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An Application on Using Multivariate Statistical Techniques to Evaluate the Sediment Quality

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ABSTRACT:

Multivariate statistical techniques have been used to evaluate the environmental risks in recent years. Felent Stream, which has international important silver mine on the basin, is exposed to agricultural, domestic and industrial pollution. The aim of this study was to evaluate the sediment quality of Felent Stream using multivariate statistical techniques. For this purpose, the accumulations of some micro and macro elements (As, Cr, Cu, Pb, Zn, Ca, K, Mg, Mn, Na and P) in the sediment of Felent Stream were investigated seasonally and Pearson Correlation Index, One Way Anova Test, Factor Analysis (FA) and Cluster Analysis (CA) were applied to the results in order to estimate the data properly. According to the CA, three statistically significant clusters were formed: Cluster 1 corresponded to F4, F5 and F1 that were uncontaminated areas of the basin; Cluster 2 corresponded to F6 and F7 that were moderately contaminated areas of the basin; Cluster 3 corresponded to F2 and F3 that were strongly contaminated areas of the basin. According to FA, four factors have explained 75.92% of the total variance. First factor (F1) named as "Mine - Agriculture Factor" has explained 24.05% of the total variance, second factor (F2) named as "Geologic Factor" has explained 22.09% of the total variance, third factor (F3) named as "Urban - Industrial Factor" has explained 15.1% of the total variance and fourth factor (F4) named as "Natural Factor" explained 14.67% of the total variance.

Keywords:
Felent Stream, Sediment Quality, Heavy metal, Statistical Evaluation

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INTRODUCTION

Significant quantities of heavy metals are discharged into aquatic ecosystems, which can be strongly accumulated, and biomagnified along water, sediment and aquatic food chain (Jones *et al.*, 2001; Xu *et al.*, 2004). It has been well documented that sediment may act as a sink of various pollutants and pose a risk to water quality through complicated biogeochemical exchanges (Massoudieh *et al.*, 2010). Therefore, the assessment of sediment quality is an essential component of aquatic ecosystem assessment (Yu *et al.*, 2011).

Applications of multivariate statistical techniques, such as Factor Analysis (FA) and Cluster Analysis (CA) are designed to reduce the number of variables to a small number of indices and they help to identify the important components or factors accounting for most of the variances of a system (Ouyang *et al.,* 2006; Shrestha and Kazama 2007).

Felent Stream that constitutes the study area of the present study is one of the most important branches of Porsuk Stream (Sakarya River Basin) and located in the Kütahya Province of Turkey. In addition to the mining activities and the solid waste storage area located on the downside of the basin, intensive agricultural and domestic activities carried on the watershed boundaries of the stream are the main pollution sources for the region (Tokatlı *et al.*, 2013).

In the present study, arsenic, chromium, copper, lead, zinc, calcium, potassium, magnesium, manganese, sodium and total phosphorus accumulations in sediment of Felent Stream Basin were investigated by implemented seasonally field studies. Also, some mono and multi statistical techniques (Factor Analysis, Cluster Analysis and One Way Anova Test) were used to evaluate the sediment quality of the basin.

MATERIALS AND METHODS

Study Area and Collection of Samples

The map of the watershed of Felent Stream Basin and the selected stations were given in Figure 1. Sediment samples were collected seasonally from the Felent Stream and Enne Dam Lake in the year of 2011 by using sediment dipper and Ekman grab taking small portions from the center of the dipper and grab with a polyethylene spoon to avoid contamination by metallic parts of the grab.

Chemical Analysis

Sediment samples were dried at 105°C for macro and micro element analysis (As, Cr, Cu, Pb, Zn, Ca, K, Mg, Mn, Na and P) for 3 hours by using a drying oven. Then, 0.25 g of each sediment samples were placed to Pyrex reactors (CEM Mars Xpress 5 microwave digestion unit). $HClO_4$:HNO_3 acids (1:3 proportions) were inserted to the reactors respectively and the sediment samples were mineralized for thirty minutes at 200°C. Then, the all the samples were filtered in such a way so as to make their volumes to 100 ml with ultra-pure distilled water.

All macro and micro element accumulations in sediment samples were investigated by using an Inductively Coupled Plasma-Optic Emission Spectrophotometer (ICP - OES) (Varian 720 ES). The element analysis were calculated as means of triplicate measurements. The wavelengths of ICP-OES used for the element analysis were given in Table 3 (EPA, 1998; EPA, 2001).

Statistical Analysis

Cluster Analysis (CA) was applied to the results to classify the stations according to the heavy metal accumulations by using the Past package program. One Way Anova Test was applied to the results to determine the significant differences of element accumulations detected in different stations Pearson Correlation Index was applied to the results to determine the relations between heavy metals and also Factor Analysis (FA) was

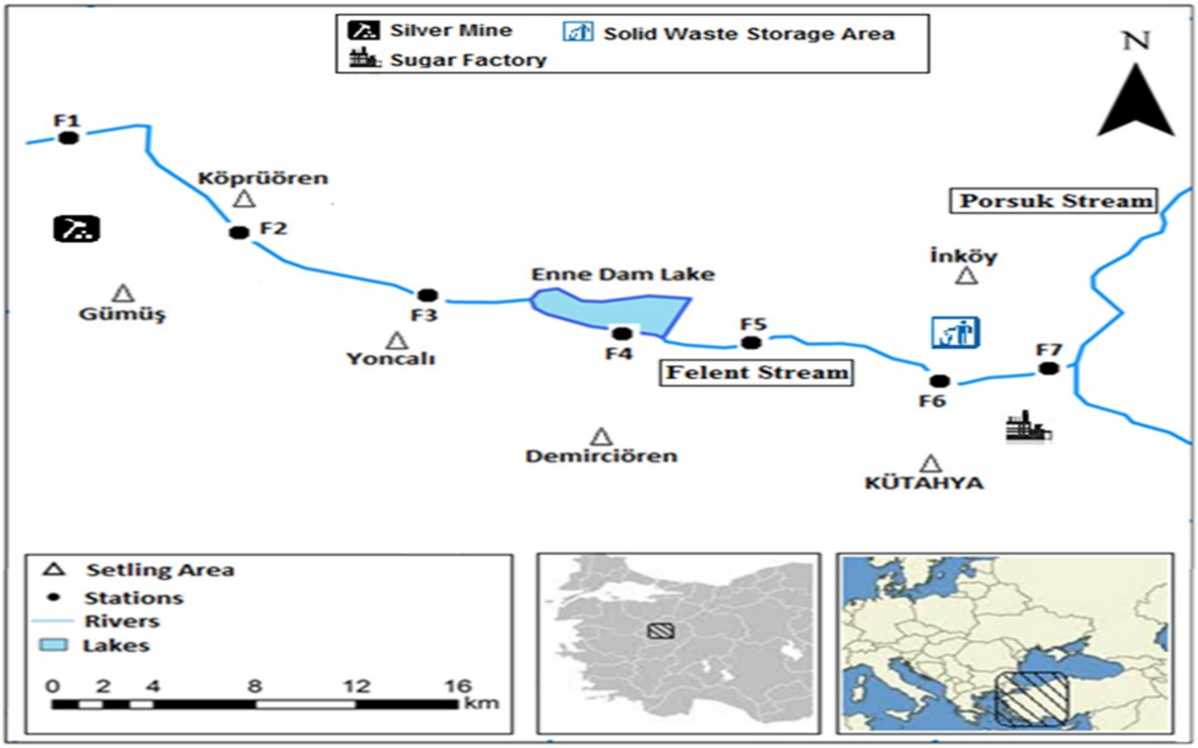

Figure 1.Study area and sampling points

applied to the results to determine the effective varifactors on Felent Stream Basin according to correlated variables by using the SPSS 17 package program.

RESULTS AND DISCUSSION

Element Accumulations in Sediment and One Way Anova Test

The annual averages of element levels observed in sediment of Felent Stream Basin and the results of One Way Anova Test that compares the element accumulations of stations were given in Table 1. According to the results of One Way Anova Test, no statistically significance stational differences were identified in terms of total chromium, copper, potassium, magnesium, manganese and sodium. Statistically significance differences were identified between F2 and F3 station with all the other stations in terms of arsenic levels; between F2 station with F1, F4, F5 and F7 stations in terms of lead levels; and between F7 station with F1, F2, F4 and F5 stations in terms of total phosphorus levels ($p<0.05$).

The upstream sections of the basin (especially in F2 and F3 stations) had the highest mean concentrations of arsenic, chromium, lead, zinc and potassium while the downstream sections of the basin (especially in F6 and F7 stations) had the highest mean concentrations of copper, calcium and total phosphorus.

Pearson Correlation Index

High correlations between specific heavy metals may reflect similar levels of contamination in the sediments or release from the same sources of pollution (Li *et al.*, 2009). The relationships between macro and micro element concentrations in sediment of Felent Stream Basin were determined by using seasonal values, ($n = 28$ for all parameters) and all identified relations were given in Table 2. It was found that, the relations between arsenic – potassium, arsenic – lead, arsenic – zinc, chromium – potassium, chromium – manganese,

Table 1.Micro and macro element concentrations in sediment (mg/kg)

Elements (Wavelengths/nm)		Mining – Agricultural Sections (Upstream)			Lenthic Section	Urban Sections (Downstream)		
		F1 (Source of stream)	F2 (Köprüören Village)	F3 (Yoncalı Village)	F4 (Reservoir)	F5 (Output of reservoir)	F6 (Solid waste storage area)	F7 (Estuary of stream)
As	mean	15.56[a]	89.28[b]	119.90[b]	27.12[a]	14.84[a]	17.64[a]	18.53[a]
(193.759)	SD	6.78	49.02	25.32	13.81	7.24	2.09	3.61
Cr	mean	48.38[a]	51.63[a]	62.69[a]	53.47[a]	33.42[a]	46.29[a]	40.73[a]
(205.552)	SD	29. 84	27.81	24.32	21.51	14.72	34.29	16.96
Cu	mean	9.62[a]	12.97[a]	19.53[a]	22.29[a]	15.47[a]	163.48[b]	67.16[ab]
(324.754)	SD	3.52	6.27	1.18	17.51	6.40	165.85	83.02
Pb	mean	11.73[a]	230.75[b]	114.31[ab]	11.29[a]	8.52[a]	123.66[ab]	42.08[a]
(220.353)	SD	4.90	123.24	37.97	5.43	1.43	71.96	11.79
Zn	mean	39.31[a]	343.25[b]	250.06[bc]	54.69[a]	56.13[a]	138.00[c]	97.29[ac]
(213.856)	SD	16.01	127.36	92.25	23.93	19.29	32.20	26.23
Ca	mean	38642[ab]	50359[ab]	43148[ab]	46654[ab]	27865[a]	72028[b]	57922[ab]
(315.887)	SD	16865	11015	21946	16205	15282	19945	14832
K	mean	2414[a]	2516[a]	3467[a]	3107[a]	1500[a]	1404[a]	1687[a]
(766.491)	SD	1548	1061	605	2283	249	388	378
Mg	mean	20424[a]	13598[a]	9633[a]	11225[a]	8679[a]	17367[a]	11256[a]
(279.079)	SD	2536	3463	2714	3502	4700	12745	2765
Mn	mean	232.42[a]	318.40[a]	385.30[a]	430.68[a]	334.75[a]	335.58[a]	279.00[a]
(257.610)	SD	140.62	123.17	87.04	112.73	98.76	122.73	62.39
Na	mean	215.49[a]	117.93[a]	170.95[a]	156.35[a]	113.98[a]	237.63[a]	217.00[a]
(588.995)	SD	158.66	59.13	72.53	110.53	85.70	118.53	72.98
P	mean	405.25[a]	416.95[a]	676.93[ab]	415.18[a]	385.88[a]	737.34[ab]	892.27[b]
(214.914)	SD	209.16	96.44	175.50	330.18	161.25	120.47	128.79

*** The values marked with different letters in the same line are statistically different ($p < 0.05$)**

magnesium – sodium and lead – zinc levels were directly proportional ($p<0.01$).

Factor Analyses

Factor Analyses (FA) were used to determine the effective varifactors on Felent Stream Basin by using correlated variables. A total of eleven variables were used to determine the varifactors. Eigenvalues higher than one were taken as a criterion to evaluate the principal components required for explaining the sources of variance in the data.

The percentage variance counted as cumulative percentage variance and component loadings (unrotated and rotated) were given in Table 3. According to rotated cumulative percentage variance, four factors have explained 75.92% of the total variance.

The parameter loadings (> 0.5) for four components before and after rotation were given in Table 4. Liu (Liu *et al.*, 2003) classified the factor loadings as "strong (> 0.75)", "moderate (0.75 – 0.50)" and "weak (0.50 – 0.30)", according to loading values.

First factor (F1) named as "Mine – Agriculture Factor" has explained 24.05 % of the total variance, and it was related to the variables of Zn, Pb and As parameters. All parameters were "strong positively" loaded with this factor. Arsenic that may exist in several valences and in a number of inorganic and organic forms is a very powerful toxicant. A large amount of information is also available on the toxic effects of lead on human health. Nervous, hematological and cardiovascular systems are the most sensitive target systems and kidney is one of the most sensitive target tissues for lead toxicity (ATSDR, 2005a; 2007). According to a study performed in Emet Stream (Turkey), lead bioaccumulations in fishes of Emet Stream detected in liver and kidney tissues of three fish species (*Squalius cii, Capoeta tinca* and

Table 2. Pearson Correlation Index coefficients

	As	Ca	Cr	Cu	K	Mg	Mn	Na	P	Pb	Zn
As	1										
Ca	-.016	1									
Cr	**. 460***	.104	1								
Cu	-.186	.071	-.314	1							
K	**. 479****	-304	**.538****	-.136	1						
Mg	-.092	.267	.134	-.053	.006	1					
Mn	.361	.040	**.690****	-.154	**.461***	-.113	1				
Na	-063	.137	.344	.161	.361	**.530****	.249	1			
P	-042	.314	-.236	.359	-.013	.070	-.217	.311	1		
Pb	**. 697****	.182	.246	.280	.166	.053	.146	-.007	-.003	1	
Zn	**.786****	.044	.278	-.066	.284	-.044	.130	-.123	.087	**.813****	1

*: Correlation is significant at the 0,05 level ($p<0.05$);
**: Correlation is significant at the 0,01 level ($p<0.01$)

Barbus oligolepis) were significantly higher than detected in muscle and gill tissues (Tokatlı *et al.,* 2012a). As it is known, pesticides used in agricultural applications contain significant quantities of lead and arsenic and mankind are being exposed to arsenic and lead since these arsenic containing pesticides are widely used in agriculture. Also fertilizers have a significant impact on zinc transition to the soil and sediment. Although zinc is an obligatory element for the function of a number of metalloenzymes and it is an essential nutrient for humans and animals, plus quantity of zinc accumulations may cause toxic effects for human (ATSDR, 2005a; 2005b; 2007).

Second factor (F2) named as “Geologic Factor” has explained 22.09 % of the total variance, and it was related to the variables of K, Cr, Mn and Na parameters. K and Cr parameters were “strong positively” loaded with this factor and Mn and Na parameters were “moderate positively” loaded with this factor. Long term exposure of chromium that is often being accumulated in aquatic organisms can cause especially kidney and liver damage in terms of tissues, and circulatory and nerve damage in terms of systems (ATSDR, 2000). Chromium can be found in compounds with other elements such as nickel, magnesium and manganese (Fishbein, 1981). High correlation coefficients between Cr with Mn concentrations in sediment were stated in another study conducted in the region (Tokatlı, 2012). As similar to this information, significant positive correlations were identified between Cr and Mn levels in the present study ($p<0.01$). According to data, detected uniform Cr – Mn accumulations in terms of stations reflect that the main Cr – Mn source of the system can be the geological structure of the Felent Stream Basin.

Third factor (F3) named as “Urban – Industrial Factor” has explained 15.1 % of the total variance, and it

Table 3.Extracted values of various FA parameters

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.286	29.872	29.872	3.286	29.872	29.872	2.646	24.057	24.057
2	1.949	17.719	47.591	1.949	17.719	47.591	2.431	22.096	46.153
3	1.937	17.610	65.201	1.937	17.610	65.201	1.661	15.100	61.253
4	1.180	10.727	75.928	1.180	10.727	75.928	1.614	14.675	75.928

Table 4.Values of component matrix and rotated component matrix

	Component Matrix				Rotated Component Matrix			
	F1	F2	F3	F4	F1	F2	F3	F4
Zn	.740		-.558		.931			
Pb	.675		-.561		.908			
As	.867				.848			
K	.673					.836		
Cr	.760					.757		
Mn	.634					.718		
Na		.616	.637			.647		
Cu		.525		.524			.811	
P		.698					.753	
Ca		.595		-594				.792
Mg		.561						.759

was related to the variables of Cu and P parameters. All parameters were “strong positively” loaded with this factor. As it is known, copper is an essential nutrient for humans and animals, but it can cause anemia, liver and kidney damage, stomach and intestinal irritation, when it is accumulated in high levels and two of the most important ways to enter the environment for copper are domestic waste water and industrial activities (ATSDR, 2004). Although the drainage water of agricultural lands may cause significant raises of phosphorus levels in aquatic ecosystems, sewage and industrial effluents provide a greater risk of lothic eutrophication than agricultural activities, even in rural areas with high agricultural phosphorus losses (Jarvie *et al.*, 2006). As similar to this literature information, although total phosphorus accumulations in sediment of the entire basin were in a relatively high level, phosphorus concentrations were significantly rising after the discharges of a sugar factory and sewage waste waters of Kütahya province to the system (in F7 station). According to the results of One Way Anova Test, total P accumulations in sediment of F7 stations were statistically higher than F1, F2, F4 and F5 stations ($p<0.05$).

Fourth factor (F4) named as “Natural Factor” has explained 14.67 % of the total variance, and it was related to the variables of Ca and Mg parameters. All parameters were “strong positively” loaded with this factor.

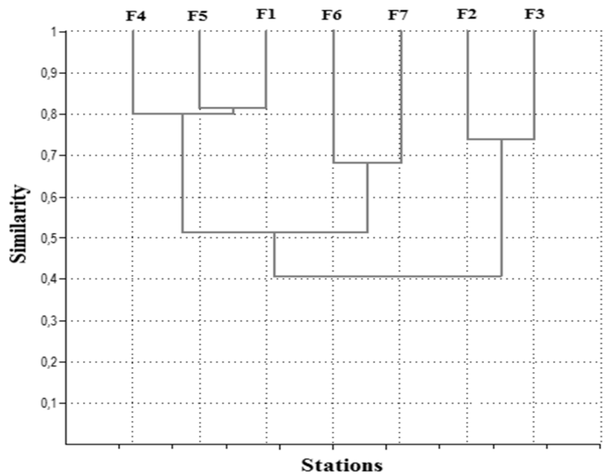

Figure 2.CA similarity diagram

In a study performed in Felent Stream in order to evaluate the water quality in a statistical approach (factor analysis) by using physiochemical and chemical parameters, three factors explained 96.54% of the total variance. As similar to the present study, variables of arsenic and zinc parameters detected in water were strong positively loaded with the same factor with an explaining of 23.31% of the total variance (Tokatlı *et al.*, 2012b).

Cluster Analyses

Cluster Analyses (CA) were used to determine the similarity groups between the stations. The diagram of CA calculated by using toxic element concentrations (As, Cr, Cu, Pb and Zn) in sediment was given in Figure 2. According to the CA, three statistically significant clusters were formed: Cluster 1 corresponded to F4, F5 and F1 that were uncontaminated areas of the basin; Cluster 2 corresponded to F6 and F7 that were moderately contaminated areas of the basin; Cluster 3 corresponded to F2 and F3 that were strongly contaminated areas of the basin.

In a study performed in Uluabat Lake, cluster analysis was used to classify the stations based on the water quality by using some physiochemical and microbiological parameters. According to results of this study, two statistically significant clusters were formed (Iscen *et al.*, 2008)

Table 5.CA similarity – distance coefficients

	F1	F2	F3	F4	F5	F6	F7
F1	1						
F2	**0.28544**	1					
F3	0.35466	0.7371	1				
F4	0.80905	0.33923	0.42334	1			
F5	**0.81352**	0.29155	0.36799	0.78979	1		
F6	0.37043	0.49073	0.57618	0.4346	0.40637	1	
F7	0.57928	0.42587	0.52272	0.64599	0.64769	0.68133	1

The highest similarity was determined between F1 and F5 stations, (81.35 %) and the lowest similarity was determined between F1 and F2 stations (28.54 %) (Table 5).

CONCLUSIONS

The aim of this study was to determine the natural and anthropogenic impacts on the watershed of the Felent Stream on the basis of seasonal investigations at seven stations. Heavy metal concentrations in the surface sediments were determined and the results were evaluated by using some monovariate (One Way Anova and Pearson Correlation Index) and multivariate (Factor and Cluster Analyses) statistical techniques.

In general, heavy metal accumulations in the sediment of upstream of the basin were higher than in the downstream. Furthermore, sediment heavy metal concentrations were much lower in the reservoir compared to the watershed, perhaps due to the resting of the water in the reservoir for a long time.

Factor Analyses illustrated that heavy metals (As, Cr, Cu, Pb and Zn) in the watershed originated from anthropogenic activities were presumably mining, agricultural, urban and industrial activities, and originate from environmental interactions were presumably geographic structure and natural possesses.

Cluster Analyses illustrated that source of Felent Stream (F1 station), Enne Dam Lake (F4 station) and output of reservoir (F5 station) were unpolluted areas; solid waste storage area (F6 station) and estuary of stream (F7 stations) were moderately polluted areas; and Köprüören (F2 station) and Yoncalı (F3 stations) Villages were polluted areas, these have the similar sediment characteristics in terms of heavy metal contamination (As, Cr, Cu, Pb and Zn).

In brief, heavy metal pollution caused from mining, agricultural, urban and industrial activities is a significant problem for the Felent Stream Basin and the study clearly presents the necessity and availability of multivariety statistical techniques on sediment quality assessment.

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