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UTILIZATION OF ENVIRONMETRIC & INDEX METHODS AS WATER QUALITY COMPARATIVE ASSESSMENT TOOLS FOCUSING ON HEAVY METAL CONTENT

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Abstract: In the study suitability of water quality index approach and environmetric methods in fingerprinting heavy metal pollution as well as comparison of spatial variability of multiple contaminants in surface water were assessed in the case of The Gediz River Basin, Turkey. Water quality variables were categorized into two classes using factor and cluster analysis. Furthermore, soil contamination index was adapted to water pollution index and used to find out the relative relationship between the reference standards and the current situation of heavy metal contamination in water. Results revealed that surface water heavy metal content was mainly governed by metal processing, textile and tannery industries in the region. On the other hand, metal processing industry discharges mainly degraded quality of water in Kemalpasa and Menemen. Furthermore, Kemalpasa region has been heavily affected from tannery and textile industries effluents. Moreover, pollution parameters have not been influenced by changes in physical factors (discharge and temperature). This study indicated the effectiveness of water quality index approach and statistical tools in fingerprinting of pollution and comparative assessment of water quality. Both methods can assist decision makers to determine priorities in management practices.

INTRODUCTION

In the last few decades, there has been a tremendous increase in the demand for fresh water due to rapid growth of population and the accelerated pace of industrialization [19]. In parallel to an increasing demand, surface water bodies are prone to impacts from human activities, which may result in degradation of the resource. The best way to minimize adverse impacts on water quality is to plan basin development activities (including industrial, residential and agricultural) and manage protection measures by monitoring quality effectively [10]. However, water quality assessment is quite difficult due to the spatial variability of multiple contaminants and a wide range of indicators that could be measured.

Modern concepts of estimation of pollution impacts require not only careful organization of water quality monitoring of water bodies (surface waters, coastal sediments and benthic organisms, seawaters and plants) but also a reliable monitoring,

data treatment, classification and modeling. Since the analytical data from ecological systems possess a multivariate nature, environmetric methods, which are application of multivariate statistical techniques, are successful approach for their interpretation [15]. On the other hand, water quality index value makes the information more easily and rapidly understood by a) using measurements in a single metric, and b) facilitating comparison between different sampling sites and/or events [5, 7].

A lot of studies abound in the literature on pollution of water sources [e.g. 1, 2, 4, 11, 12, 18 and 20]. All these researchers used various methods (e.g. water quality indexing, statistical tools) to assess water quality focusing on heavy metal pollution. They indicated that the application of multivariate statistical methods and water quality index approach made it possible to interpret and model the complex data sets from river water monitoring sites in a more appropriate way.

The aim of the study is not only to assess the present water quality focusing on heavy metal content along the Gediz River and its tributaries but also to examine emissions from industrial sources and spatial differences between monitoring sites. The assessment was carried out by the use of factor analysis (FA), cluster analysis (CA), water quality index (WQI) method, correlation analysis and frequency histograms.

STUDY AREA

The Gediz River Basin is located in western Anatolia in the Aegean region neighboring the city of Izmir. The Gediz River, 401 km long, drains an area of 17 500 km^2 and flows from east to west into the Aegean Sea just north of Izmir (Fig. 1).

Annual average discharge of the river is about 60 m^3/s. Agricultural lands and forest cover about 88% of the total area and residential and industrial area is almost 10% of the total land uses [16].
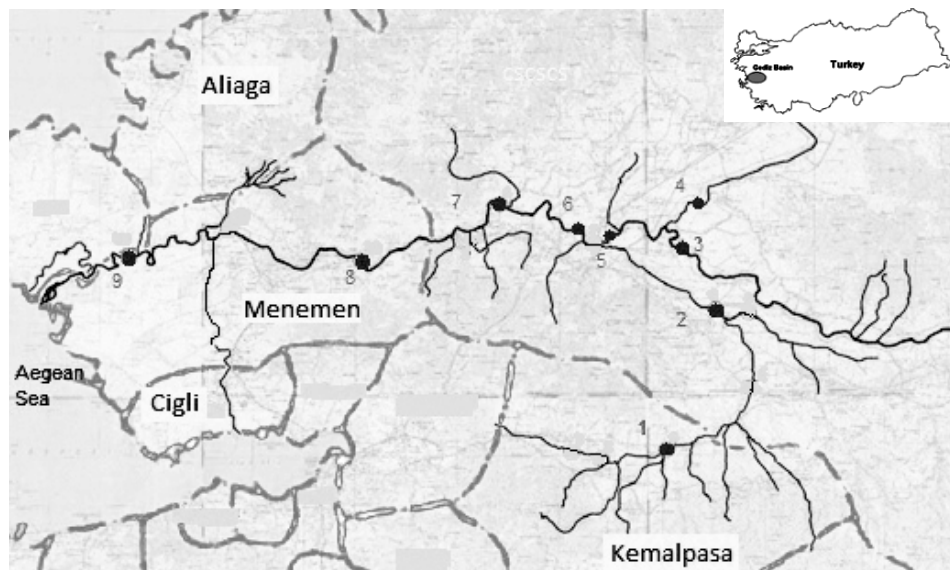

Fig. 1. Gediz River and monitoring stations

Wastewater discharges from urban areas and industries within the basin seriously degrade the quality of the surface water. There are several organized districts and individual companies along Nif Creek and downstream part of the river. The study focused on impacts of discharges on water quality focusing on heavy metal content in this region.

In the study area, Kemalpasa Organized Industry Region, there are mainly metal processing, chemical, plastic and paper producing companies. On the other hand, there are leather and tannery processing companies in the organized district located in Menemen. Izmir Atatürk Organized Industry Region dominantly comprises textile, metal processing, electric and electronic, construction material, chemical and food industries, etc. In addition to these industrial regions, there are individual companies spread all over the region [16].

STUDY METHOD

In the study, the measured parameters of heavy metals – aluminum, boron, cadmium, iron, mercury, nickel, lead, total chromium and zinc were subject to examination by environmetric methods and water quality index calculation. Water samples were collected on a monthly basis from nine monitoring stations for two years and analyzed according to "Standard Methods for the Examination of Water and Wastewater [3]" at the laboratory. The determination of heavy metals was carried out by atomic absorption spectrophotometry (AAS). Overall objective of the study was water pollution fingerprinting, determination of spatial differences and also analyzing impact of physical factors on water quality.

Factor and cluster analysis were applied in order to explain the behavior and sources of water pollutants. Factor analysis was performed by examining the pattern of correlations (or covariances) between the observed measures. Measures that are highly correlated (either positively or negatively) are likely to be influenced by the same factors, while those that are relatively uncorrelated are likely to be influenced by different factors [9].

Cluster analysis encompasses a number of different algorithms and methods for grouping objects of similar kind into respective categories. In other words, the method is an exploratory data analysis tool which aims to sort different objects into groups in a way that the degree of association between two objects is maximal if they belong to the same group and minimal otherwise. The joining or tree clustering method uses the dissimilarities (similarities) or distances between objects when forming the clusters. Similarities (dissimilarities) can be based on a single dimension or multiple dimensions, with each dimension representing a rule or condition for grouping objects. A typical result of this type of clustering is the hierarchical tree [14].

Correlation is the mutual relationship between two variables. Direct correlation exists when increase or decrease in the value of one parameter is associated with a corresponding increase or decrease in the value of another parameter [8]. In the study the method was used to determine interdependence between particular variables.

Water quality index and frequency histograms were applied to assess present level of pollution by relating to standards and also to determine spatial differences in water quality. In this scope single contamination index used in the literature [12] to investigate heavy metal contamination in soils was adapted to water quality index by referencing Turkish Water Pollution Control Regulation. The objective was to find out a relative relationship between the national standards and the current situation of heavy metal contamination in water. In this method WQI_i was defined as the quality index of variable i and C_i as parameter

concentration (Tab. 1). Moreover, X_a, X_p, and X_c represented the limits for Class I, II and III waters defined by the regulation respectively (see Tab. 2). In this classification "Class I" water represented the best quality and "Class IV" heavily polluted waters.

Furthermore, frequency histograms were also plotted using combined data of each variable with size class interval of "1" to allow for distinctions for water quality classes.

RESULTS AND DISCUSSION

Water Pollution Fingerprinting and Investigation of Spatial Differences

In the study data set was analyzed using factor analysis-FA (extraction method – principal component analysis, rotation method – Varimax with Kaiser Normalization) with a view

Table 1. Water quality index [12]

Variable concentration			
$C_i \leq X_a$	Quality index formula	$WQI_i = C_i/X_a$	(1)
	Index range	$WQI_i \leq 1$	
	Water Quality Class represented	I	
$X_a < C_i \leq X_c$	Quality index formula	$WQI_i = 1 + (C_i - X_a)/(X_c - X_a)$	(2)
	Index range	$1 < WQI_i \leq 2$	
	Water Quality Class represented	II	
$X_c < C_i \leq X_p$	Quality index formula	$WQI_i = 2 + (C_i - X_c)/(X_p - X_c)$	(3)
	Index range	$2 < WQI_i \leq 3$	
	Water Quality Class represented	III	
$X_p < C_i$	Quality index formula	$WQI_i = 3 + (C_i - X_p)/(X_p - X_c)$	(4)
	Index range	$WQI_i > 3$ (max 4)	
	Water Quality Class represented	IV	

Table 2. Standart limits recommended by the Turkish Water Pollution Control Regulation (µg/L) [17]

Variable	Class I	Class II	Class III	Class IV
Al	300	300	1000	>1000
B	1000	1000	1000	>1000
Cd	3	5	10	>10
Fe	300	1000	5000	>5000
Hg	0.1	0.5	2	>2
Ni	20	50	200	>200
Pb	10	20	50	>50
T-Cr	20	50	200	>200
Zn	200	500	2000	>2000

to examine their correlations and influences. The objective was the identification of possible factors/sources that are responsible for variations in water quality and influence the water system. Combined data covering all sampling stations and study period was used for analysis.

Table 3 summarizes the FA results including the loadings, eigenvalue and variance explained by each factor. FA rendered two factors with eigenvalues >1 explaining 69.2% of the total variance of the data set. Factor 1 explained 40.3% of total variance and had strong positive loadings (> 0.90) on iron, aluminum, zinc and mercury. On the other hand, Factor 2, having strong positive loadings on total chromium, cadmium and nickel, explained 28.9% of the total variance.

Table 3. Rotated component matrix

Variable	Factor Component	
	1	2
Pb	1.536E-02	.353
TCr	.159	.902
Zn	.927	.241
Hg	.911	-2.936E-02
Cd	9.597E-02	.881
B	-.154	.282
Fe	.960	1.702E-02
Ni	.226	.861
Al	.952	7.282E-02
Total variance explained (%)	40.28	69.16

Cluster analysis is another data reduction method that is used to classify entities with similar properties. The method divides a large number of objects into a smaller number of homogeneous groups on the basis of their correlation structure [24].

In addition to factor analysis, classification of water quality variables was made by the use of cluster analysis (z-transformation of the input data, squared Euclidean distance as similarity measure and between groups method of linkage) and a dendogram was generated. According to results shown in Figure 2 two associations were evident. The association between iron, aluminum, zinc and mercury were significant. Another group comprised variables – total chromium, nickel and cadmium. This result was in accordance with outcome of FA. Therefore, both FA and CA showed that water quality variables can be grouped into two main clusters (groups).

Pollution of surface water by industrial processes is a widespread and very serious environmental issue. Heavy metals are metallic elements (e.g., cadmium, chromium, copper, lead, mercury, nickel and zinc), many of which are toxic at relatively low concentrations and are found in industrial wastewaters [23]. The primary human-related
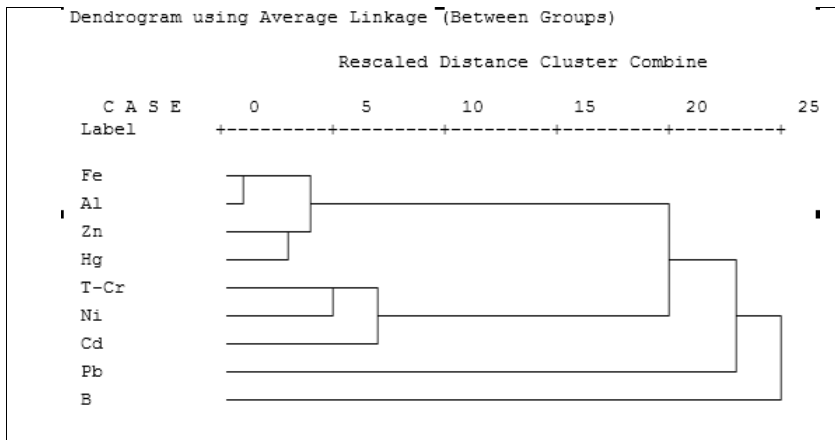
Fig. 2. Hierarchical dendrogram for variables clustering

mercury sources include coal combustion, chlorine alkali processing, waste incineration, and metal processing [21]. On the other hand, the main inorganic pollutants from metal molding and casting industry are copper, lead and zinc. Wastewater coming from non-ferrous metals manufacturing industry also includes aluminium, antimony, chromium, lead, magnesium, nickel, silver, tin, and zinc, as inorganic pollutants. [23].

Use of Cd, Cr and Pb in electroplating factory, plastic industry and in alloy preparation are quite common [22]. The tannery industry, which uses a variety of chemicals in the tanning process is recognized as a major contributor of heavy metals to the environment and poses serious environmental threats worldwide [4]. For example, chromium (Cr), when used in the productive cycle, is one of the most problematic pollutants discharged by the tanning industry [6]. The heavy metal constituents in wastewater from textile industry are chromium, copper and zinc [23]. Heavy metals such as lead, chromium, cadmium and copper are widely used for production of color pigments of textile dyes [13].

Based on these statements and considering the profile of production companies located in the region, it was concluded that Group I can represent impact of effluent dominated by metal processing industry. Besides Group II variables can be indicator of discharges from textile and tannery industries.

Accordingly, further analysis techniques have been carried out and results presented for two groups of variables representing "Group I-metal processing industry impact" and "Group II- textile and tannery industries impact" separately.

Water quality classification and spatial variability for the Group I
The simple linear correlation analysis has been carried out to find out a correlation between parameters classed under Group I. The correlation matrix was presented in Table 4.

The positive high correlations were found between zinc, mercury, iron and aluminum. The result was indicator of human induced changes in heavy metal content in surface water. In other words, high positive correlation between parameters can be explained by effect of industrial discharge containing these pollutants.

Table 4. Correlation coefficients between Group I variables

	Zn	Hg	Fe	Al
Zn	1.0	0.7	0.6	0.8
Hg		1.0	0.5	0.8
Fe			1.0	1.0
Al				1.0

Classification of water quality has also been made using WQI method. The unit indices that represent water quality class were determined from the values of individual parameters using formulas given in Table 1. Relative frequency histograms illustrating distribution of index scores of Group I variables are depicted in Figure 3.
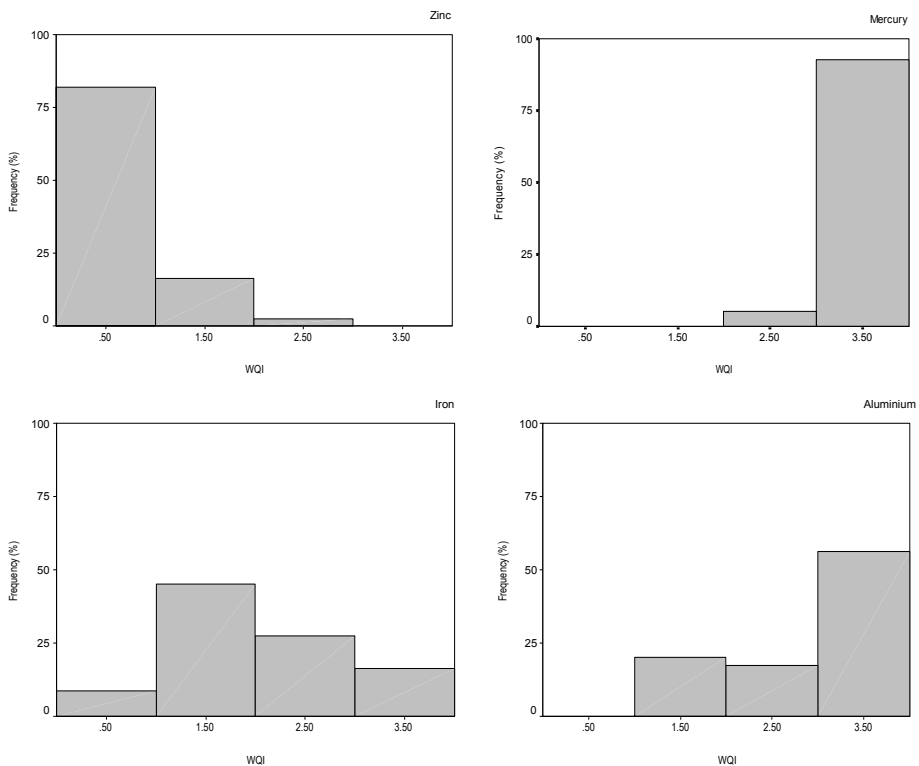

Fig. 3. Relative frequency histograms for Group 1 variables

The highest proportion of the samples represented "Class IV water" for mercury and aluminum, both of which were determined as the most serious threat among Group I parameters. In contrast, index score of samples analyzed for zinc were dominantly 1 and 2. Therefore, zinc was not a serious risk among Group I variables.

Furthermore, spatial differences among monitoring stations were analysed. In this scope, complying with Turkish Water Pollution Control Regulation, 90th percentile of

each data set was determined as the characterictic value. In addition to 90th percentile, median values were used for comparison and results are presented in Table 5.

Based on the median and 90th percentile values, it was concluded that the sites "1, 2, 6, 7, 8 and 9" appeared to be the most influenced parts from metal industry discharges. In contrast, Sites 3, 4 and 5 were the regions reflecting impact of discharges at minimum level.

As mentioned before, water quality classes were defined by assigning each sampling value to a number between 0 and 4. In this case, index scores greater than "4" were set to upper class limit value index score which is "4". In the study, to give an idea about the extreme values (classified under Class IV and having index score greater than 4), the ratio of water quality parameters sampling values to Class IV reference values was analyzed. The range of exceedance rates is presented in Table 6.

Based on these values it was concluded that mercury was the most critical parameter with high ratios at the stations 1-3-4-5 and 7. The second critical variable was Al with relatively lower values.

Water quality classification and spatial variability for the Group II

Correlation analysis and WQI calculation have been performed for Group II variables. Correlation matrix is presented in Table 7. It is evident that Group II variables were significantly positively correlated. This could be explained by effect of "tannery-textile industrial discharges" on surface water.

Table 5. Median and 90th percentiles of data sets comprising index values for Group I variables at monitoring stations

Variable		Monitoring Sites								
		1	2	3	4	5	6	7	8	9
Zn	Median	1.0	0.6	0.3	0.3	0.3	0.3	0.4	0.4	0.4
	90th percentile	1.9	1.8	1.0	0.6	1.0	1.3	0.8	1.0	1.2
Hg	Median	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
	90th percentile	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Fe	Median	2.0	3.8	1.3	0.9	1.2	1.5	2.1	1.5	1.5
	90th percentile	2.8	4.0	2.3	1.2	1.7	2.1	3.0	2.4	3.3
Al	Median	3.9	4.0	3.5	2.0	4.0	4.0	4.0	2.1	2.4
	90th percentile	4.0	4.0	4.0	2.2	4.0	4.0	4.0	4.0	4.0

Table 6. Exceedance over the threshold values (Class IV waters) for Group I variables

Variable	Monitoring Sites								
	1	2	3	4	5	6	7	8	9
Zn	-	-	-	-	-	-	-	-	-
Hg	5-10	1-5	5-10	5-10	5-10	1-5	5-10	1-5	1-5
Fe	-	1-5	-	-	-	-	-	-	-
Al	1-5	5-10	1-5	-	1-5	1-5	1-5	1-5	1-5

Table 7. Correlation coefficients between Group II variables

	T-Cr	Cd	Ni
T-Cr	1.0	0.5	0.7
Cd		1.0	0.6
Ni			1.0

Frequency histograms plotted for three variables are depicted in Figure 4. In these histograms, while more than 75% of the samples analyzed for cadmium belonged to Class IV, water quality class for nickel was mainly Class III and Class IV with lower frequency. On the other hand, the variability of concentrations for chromium was higher than for the others. Samples represented Class II–IV waters with about 25% and Class III waters with 50% frequency.

Spatial differences among sites based on index scores of Group II variables were also analyzed (using the median and 90th percentile of each data set) and results are presented in Table 8. Based on these values it can be concluded that stations "1 and 2" were heavily affected from tannery and textile industry effluent. In contrast, other sites were influenced from discharges to a lesser extent.
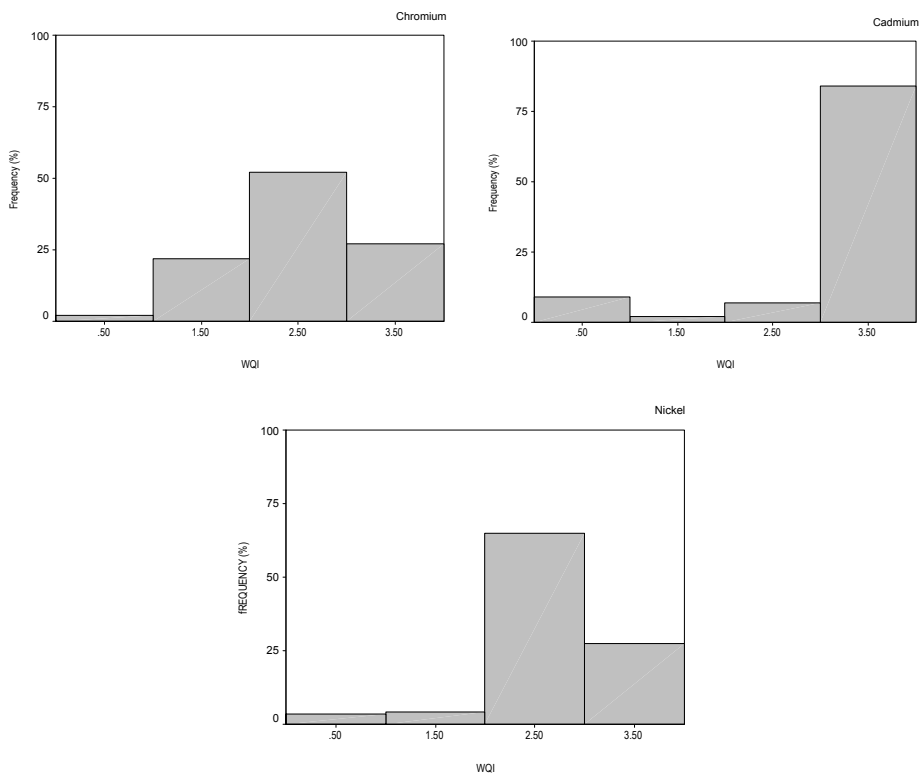

Fig. 4. Relative frequency histograms for Group 2 variables

What is more, exceedance ratios over the threshold values (Class IV waters) for Group II variables sampling results changed mainly between 1 and 5 (see Table 9). Sites 4 and 5 had no value exceeding threshold for total chromium and nickel.

Influence of Water Quality from Physical Parameters (Discharge and Temperature)

Although the variables analyzed for total chromium, zinc, mercury, cadmium, nickel and aluminum could be naturally found in surface water, their high level of concentrations in the study area was the evidence of industrial discharges to the river.

The correlation study was performed to measure strength of the relation between water quality variables and physical parameters. Results presented in Table 10 show that pollution parameters have not been influenced by changes in physical factors (discharge and temperature).

CONCLUSION

This study evaluated the applicability of the water quality index and also environmetric methods for the study area using heavy metal observations. Overall objective was water

Table 8. Median and 90th percentiles of data sets comprising index values for Group II variables at monitoring stations

Variable		Monitoring Sites								
		1	2	3	4	5	6	7	8	9
T-Cr	Median	3.1	2.4	2.4	2.4	2.3	2.7	2.5	2.3	2.3
	90th percentile	4.0	3.4	3.1	2.7	3.3	2.9	3.7	3.2	3.7
Cd	Median	4.0	4.0	3.3	4.0	4.0	3.5	3.0	3.0	3.0
	90th percentile	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Ni	Median	3.9	2.7	2.3	2.3	2.2	2.3	2.3	2.3	2.3
	90th percentile	4.0	4.0	2.9	2.4	3.4	2.5	2.9	2.9	3.7

Table 9. Exceedance over the threshold values (Class IV waters) for Group II variables

Variable	Monitoring Sites								
	1	2	3	4	5	6	7	8	9
T-Cr	1-5	1-5	1-5	-	-	1-5	1-5	1-5	1-5
Cd	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5	1-5
Ni	1-5	1-5	-	-	-	1-5	1-5	1-5	1-5

Table 10. Correlation coefficients between physical variables (Q; T) and water quality parameters

	T-Cr	Zn	Hg	Cd	Fe	Ni	Al
Q	-.03	-.07	-.06	-.05	.22	-.11	-.07
T	.06	-.04	-.06	-.06	-.11	-.01	.06

pollution fingerprinting, determination of spatial differences and also analyzing impact of physical factors on water quality.

Factor and cluster analysis offered a valuable tool for estimation of contaminant sources. Two groups were extracted and Group I included iron-aluminum-zinc and mercury variables which could be mainly found in metal industry discharge. On the other hand, the existence of total chromium, nickel and cadmium in Group II was explained by the influence of surface water quality from tannery and textile industry effluent. Therefore, it was concluded that heavy metal content of surface water in the region was mainly governed by metallic, tannery and textile industry discharges. Water quality analyzed for both groups mainly belonged to Class III and IV, which represented polluted and heavily polluted waters. Spatial differences were also examined and results revealed that although variability of level of impact from both groups of pollutants, Kemalpasa and Menemen appeared to be the most effected region from metal industry discharges. In contrast, upstream part was influenced by pollution to a lesser extent. Similarly, textile and tannery industries effluents affected water quality dominantly at Kemalpasa region. Correlation analysis examined the relation between quality variables and physical parameters (discharge and temperature). Results showed that pollution parameters were not affected from changes in discharge and temperature. The study showed that there was need to monitor water quality on a regular basis and extract information from data sets using environmetric methods and index approach for basin specific management decisions.

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