs) are used to describe the differences between two or more groups and identifying the relative contribution of all variable for separation of the groups.
- **prediction or allocation of observations to group:** linear or quadratic functions of the variable (classification functions – CFs) are used to assign an observation to one of the groups [1].

The Mann-Whitney U test is a non-parametric significance test used to investigate whether the differences between two data sets are really significant or not. The null hypothesis is that both samples are drawn from populations with the same distributions. The alternative hypothesis is that the parent populations from which the samples are taken
have different medians. The method assumes that the distributions have the same form but have different medians [23].

**Trend analysis**

Trend detection of water quality variables is a critical step in assessing the environmental condition of a given system. For example, positive identification of contaminant concentration trends can assist in both proving plume migration and demonstrating evidence of contaminant degradation [4].

Mann Kendall Test is a non-parametric statistical test used to assess trends in data sets. The rank-based non-parametric Mann-Kendall has been commonly used to assess the significance of trends in hydro-meteorological time series (such as water quality, stream flow, temperature and precipitation). The main advantage of the method is that compared with parametric statistical tests, the non-parametric tests are thought to be more suitable for non-normally distributed data [26]. It is based on the difference between the numbers of pairwise differences (number of positive signs minus those that are negative). If the difference is a large positive/negative value, then there is evidence of an increasing/decreasing trend in the data. The null hypothesis 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 $z_a$ where “a” is the level of statistical significance [3].

One of the difficulties in the interpretation of environmental field data is the quantification of trends (e.g. calculation of slope). Sen’s Slope estimator is a non-parametric method used in determining the presence of slope. The method requires a time series of equally spaced data. It proceeds by calculating the slope as a change in measurement per change in time [4]. The Sen’s Slope estimator is the median of all pair wise slopes in the data set [8].

**RESULTS**

In the study, water quality variables were divided into three groups as:

- **physical-inorganic** (Cl, NO$_3$-N, pH, DO, color, SO$_4$ and TDS),
- **organic** (BOD and COD) and
- **inorganic pollution** (Al, Fe, Mn, Cu, Ba, B and Zn) parameters.

Statistical methods were performed using SPSS 15, Minitab 15 and NCSS 2000 software packages and analysis results were presented for each group separately.

Descriptive statistics of variables were given in Table 1.

**Physical inorganic parameters**

The objective of discriminant analysis-DA performed for physical-inorganic parameters was to determine the most significant variables associated with the differences between reservoirs.

Homogeneity of variances was checked using Box M test. Based on the result it was concluded that the null hypothesis stating there was no differences between variances of groups was accepted (p=0.229 and >0.05). Therefore, the variances were equal and the prerequisite of discriminant analysis was met.

As was presented in Table 2, the value of Wilks’ lambda for the discriminant function was quite small (0.100). This suggested that DA for this group of variables was valid and
effective. Moreover, classification function-CF’s coefficients given in Table 3 showed that DA gave the best result to identify the relative contribution for all parameters in discriminating (distinguishing) the two reservoirs (affording 100% correct assignations). F-test was also conducted to identify the most discriminating variables. Results indicated that all the discriminant variables were significant except SO_4 and NO_3 (p>0.05) to distinguish both reservoirs (see Table 4). Therefore two reservoirs were discriminated using one discriminant function-DF which was defined by five (discriminant) variables (SO_4 and NO_3 were not included). The standardized DF was created using the discriminant procedure in SPSS 15.

DF: 0.968 (Cl) – 0.395 (pH) – 0.032 (DO) – 0.173 (color) – 0.024 (TDS)

The relationship between the discriminant variables and the function was also represented by pearson coefficients and presented in Table 5. Based on the coefficients it can be concluded that Cl was the most important variable discriminating between reservoirs. The order of inclusion in the model was Cl, color, pH, DO and TDS.

The effectiveness of pollution prevention programs in the region was examined using trend analysis. Mann-Kendall test results presented in Table 6 showed upward trend for the parameters Cl and SO_4 in the Tahtali reservoir. In contrast no upward trend was observed in the Balcova reservoir.

It is known that increasing concentrations of sodium and chloride in surface water are strongly related to urbanization and population density. They can have a significant impact on drinking water and salinity of aquatic ecosystems [20]. Therefore increasing trend for Cl in the Tahtali reservoir was explained by impact of urbanization on surface water quality in the region.
Table 2. Test results for discriminant function created for physical-inorganic variables

| Value                  |       |
|------------------------|-------|
| Eigenvalue             | 8.999 |
| Canonical correlation  | 0.949 |
| Wilks lambda-λ         | 0.100 |
| Chi-square             | 60.996|
| p                      | 0.000 |
| % of variance          | 100   |

Table 3. Classification function coefficients and % correct values

| Tahtali reservoir | Balcova reservoir |
|-------------------|-------------------|
| Cl                | -3.415            | -8.646            |
| NO3-N             | 72.811            | 78.135            |
| PH                | 416.948           | 435.598           |
| DO                | -14.996           | -14.839           |
| Colour            | -8.451            | -8.533            |
| SO4               | 1.026             | 2.533             |
| TDS               | -0.149            | -0.218            |
| Constant          | -1544.586         | -1606.169         |
| % correct         | 100               | 100               |
| Total % correct   | 100               |                   |

Table 4. Wilks’ lambda and p values for physical-inorganic parameters

| Discriminant variable | Wilks’ Lambda | p   |
|-----------------------|---------------|-----|
| Cl                    | 0.158         | 0.00|
| NO3-N                 | 1.000         | 0.93|
| PH                    | 0.783         | 0.01|
| DO                    | 0.824         | 0.02|
| Color                 | 0.564         | 0.00|
| SO4                   | 0.918         | 0.11|
| TDS                   | 0.879         | 0.05|

Table 5. Structure matrix for physical-inorganic parameters

| Discriminant variable | Pearson coefficients |
|-----------------------|----------------------|
| Cl                    | 0.88                 |
| Color                 | -0.34                |
| pH                    | -0.20                |
| DO                    | -0.18                |
| TDS                   | -0.14                |
Organic variables
In the study due to high correlations between BOD and COD, discriminant analysis could not be applied. Instead, Mann-Whitney U-test was performed to examine if the differences between two reservoirs for this group of variables were really significant. Based on the Mann-Whitney U-test results given in Table 7, it was concluded that the difference between two reservoirs regarding organic pollutants was statistically significant (p ≤ 0.05). Concentrations at Tahtali Reservoir were slightly higher (see Table 1).

Additionally significance of trends was tested using the non-parametric Mann-Kendall test. Magnitude of the detected trend was investigated. Results showed that there was no trend at both sites. The result was evidence of effective pollution control measures taken by local authorities.

Table 7. Mann-Whitney U test results

| Variable | p   |
|----------|-----|
| BOD      | 0.01|
| COD      | 0.05|

Inorganic pollution variables
Results of the DA applied to inorganic pollution parameters (Al, Fe, Cu Mn Ba, B, Zn and F) showed that there was no significant function for differentiating water quality for this group of variables (p > 0.05) (Table 8).

The second step of statistical analysis was examination of trends. Mann Kendall test results and Sen’s Slope estimators for inorganic pollution parameters presented in Table 9 revealed that there was no significant increasing trend in variables.
Heavy metals in surface water originate from direct inputs (wastewater treatments, industry) but also from nonpoint sources including the contribution from groundwater and, initially leaching from soils to groundwater. The magnitude of the pathway soil – groundwater-surface water remains largely unknown but is believed to be quite substantial for such elements as Cd, Cu and Zn [14].

These statements and results of the trend analysis yielded that measures taken by local authorities to prevent inorganic pollutant inputs to surface water in the region were effective.

Table 8. Test results for discriminant function created for inorganic pollution variables

| Value               | Value |
|---------------------|-------|
| Eigenvalue          | 0.449 |
| Canonical correlation| 0.310 |
| Wilks lambda-λ      | 0.690 |
| p                   | 0.225 |

Table 9. Mann Kendall test results and Sen’s Slope estimators for inorganic pollution parameters

| Variable | Reservoir | Trend detection | Sen’s slope |
|----------|-----------|-----------------|-------------|
| Al       | Tahtali   | –               |             |
|          | Balcova   | –               |             |
| Fe       | Tahtali   | –               |             |
|          | Balcova   | –               |             |
| Mn       | Tahtali   | –               |             |
|          | Balcova   | –               |             |
| Cu       | Tahtali   | up              | 0.0003      |
|          | Balcova   | –               |             |
| Ba       | Tahtali   | –               |             |
|          | Balcova   | –               |             |
| B        | Tahtali   | –               |             |
|          | Balcova   | –               |             |
| Zn       | Tahtali   | up              | 0.0007      |
|          | Balcova   | up              | 0.0035      |
| F        | Tahtali   | –               |             |
|          | Balcova   | –               |             |

CONCLUSION

In the study discriminant analysis, Mann Whitney U tests, Mann Kendal test and Sen’s Slope estimator techniques were applied to investigate water quality differentiation caused by anthropogenic and natural factors between Tahtali and Balçova reservoirs in western Turkey. These techniques were performed for three groups of variables:
physical-inorganic (Cl, NO$_3$-N, pH, DO, color, SO$_4$ and TDS), organic (BOD, COD) and inorganic pollution (Al, Fe, Mn, Cu, Ba, B and Zn) parameters separately. Test results for physical-inorganic variables showed that Cl was the most important parameter discriminating between Tahtali and Balcova reservoirs. In contrast, SO$_4$ and NO$_3$ were not significant to distinguish between both reservoirs. Among the organic pollution parameters, difference for COD and BOD levels was statistically significant at both sites. Furthermore, there was no significant function differentiating water quality for inorganic pollution parameters. Increasing trend for Cl and also slightly higher concentrations observed for the variables discriminating reservoirs was explained by negative effects of urbanization to the Tahtali reservoir water quality. Since the Tahtali region is more populated compared to Balcova basin the result was reasonable. In general no trend in pollution indicators at both sites was indication of effective management practices by local authorities. The main outcome of the study is that statistical methods are successful tools to investigate spatial and temporal changes in water quality and to determine priorities in management activities.

ACKNOWLEDGEMENTS
The author wish to thank to members of the Izmir Water and Sewerage Authority (IZSU) for their assistance in providing necessary data for the study.

REFERENCES
[1] Alkarkhi, A.F.M., Ahmad, A., Ismail, N., Easa, A. & Omar, K. (2008). Assessment of surface water through multivariate analysis, *Journal of Sustainable Development*, 1, 3 27–33.
[2] APHA (2005). Standard methods for the examination of water and waste water. 21st edition, American Public Health Association, Washington 2005.
[3] Boyacioglu, H. & Boyacioglu, H. (2008). Investigation of temporal trends in hydrochemical quality of surface water in Western Turkey, *Bulletin of Environmental Contamination and Toxicology*, 80, 469–474.
[4] Brauner, J.S. (2012). Non-parametric estimation of Slope: Sen’s method in environmental pollution. Environmental sampling and monitoring primer, accessed on 25 june 2012 from http://www.webapps.cee.vt.edu/ewr/environmental/teach/smprimer/sen/sen.html.
[5] Caliskan, A. (2008). Modelling of hydrodynamics and sedimentation in a stratified reservoir: Tahtali Reservoir, Izmir, Master thesis, The Graduate School of Engineering and Sciences of Izmir Institute of Technology 2008.
[6] Feng, H., Han, X.F., Zhang, W.G. & Yu, L.Z. (2004). A preliminary study of heavy metal contamination in Yangtze River intertidal zone due to urbanization, *Marine Pollution Bulletin*, 49, 910–915.
[7] Fisher, D.S., Steiner, J.L., Endale, D.M., Stuedemann, J.A., Schomberg, H.H., Franzluebbers, A.J. & Wilkinson, S.R. (2000). The relationship of land use practices to surface water quality in the Upper Oconee Watershed of Georgia, *Forest Ecology and Management*, 128, 39–48.
[8] Hirsch, R.M., Alexander, R.B. & Smith, R.A. (1991). Selection of methods for the detection and estimation of trends in water quality, *Water Resources Research*, 27, 5, 803–813.
[9] Karadas, D. & Elci, A. (2009). Modeling of the Izmir-Tahtali Lake buffer zones supported by GIS in terms of groundwater contaminant. Proceedings of Congress on Geographical Information Systems. 2009. Organised by Union of Chambers of Turkish Engineers and Architects.
[10] LeBlanc, R.T., Brown, R.D. & Fitz Gibbon, J.E. (1997). Modeling the effects of land use change on the water temperature in unregulated urban streams, *Journal of Environmental Management*, 49, 445–469.
[11] Ouyang, T., Zhu, Z., Kuang, Y. (2006). Assessing impact of urbanization on river water quality in the Pearl River Delta Economic Zone, China, *Environmental Monitoring and Assessment*, 120, 1–3, 313–325.
[12] Pejman, A.H., Nabi Bidhendi, G.R., Karbassi, A.R., Mehrdadi, N. & Esmaeili Bidhendi, M. (2009). Evaluation of spatial and seasonal variations in surface water quality using multivariate statistical techniques, *International Journal of Environmental Science and Technology*, 6, 3, 467–476.
[13] Ren, W.W., Zhong, Y., Meligrana, J., Anderson, B., Watt, W.E., Chen, J.K. & Leung Hok-Lin. (2003), Urbanization, land use, and water quality in Shanghai 1947–1996, Environment International, 29, 649–659.

[14] Rômkens, P.F.A.M. (2002). Contribution of agriculture to the heavy metal loads of Dutch surface waters, Agricultural Effects on Ground and Surface Waters: Research at the Edge of Science and Society, Proceedings of a symposium held at Wageningen, October 2000, IAHS Publ. no. 273.

[15] Shrestha S. & Kazama F. (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan, Environmental Modelling & Software, 22, 464–475.

[16] Simeonov, V., Simeonova, P., Tsakovski, S. & Lovchinov, V. (2010). Lake water monitoring data assessment by multivariate statistics, Journal of Water Resource and Protection, 2, 353–361.

[17] Singh, K.P., Amalik, A. & Singh, V.K. (2006). Chemometric analysis of hydro-chemical data of an alluvial river: A case study, Water Air & Soil Pollution, 170, 1–4, 383–404.

[18] Sojka, M., Slepak, M., Ziola, A., Frankowski, M., Blazejewska, S.M. & Siepak, J. (2008). Application of multivariate statistical techniques to evaluation of water quality in the Mala Welna River (Western Poland), Environmental Monitoring and Assessment, 147, 1–3, 159–170.

[19] State Hydraulic Works, (2012), Balcova Reservoir, http://www.dsi.gov.tr (16.06.2012).

[20] Steele, M. & Aitkenhead-Peterson, J.A. (2010). Long-term sodium and chloride surface water exports from a humid subtropical urban gradient, American Geophysical Union, Fall Meeting 2010, abstract #B43A-0447.

[21] Su, S., Zhi, J., Lou, L., Huang, F., Chen, X., Wu, J., (2010). Spatio-temporal patterns and source apportionment of pollution in Qiantang River (China) using neural-based modeling and multivariate statistical techniques, Physics and Chemistry of the Earth, Parts A/B/C (in press).

[22] Tang, Z., Engel, B.A., Pijanowski, B.C. & Lim, K.J. (2005). Forecasting land use change and its environmental impact at a watershed scale, Journal of Environmental Management, 76, 35–45.

[23] USEPA, (2000), United States Environmental Protection Agency. Nutrient Criteris Technical Guidance Manual. Rivers and streams. EPA-822-B-00-002.

[24] Wang, J., Da, L., Song, K. & Li, B.L. (2008). Temporal variations of surface water quality in urban, suburban and rural areas during rapid urbanization in Shanghai, China, Environmental Pollution, 152, 387–393.

[25] Yin, Z.Y., Walcott, S., Kaplan, B., Cao, J., Lin, W.Q., Chen, M.J., Liu, D.S. & Ning, Y.M. (2005). An analysis of the relationship between spatial patterns of water quality and urban development in Shanghai, China, Computers. Environment and Urban Systems, 29, 197–221.

[26] Yue, S., Pilon, P. & Cavadias, G. (2002). Power of the Mann-Kendall and Spearman’s rho tests for detecting monotonic trends in hydrological series, Journal of Hydrology, 259, 1–4, 254–271.

[27] Zhang, Q., Li, Z., Zeng, G., Li, J., Fang, Y., Yuan, Q., Wang, Y. & Ye, F. (2009). Assessment of surface water quality using multivariate statistical techniques in red soil hilly region: a case study of Xiangjiang watershed, China, Environmental Monitoring and Assessment, 152, 123–131.

[28] Zhao, J., Fu, G., Lei, K. & Li, Y. (2011). Multivariate analysis of surface water quality in the Three Gorges area of China and implications for water management, Journal of Environmental Sciences, 23, 9, 1460–1471.

[29] Zhou, F., Liu, Y. & Guo, H. (2007). Application of multivariate statistical methods to water quality assessment of the watercourses in Northwestern New Territories, Hong Kong, Environmental Monitoring and Assessment, 132, 1–3, 1–13.