

Application of environmetric methods to investigate control factors on water quality

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Abstract: In the study, environmetric methods were successfully performed a) to explore natural and anthropogenic controls on reservoir water quality, b) to investigate spatial and temporal differences in quality, and c) to determine quality variables discriminating three reservoirs in Izmir, Turkey. Results showed that overall water quality was mainly governed by “natural factors” in the whole region. A parameter that was the most important in contributing to water quality variation for one reservoir was not important for another. Between summer and winter periods, difference in arsenic concentrations were statistically significant in the Tahtalı, Ürkmez and iron concentrations were in the Balçova reservoirs. Observation of high/low levels in two seasons was explained by different processes as for instance, dilution from runoff at times of high flow seeped through soil and entered the river along with the rainwater run-off and adsorption. Three variables “boron, arsenic and sulphate” discriminated quality among Balçova & Tahtalı, Balçova & Ürkmez and two variables “zinc and arsenic” among the Tahtalı & Ürkmez reservoirs. The results illustrated the usefulness of multivariate statistical techniques to fingerprint pollution sources and investigate temporal/spatial variations in water quality.

Introduction

The state of water quality is the result of complex natural and man-made conditions and the consequent interactions in both time and space. Accordingly, abstracting the essence of water quality conditions is often very difficult. The purpose of monitoring is generally laid down by directives, water quality standards, action plans etc. and aim at assessing the environmental state and detecting trends (EEA 2011). Due to spatial and temporal variations in quality, a monitoring program, providing a representative and reliable estimation of the surface waters is necessary. Various methods can be applied to characterize and evaluate freshwater sources by interpreting complex data sets, created by long-term water quality monitoring programs (Zhang et al. 2009). Since the state of an ecosystem is dependent simultaneously on many factors and parameters, these systems are multivariate in nature (Simeonov et al. 2010). Therefore the interpretation of the monitoring data sets has to be performed by use of the multivariate statistical methods rather than univariate (Voza et al. 2015).

In the present study, a data matrix obtained from three reservoirs “Tahtalı, Balçova and Ürkmez” in Izmir, Turkey, during 4 years of monitoring program, on monthly basis, was subjected to different environmetric techniques. Overall objective of the study was a) to extract parameters that are

most important in assessing variation in water quality, b) to investigate seasonal differences in water quality, c) to investigate dissimilarities between reservoirs, and d) to determine parameters discriminating water quality. In this scope the data sets were subjected to principal component analysis, Student's t-test and discriminant analysis.

Study Area

Tahtalı, Balçova and Ürkmez reservoirs provide drinking water to the city of Izmir, the third largest metropolitan area in Turkey with a population of over 3 million. Tahtalı Basin covers an area of approximately 550 km² and the capacity of the reservoir located within the basin is 285 million m³ providing about 5 million m³ water per month. 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% is residential area. Balçova Reservoir is located on Ilıca River with the capacity of 7.6 million m³ and produces about 1.2 million m³ water per month to the city (as of May–August 2015). Land use structure in the Balçova Basin is as follows: forested area – 26.8%, urban settlement area – 48.4%, greenhouse agriculture 3.8%, citrus-fruit orchards 11.8% and other uses (olive growth, rainfed agricultura etc.) (Bolca et al. 2007). Ürkmez Reservoir with 30.81 km² drainage area has 8.25 million m³ water storage capacity. On average 1.5 million m³ water per month is generated from the reservoir

(as of August–October 2015). Land use distribution in the region is 41.2% forest, 34.2% pasture, 13.7% agricultural land, 9.7% settlement and water body 1.3% (Boyacıoğlu 2014, Gülersoy 2014, İZSU 2016). The location of the reservoirs is seen in Fig. 1.

Study method

Water quality analysis

In the study, water quality samples were obtained from the Tahtalı, Balçova and Ürkmez reservoirs abstraction structures on a monthly basis for 4 years. Water quality samples were analyzed at the laboratory for metals and inorganic pollution parameters. In this scope iron-Fe, manganese-Mn, copper-Cu, zinc-Zn, fluoride-F, boron-B, arsenic-As, chromium-Cr, lead-Pb, barium-Ba, chloride-Cl and sulphate-SO₄ concentrations in water samples were determined according to procedures described in Standard Methods for Examination of Water and Waste Water (APHA 2005).

Statistical analysis

In the study data sets were subjected to principal component analysis, Student's t-test and discriminant analysis.

Factor analysis was employed on the variables that are correlated to isolate or determine specific factors that are associated with such groupings of physico-chemical characteristics so as to establish their origin. It is multivariate statistical method that reduces the complexity of large data set and eliminates redundant information. The method attempts to explain the correlations between the observations in terms of the underlying factors, which are not directly observable.

There are three stages in factor analysis:

- for all the variables a correlation matrix is generated (this step is the determination of the parameter correlation

matrix. It is used to account for the degree of mutually shared variability between individual pairs of water quality variables),

- factors are extracted from the correlation matrix based on the correlation coefficients of the variables (eigenvalues and factor loadings for the correlation matrix are determined. Eigenvalues correspond to an eigenfactor which identifies the groups of variables that are highly correlated among them. Lower eigenvalues may contribute little to the explanatory ability of the data. Once the correlation matrix and eigenvalues are obtained, factor loadings are used to measure the correlation between the variables and factors),
- to maximize the relationship between some of the factors and variables, the factors are rotated (factor rotation is used to facilitate interpretation by providing a simpler factor structure) (Singovszka and Balintova 2012, Gao et al. 2011).

Student's t-test is one of the most commonly used techniques for testing a hypothesis on the basis of a difference between sample means. The difference in concentrations between summer and winter seasons has been examined using Student's t test at a significant level of 0.05.

Discriminant analysis was used to classify cases into categorical dependent values and also determine variables that discriminate between naturally occurring groups. The method constructs a discriminant function for each group given several quantitative (independent) variables and categorical (dependent) variables (Singh et al. 2004, Juahir et al. 2010). In the stepwise method, the first variable included in this analysis is the largest acceptable value for the selection criterion. The selection criterion is the minimization of Wilks lambda. Stepwise discriminant analysis was proved to be the most

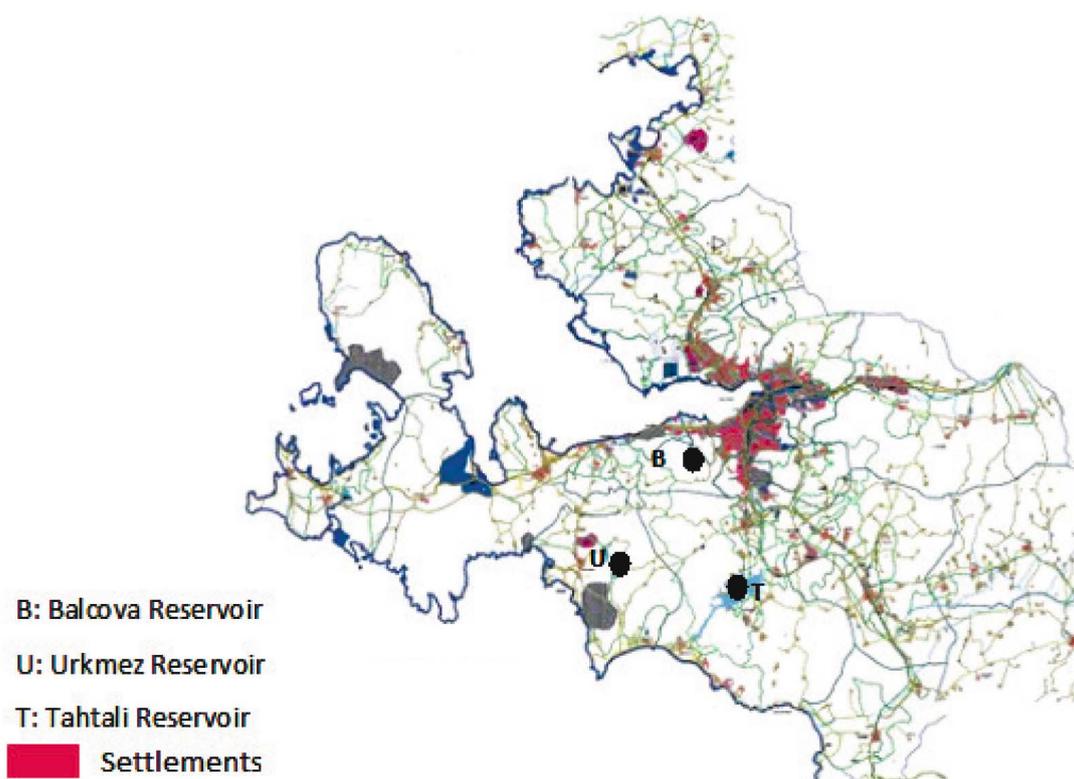


Fig. 1. Location of water reservoirs

effective mode for reducing the dimensionality of the large dataset (Aris et al. 2013).

In the study all mathematical and statistical computations were made using SPSS Statistics (version 21).

Results and discussion

Investigation of natural & antropogenic controls and variations (spatial & temporal)

Descriptive statistics (mean, median, standard deviation, skewness, minimum and maximum) of water quality data sets belonging to three reservoirs are presented in Table 1. In order to avoid the influence of occasional extreme pollution events during the period of study, outliers were screened by using box plots.

Factor analysis was used to identify the key variables with the highest influence on water quality characteristics. It was applied to standardized data set (through z-scale transformation) to avoid misclassifications arising from the different orders of magnitude of both numerical values and variance of the parameters analyzed. The correlation matrix of variables representing three reservoirs water quality was generated and factors extracted by the Centroid method, rotated by Varimax rotation for the data set. Calculated eigenvalues, percent total variance, factor loadings and cumulative variances are given

through Tables 2–4. In the study positively correlated variables with each factor and occurrence of which in surface waters were the basis to determine most important parameters in assessing variation in water quality.

The difference in concentrations between summer (June–July–August) and winter seasons (December–January–February) has also been examined using Student's t-test at 0.05 significance level. Mean and p values (results of the-test) of variables are shown in Table 5.

Each reservoir data set was evaluated individually in the following sections.

Tahtalı Reservoir

The factor analysis generated four significant factors for Tahtalı Reservoir. The factors and positively correlated variables with these factors are:

- Factor 1 (F1): B, As, F
- Factor 2 (F2): Cr, Cu
- Factor 3 (F3): Ba, Mn
- Factor 4 (F4): Zn

Four principal factors were identified as responsible for the data structure explaining 80% of the total variance (Table 1). F1 was positively correlated with “B, As, F” and F2 had a high positive loading on “Cr and Cu”. F1 and F2 explained ≈51% of the total variance (≈27% for F1 and ≈24% for F2).

Table 1. Descriptive statistics of Tahtalı, Balçova and Urkmez Reservoirs (in mg/l)

	Fe	Mn	Cu	Zn	F	B	As	Cr	Pb	Ba	Cl	SO ₄
Tahtalı Reservoir												
Mean	0.06674	0.03311	0.00102	0.00811	0.16	0.05029	0.00408	0.00044	0.00042	0.02521	20	22
Median	0.05435	0.02274	0.00088	0.00717	0.13	0.05017	0.00384	0.00036	0.00042	0.02502	20	22
Std. Deviation	0.03544	0.02775	0.00059	0.00504	0.10	0.00558	0.00108	0.00026	0.00023	0.00474	1	5
Skewness	1.36	1.43	0.83	1.62	0.61	-1.59	0.54	1.02	0.59	-0.11	0.22	-0.15
Minimum	0.01640	0.00540	0.00020	0.00210	0.00	0.02700	0.00260	0.00010	0.00000	0.01120	17	10
Maximum	0.18650	0.11966	0.00250	0.02750	0.46	0.05960	0.00660	0.00110	0.00100	0.03700	23	34
Balçova Reservoir												
Mean	0.08204	0.08836	0.00099	0.01152	0.18	0.01860	0.00110	0.00062	0.00039	0.01838	16	28
Median	0.06736	0.03659	0.00096	0.00855	0.15	0.01786	0.00097	0.00058	0.00035	0.01832	16	29
Std. Deviation	0.03925	0.10366	0.00042	0.00778	0.10	0.00438	0.00042	0.00020	0.00018	0.00208	2	5
Skewness	0.88	1.53	0.44	1.67	0.85	0.78	1.29	0.23	0.56	0.07	0.37	-0.30
Minimum	0.03030	0.00570	0.00010	0.00200	0.01	0.01110	0.00050	0.00020	0.00010	0.01350	13	15
Maximum	0.18400	0.37740	0.00200	0.03630	0.48	0.02940	0.00240	0.00090	0.00080	0.02270	20	37
Urkmez Basin												
Mean	0.22710	0.10312	0.00132	0.00450	0.16	0.04089	0.00268	0.00125	0.00049	0.02429	19	21
Median	0.18261	0.03479	0.00123	0.00407	0.15	0.03989	0.00264	0.00118	0.00047	0.02443	19	21
Std. Deviation	0.18794	0.12416	0.00063	0.00247	0.08	0.00841	0.00090	0.00083	0.00023	0.00476	2	7
Skewness	1.15	1.32	1.72	0.51	0.96	0.62	0.01	0.85	0.37	1.43	0.32	0.00
Minimum	0.01600	0.00280	0.00020	0.00020	0.03	0.02720	0.00030	0.00020	0.00010	0.01500	16	10
Maximum	0.76930	0.38950	0.00370	0.01020	0.42	0.06520	0.00500	0.00340	0.00100	0.04340	24	34

Table 2. Factor loading matrix and total variance explained (Tahtali Reservoir)

Tahtali Reservoir	Factor			
	F1	F2	F3	F4
B	.855	-.091	-.017	.135
As	.845	-.040	-.393	.043
Pb	-.745	-.103	.077	.181
Fe	-.635	.528	-.090	.392
F	.603	-.284	.336	.411
Cr	-.203	.905	.233	.205
Cu	.141	.877	-.082	-.101
Cl	.099	-.836	.202	.156
SO ₄	.125	.111	-.858	-.047
Ba	-.416	-.192	.717	.061
Mn	.395	.362	.704	-.124
Zn	-.002	-.021	-.007	.964
Eigen value	3.18	2.85	2.13	1.40
% total variance	26.52	23.73	17.75	11.68
Cumulative %	26.52	50.25	68.00	79.69

Table 3. Factor loading matrix and total variance explained (Balcova Reservoir)

Balcova Basin	Factor				
	F1	F2	F3	F4	F5
Cr	.866	.031	.018	.054	.147
Fe	.785	.185	.012	.210	.356
B	.693	.544	-.044	-.202	-.258
Mn	-.536	.359	-.513	.247	.308
As	.016	.879	.200	-.182	.192
Cu	.171	.691	-.185	.242	-.025
SO ₄	.089	.594	.116	-.590	-.072
F	.090	.255	.820	.082	.186
Pb	-.070	.169	-.778	.146	.171
Zn	-.328	.064	.677	.408	-.186
Ba	.129	.022	.076	.943	.011
Cl	.195	.036	-.096	-.005	.924
Eigen value	2.35	2.16	2.11	1.67	1.30
% total variance	19.56	18.01	17.55	13.93	10.87
Cumulative %	19.56	37.57	55.12	69.05	79.91

Table 4. Factor loading matrix and total variance explained (Urkmez Reservoir)

Urkmez Basin	Factor				
	F1	F2	F3	F4	F5
Fe	.893	.104	-.132	-.172	.207
Cr	.845	.343	.200	-.141	.199
Cu	.755	-.301	.079	.108	-.268
B	-.620	.430	-.028	.321	-.437
As	.075	.875	.191	.153	.039
Zn	.025	-.872	-.136	.338	-.066
Cl	.081	.031	.922	.077	.114
Ba	-.152	.533	.783	.015	-.123
F	-.077	.037	.160	.945	.037
SO ₄	-.295	-.289	-.533	.643	-.265
Mn	.087	.022	.045	.016	.971
Pb	.194	.241	.496	-.490	.538
Eigen value	2.64	2.36	2.14	1.86	1.68
% total variance	21.99	19.66	17.85	15.46	14.02
Cumulative %	21.99	41.65	59.50	74.96	88.99

Fingerprinting of pollution

Inorganic contamination of aquatic environment is caused by naturally occurring substances (fluoride, arsenic and boron), industrial waste (mercury, cadmium, chromium, cyanide and others), agricultural and domestic waste (nitrogen compounds) (UNESCO 2010). Due to the extensive occurrence of clay-rich sedimentary rocks on the Earth's land surfaces, the majority of boron mobilized into soils and the aquatic environment by weathering probably stems from this source. Natural weathering is estimated to release more boron into the

environment than industrial sources (CCME 2009). Boron concentrations in fresh surface water range from <0.001 to 2 mg/l in Europe, with mean values typically below 0.6 mg/l. Similar concentration ranges have been reported for water bodies within Pakistan, Russia and Turkey, from 0.01 to 7 mg/l, with most values below 0.5 mg/l (WHO 2003a). Arsenic is commonly found in natural waters and its concentration depends on type of geological environment and degree of pollution in a given area. The natural concentration can vary from decimal correspondence to tens of µg/ml (Niedzielski

et al. 2002). However, in areas with volcanic rock and sulfide mineral deposits in areas containing natural sources, levels as high as 12 mg/l have been reported near anthropogenic sources (e.g mining and agrochemical manufacture) (WHO 2011). Fluorides are released into the environment naturally through the weathering and dissolution of minerals, in emissions from volcanoes and in marine aerosols. They are also released into the environment via coal combustion and process waters and waste from various industrial processes. The use of fluoride containing pesticides as well as the controlled fluoridation of drinking-water supplies also contribute to the release of fluoride from anthropogenic sources. Fluoride levels in surface waters vary according to location and proximity to emission sources. Surface water concentrations generally range from 0.01 to 0.3 mg/l (WHO 2002).

Based on a) these statements, b) components of first factor F1 – B, As, Pb c) level of concentrations presented in Table 1, and also d) antropogenic activities in the region, it can be concluded that Tahtali Reservoir water quality is mainly governed by “natural factors”.

Moreover, F2 comprised Cr and Cu and explained 24% of the total variance. Chromium is widely distributed in the Earth's crust. The natural total content of surface waters is approximately 0.5–2 µg/l and the dissolved content is 0.02–0.3 µg/l. Most surface waters contain between 1 and 10 µg of chromium per litre (WHO 2003b). Copper is an abundant trace element that occurs naturally in the Earth's crust and surface waters. It can be found as a pure metal in nature and has a high thermal and electrical conductivity. Copper compounds are generally found as copper (II) salts. (USEPA 2007). Urban stormwater runoff represents an important source of heavy metals to receiving surface waters. The primary source of many metals in urban runoff is vehicle traffic. Concentrations of copper, lead and cadmium appear to be directly correlated to traffic intensity on surfaces such as highways, streets and parking lots (Prestes et al. 2006).

Considering the level of concentrations for both variables in summer and winter seasons, it cannot be argued that these

are indicators of urban runoff effect. Therefore similar to F1, this grup-F2 can also be the representation of “natural effects” rather than urbanisation on water quality.

Furthermore, results of the Student's t-test given in Table 5 showed that among factor components of F1 and F2, only difference in “Arsenic” concentrations was statistically significant between summer and winter periods (P value was 0). Mean values were 0.0035 in winter and 0.0051 in summer. This has been attributed to dilution from runoff at times of high flow (winter season) in the region.

Balçova Reservoir

Factor analysis results performed for Balçova Reservoir water quality data set produced the following factors. Positively correlated variables with these factors are:

- Factor 1 (F1): Cr, Fe, B
- Factor 2 (F2): As, Cu, SO₄
- Factor 3 (F3): F, Zn
- Factor 4 (F4): Ba
- Factor 5 (F5): Cl

Cr, Fe and B marked F1 and explained 20% of the total variance (with factor loadings 0.87, 0.79 and 0.69, respectively). The F2 had a high positive loading on As, Cu, SO₄ (with factor loadings 0.88, 0.69 and 0.59) and explained 18% of the total variance.

Fingerprinting of pollution

Natural occurrence of chromium, boron, arsenic and copper in surface waters has already been explained previously. Moreover, iron is the second most abundant metal in the Earth's crust of which it accounts for about 5% (WHO 2003c). Sulphates are discharged into the aquatic environment in wastes from industries that use sulphates and sulphuric acid. Acid rock drainage is also a significant source of sulphate generation. Sulphate fertilizers are also a major source of sulphate to ambient waters (BCME 2000).

Considering a) first two factor components- “Cr, Fe, B, As, Cu and SO₄”, b) level of concentrations of these variables

Table 5. Mean concentrations and results of Student's t tests

Variable	Reservoir								
	Tahtali			Balçova			Ürkmez		
	Winter	Summer	P	winter	summer	P	winter	summer	P
Fe	0.0838	0.0549	0.024	0.0954	0.064	0.019	0.1939	0.2434	>0.05
Mn	0.0197	0.0483	0.011	0.0618	0.1143	>0.05	0.0266	0.1981	0.000
Cu	0.001	0.0012	>0.05	0.0012	0.0009	>0.05	0.0013	0.0011	>0.05
Zn	0.0078	0.0098	>0.05	0.0087	0.0125	>0.05	0.004	0.0045	>0.05
F	0.14	0.18	>0.05	0.15	0.18	>0.05	0.17	0.17	>0.05
B	0.0498	0.053	>0.05	0.0193	0.0196	>0.05	0.0459	0.0374	0.011
As	0.0035	0.0051	0.000	0.0011	0.0012	>0.05	0.0031	0.0022	0.000
Cr	0.0005	0.0003	>0.05	0.0007	0.0005	>0.05	0.0013	0.0013	>0.05
Pb	0.0004	0.0004	>0.05	0.0004	0.0004	>0.05	0.0004	0.0005	>0.05
Ba	0.0255	0.024	>0.05	0.0171	0.0191	0.032	0.0253	0.0232	>0.05
Cl	20	20	>0.05	17	16	>0.05	20	18	0.034
SO ₄	24	21	>0.05	30	28	>0.05	25	19	0.007

presented in Table 1, and c) source of these substances in water, it can be concluded that Balçova reservoir water quality is mainly controlled by “natural factors”.

Furthermore, among components of the first two factors (F1 and F2), difference in iron concentrations in summer and winter periods was statistically significant (p value was 0.019). Higher mean values were observed in winter (0.083 mg/L) and lower in summer (0.055 mg/L). Higher iron levels in winter could be explained by seepage through soil and entrance to the river with the rainwater run-off process (Kaur and Mehra 2012).

Ürkmez Reservoir

Factor analysis results performed for Ürkmez Reservoir water quality data set generated five factors explaining 89% of the total variance. Positively correlated variables with these factors are:

- Factor 1 (F1): Fe, Cr, Cu
- Factor 2 (F2): As
- Factor 3 (F3): Cl, Ba
- Factor 4 (F4): F, SO₄
- Factor 5 (F5): Mn, Pb

F1 was positively correlated with “Fe, Cr, Cu” and F2 with “As”. Factor loadings were 0.90, 0.85, 0.76 and 0.88, respectively. Quality of water showed quite similar characteristics to Balçova reservoir with the presence of similar factor components explaining higher percentage of variance in data set.

Fingerprinting of pollution

Considering a) natural occurrence factor components that has been explained in the previous sections and b) level of concentrations, it can also be concluded that Ürkmez reservoir water quality was mainly controlled by “natural factors”. Among the factor components of F1 and F2, difference in arsenic concentrations in summer and winter periods was statistically significant. Lower levels have been observed in summer months (Table 5). This implies that adsorption process

is more important in attenuating arsenic concentrations during periods of dry weather in the region (Gault et al. 2003).

Investigation of dissimilarities between reservoirs

In the study discriminant analysis was performed on the original data based on the stepwise mode to construct the best discriminant functions. Discriminant functions with small Wilk’s Lambda and a large chi-square respectively ($p < 0.05$) indicated that the spatial discriminant analysis was credible and effective (Table 6). In other words the discriminant functions were sufficient to explain the difference of water quality among reservoirs. Classification functions obtained from analysis are shown in Table 7. The stepwise method identified “boron, arsenic and sulphate” as the most important variables discriminating Balçova & Tahtalı and Balçova & Ürkmez reservoirs (Table 7). As is presented in Table 5, boron and arsenic levels were considerably lower and sulphate was higher in the Balçova reservoir compared to the others. On the other hand, “zinc and arsenic” were the discriminating variables between Tahtalı & Ürkmez reservoirs. The levels of both variables were higher in the Tahtalı reservoir.

Conclusion

In the study, environmental methods were used to investigate a) natural and anthropogenic controls of water quality and b) seasonal & spatial variations in water quality of three reservoirs in Izmir, Turkey. Factor analysis helped to identify the factors/sources responsible for variations in reservoir water quality at three different sites. The method produced four factors in the Tahtalı, five factors in the Balçova and Ürkmez Reservoirs. For each data set a) positively correlated variables with first two factors, b) occurrence of these variables in surface waters, and c) levels in the reservoirs were the basis to fingerprint pollution. Results indicated that water quality in three reservoirs was mainly governed by “natural factors”

Table 6. Wilk’s lambda and chi-square test for the discriminant analysis of spatial variation in water quality

Reservoir	R	Eigenvalue	Wilks’ Lambda	chi-square	p-level
Balcova&Tahtali	0.94	14.917	0.063	84.405	0.00
Balcova & Ürkmez	0.88	7.461	0.118	67.268	0.00
Tahtalı & Ürkmez	0.61	1.597	0.385	28.639	0.00

Table 7. Classification function coefficients for the discriminant analysis (DA) of Table 6

Balcova&Tahtalı		Balcova&Urkmez		Tahtalı&Urkmez	
Parameters	Function	Parameters	Function	Parameters	Function
B	8.136	B	8.744	Zn	3.025
As	5.474	As	3.534	As	9.771
SO ₄	-9.699	SO ₄	-4.974		
(Constant)	41.094	(Constant)	30.485	(Constant)	31.556

rather than anthropogenic sources. Furthermore, the results of the Student's t-test showed that among the first two factor components difference in "arsenic" concentrations between summer and winter periods was statistically significant in Tahtalı reservoir. Lower levels in winter season were explained by dilution from runoff at times of high flow. Similar to the Tahtalı reservoir, "arsenic" was the variable having difference between two seasons in Ürkmez reservoir. Here the main difference was that lower levels have been observed in summer months. This implied that adsorption process was more important in attenuating arsenic concentrations during the periods of dry weather in the region. In contrast, in the Balcova reservoir iron levels showed seasonal differences. Higher iron levels in winter could be explained by seepage through soil and entrance to the river with the rainwater run-off process. Furthermore, discriminant analysis gave the best results to investigate spatial differences. For three reservoirs it yielded an important data reduction. It used only three parameters "boron, arsenic, sulphate" to discriminate quality between Balcova & Tahtalı and Balcova & Ürkmez reservoirs and two parameters "zinc and arsenic" between Tahtalı & Ürkmez reservoirs. Therefore the method allowed for a reduction in the dimensionality of the large data set delineating a few indicator parameters responsible for large variations in water quality. This study illustrated the effectiveness of multivariate statistical techniques to investigate natural & anthropogenic controls of seasonal and spatial variations in water quality.

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