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Metal pollution assessment in water and sediment of Sarıçay stream in Muğla-Turkey

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ABSTRACT

The concentrations of six heavy metals (Cr, Pb, Cu, Mn, Zn and Ni) were measured in water and sediment of Sarıçay Stream in Turkey. The decreasing trend of metals were observed in water as Mn>Zn>Cr>Cu>Ni>Pb and in sediment as Mn>Zn>Ni>Cu>Cr>Pb. The level of studied metals not exceeded the safe limits of toxicity reference value for fresh water, indicated that water from this stream is safe for organism. The assessment of pollution load index (PLI) values of metals in sediment at all sites were ranged from 0.18 to 0.21 during winter and 1.43–1.80 during summer it is supporting that the sediment of the studied stream was not contaminated on winter but contaminated on summer. Furthermore, Igeo values for Mn (3.99) and Zn (3.18) during summer indicates heavily contaminated status. Enrichment ratio (ER) values for Cr, Pb, Cu, Zn and Ni at all station were indicated no enrichment of these metals but ER values for Mn showed minor enrichment in all stations. The higher geoaccumulation factor (Igeo), pollution load index (PLI) and contamination factor (CF) values on summer indicated that Mn and Zn are the major contributors to the sediment pollution. Calculated values indices Sarıçay stream can be classified as unpolluted to moderately polluted stream environment.

Keywords: Metals, pollution index, geo-accumulation index, enrichment ratio, Turkey

INTRODUCTION

Metals are the main group of inorganic contaminants and spread over a considerable large area. Metal contaminations of land resources continue to be the focus of numerous environmental studies and attract a great deal of attention worldwide. In our century of advanced technologies and technical progress soil contamination by various pollutants is one of the most significant environmental problems and irrespective of the origin of the metals in the soil, excessive levels of many metals can result in soil quality degradation, crop yield reduction, and poor quality of agricultural products, posing significant hazards to human, animal and ecosystem health [1].

River sediments play a key role as pollutants and they reflect the history of the river pollution [2]. A number of studies on the metal distributions in river sediments and on speciation of metals have been performed [3-6].

The Sarıçay stream basin is located at the northwest part of the Muğla City in borders of Milas town. Sariçay Stream can be polluted by different types of industrial, agricultural and domestically wastewaters. Particularly, the Stream transfers domestic waters of Milas town and other sources of metal pollution, such as from car washing stations, pesticides from agricultural areas through rain-wash to Gulluk Bay [7]. Sarıçay stream had been a water source of agricultural activities for years of Milas [8]. To know the accumulation level of the metals in water and sediment is very important in order to evaluate future toxicity on living organisms. The purpose of the current study was; investigation of sediment and water contamination of the Sarıçay highway by chromium (Cr), lead (Pb), copper (Cu), manganese (Mn), zinc (Zn) and nickel (Ni) accumulation of metals depending on different distances from the highway. The degree of contamination in the sediments is illustrated with the assistance of three parameters which Enrichment Ratio (ER), Pollution Load Index (PLI) and Geo-accumulation Index (*I*geo).

EXPERIMENTAL SECTION

Description of the study area

Sarıçay stream is about 50 km in length. The basin is aligned in a northwest-southeast direction. A large part of the basin plain is made of alluvium, which is the principal aquifer in the catchments area, and consists of loose, interlayered clay, silt, sand, and gravel. Karstic cavities are observed in marbles in the area [9]. Five sampling points were selected (Figure 1) in the research area. Sampling plots were marked in Sarıçay stream approximately at 10 km meters distance from the highway. The first station (station 1) was chosen upstream in front of the dam. This station where there is agricultural activity is begun. The second station (station 2) was located in the area where far from 10 km to the Centrum. The third station (3) was chosen in Centrum area. The fourth station (station 4) was chosen after the industrial companies which produce animal nutrition, olive oil and concrete plant. The fifth station (station 5) was chosen nearest location to the sea.

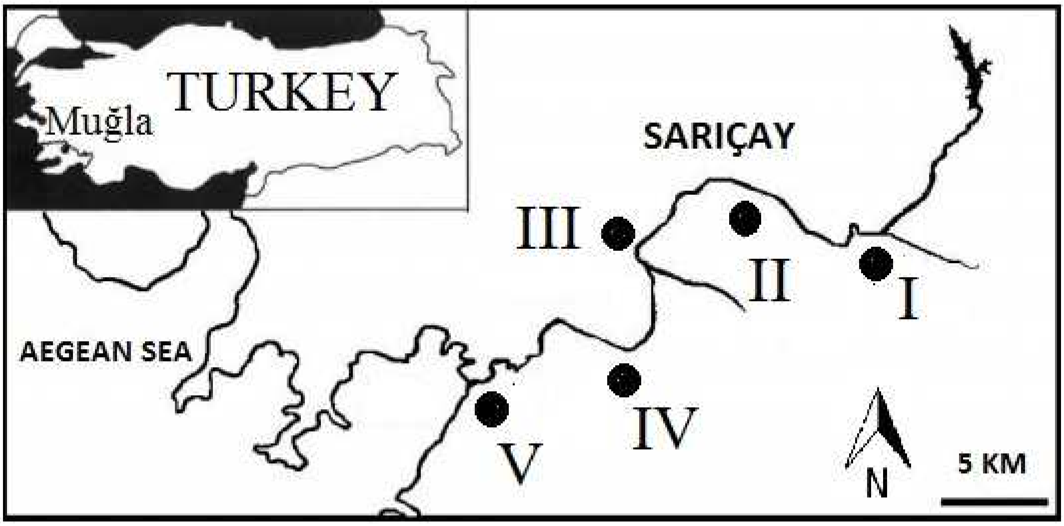

Fig 1: Sampling station of Sarıçay Stream

Sample collection and preparation

The water and sediment samples were collected from five different stations in winter (December, January and February) and summer (June, July and August) in 2014. Samples were taken from every distance in all selected sites and analyzed independently. Water samples were collected at the surface in 40 mL acid-washed polyethylene sample bottles, taking care not to incorporate sediment into the samples and during the sampling, 0.5% concentrated nitric acid was added to the water samples. Water samples were taken from the surface of the stream for metal analyses. At each point, composite sediment samples were collected using standard protocol [10]. Composite samples of mass approximately more than 250 g were collected at sampling points.

Sample digestion and metal analyses

The sediments were dried at 105°C for 24 h. The dried sediments were passed through a 60 mesh stainless screen to remove larger particles. Ultrapure (Direct-Q 8UV Germany) water was used for solution preparation. The Teflon vessel were cleaned, soaked in %5 HNO_3 for more than 1 day than rinsed with ultrapure water and dried. For metal analysis, 0.5 g of sediment sample and 20 mL water sample was treated with 7 mL 70 % HNO_3 acid and 3 mL 30% H_2O_2 in a closed Teflon vessel and was digested microwave digestion system (Berghof speedway MWS-3^+).

The operating conditions for sediments are given in Table 1. Water samples were filtered and analyzed directly. The advantage of microwave digestion against the classical method are the shorter time, less consumption of acid and keeping volatile compounds in the solution [11]. The digested solution was then filtered by using Filter papers (Sartorius-Stedim, particle retention=2-3μm) and stored in 25 mL polypropylene tubes. Lastly of digestion procedure, the vessels were cleaned by ultrapure water and dried with air.

Table 1: Operating condition to digestion the sediment with MWS-3+

Stage	1	2	3	4	5
Temperature [°C]	175	100	100	100	100
Pressure [bar]	30	0	0	0	0
Time [min]	10	10	10	10	10
Slope [min]	1	1	1	1	1
Power [%]	80	0	0	0	0

To avoid possible contamination, all equipments used were acid-soaked with 10% HCl for at least 24 h and then double rinsed with ultrapure distilled water. Standard solutions were prepared from stock solutions (Merck, multi element standard). Standard reference National Research Council Canada SPS-SW1 (for water) and WQB1 (for sediment) - National Water Research Institute were analyzed for metals. All samples were analyzed three times for Cr, Pb, Cu, Zn, Mn and Ni by AAS (Atomic Absorption Spectrometry – GBC Scientific Equipment-Avanta). The calibration curves with R2 > 0.999 were accepted for concentration calculation. The data are presented in µg/g dry weight basis. Replicate analysis of these reference materials showed good accuracy, with recovery rates for metals between 90-97 % for water and sediments.

Contamination factor (CF) and pollution load index (PLI)

Pollution load index (PLI), for a particular site, has been evaluated following the method proposed by Tomilson et al. [12]. The PLI is defined as the *n*th root of the multiplications of the contamination factor of metals (CF).

$$\text{Contamination factor (CF)} = \frac{\text{Metal concentration in sediment}}{\text{Background value of the metal}}$$

$$\text{PLI is expressed as: PLI} = (CF_1 \text{ x } CF_2 \text{ x } CF_3 \text{ x } \ldots\ldots\ldots.. \text{ x } CF_n)^{1/n}$$

Where, n is the number of metals (seven in the present study) and CF is the contamination factor. The ratio of the measured concentration to natural abundance of a given metal had been proposed as the index contamination factor (CF) being classified into four grades for monitoring the pollution of one single metal over a period of time [13-14]: low degree (CF < 1), moderate degree (1≤CF < 3), considerable degree (3≤CF < 6), and very high degree (CF≥6). Thus the CF values can monitor the enrichment of one given metal in sediments over a period of time.

Geo-accumulation index (*I*geo)

The geoaccumulation index (Igeo), introduced by Muller [15] for determining the extent of metal accumulation in sediments, has been used by various workers in their studies [16-18].

$$l\text{geo} = \text{Log2}[\frac{\text{C}n}{1.5\text{B}n}]$$

Where C_n is the measured concentration of metal *n* in the sediment and Bn is the geochemical background value of element *n* in the background sample. The factor 1.5 is introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. Geoaccumulation index (*I*geo) values were interpreted as: *I*geo≤0–practically uncontaminated; 0≤*I*geo≤1 uncontaminated to moderately contaminated; 1≤*I*geo≤2 moderately contaminated; 2≤Igeo≤3 moderately to heavily contaminated; 3≤*I*geo≤4 heavily contaminated; 4≤*I*geo≤5 heavily to extremely contaminated; and 5< *I*geo– extremely contaminated [19-21].

Enrichment ratio (ER)

Enrichment ratio analysis, a method proposed by Simex and Helz [22] to assess trace element concentration, is considered as an effective tool to evaluate the magnitude of contaminants in the environment [23].

To identify anomalous metal concentration, geochemical normalization of the heavy metals data to a conservative element, such as Al, Fe, and Si was employed. Several authors have successfully used aluminum and iron to normalize heavy metals contaminants [24-25, 18].

In this study, aluminum was used as a conservative tracer to differentiate natural from anthropogenic components.
The ER for each element was calculated to evaluate anthropogenic influences on heavy metals in sediments using the following formula:

$$\text{Enrichment Ratio (ER)} = \frac{(\text{Cx/Al})\text{sample}}{(\text{Cx/Al})\text{background}}$$

Where, Cx stands for concentration of metal 'x'. The background value is that of the world surface rock average [25] given in Table 4.

Samples having enrichment factor >1.5 was considered indicative of human influence and (arbitrarily) an ER of 1.5–3, 3–5, 5–10 and >10 is considered the evidence of minor, moderate, severe, and very severe modification [25].

Data analyses

Paired relationships for water and sediment were revealed using Spearman's rho correlation tests. These statistical calculations were performed with SPSS 20.0 for Windows while Origin 8.0 was used to draw.

RESULTS AND DISCUSSION

Metal concentration in water

The result of heavy metal concentrations in waters of the Sarıçay stream are shown in Table 2. The average concentration of metals in water followed a decreasing order of Mn> Zn> Cr> Cu> Ni> Pb. The mean concentration of Mn in water was observed 92.79 and 155.8 µg/L during winter and summer season respectively which higher in station 5 than other stations. Accumulation of Zn (28.1 µg/L) and Ni (1.2 µg/L) in water also were found much higher in station 5 on summer but interestingly the highest value of Pb was observed on winter in station 1. Considering the toxicity reference values (TRV) proposed by USEPA [27] all the metals not exceeded the limit for safe water, concluded that water from this stream is safe for organisms.

Table 2: Metal concentration (µg/L) in water sample of Sarıçay stream of the present study and permitted concentration in water (µg/L)

Sites	Cr		Pb		Cu		Zn		Mn		Ni	
	W	S	W	S	W	S	W	S	W	S	W	S
S 1	1,48± 0,29	1,60± 0,25	0,55± 0,01	0,32± 0,14	1,01± 0,09	0,73± 0,10	8,40± 2,40	17,02± 2,24	69,79± 5,86	94,59± 13,27	0,31± 0,14	0,82± 0,27
S 2	1,37± 0,24	1,71± 0,21	0,46± 0,01	0,40± 0,08	0,95± 0,05	0,75± 0,16	10,51± 2,08	18,12± 2,61	75,76± 3,98	103,55± 18,53	0,32± 0,02	0,82± 0,15
S 3	1,27± 0,23	1,92± 0,43	0,33± 0,01	0,47± 0,03	0,91± 0,05	1,40± 0,06	13,82± 4,75	20,35± 4,07	86,72± 9,15	125,40± 18,43	0,48± 0,19	0,87± 0,04
S 4	1,29± 0,08	1,98± 0,25	0,33± 0,02	0,42± 0,08	0,85± 0,03	1,11± 0,11	15,26± 5,19	23,25± 3,40	89,48± 11,76	141,38± 26,67	0,55± 0,24	1,02± 0,11
S 5	1,30± 0,11	1,96± 0,31	0,34± 0,03	0,36± 0,16	0,80± 0,06	0,83± 0,18	20,86± 5,90	28,15± 4,40	92,79± 19,02	155,83± 46,18	0,66± 0,51	1,24± 0,12
Avarage± SD	1,34± 0,19	1,83± 0,30	0,40± 0,09	0,39± 0,10	0,90± 0,09	0,96± 0,29	13,77± 5,76	21,38± 5,06	82,91± 13,10	124,16± 32,96	0,46± 0,23	0,95± 0,21
TRV	11		2,5		9		118		-		52	

Total metals in sediment

Metal concentrations of sediments in stations and comparison of metals in sediment (µg/g) with different other studies in Aegean part of Turkey are presented in Table 3 and 4. A wide range of metal accumulation in sediment was observed among sampling sites. The average concentration of metals in sediment were in the decreasing order of Mn>Zn>Ni>Cu>Cr>Pb. Metal accumulation in water and sediment almost in the same order. Just Cr and Ni were different place in ranking of metals. Conspicuously, all metals in sediment were found highly on summer season. In highly polluted station for Mn and Zn were Station 5, on the other hand, domestically and agricultural activities are the primary culprit. High values for Cr, Pb, Cu and Ni concentrations were observed in station 1. Factors such as, geomorphological setup, pH, salinity, hardness might have played a crucial role in high accumulation of these metals in station 1. It should be noted that station 1 where there is agricultural and urban activity is begun.

Table 3: Metal concentration (µg/g) in sediment of Sarıçay stream

	Cr		Pb		Cu		Zn		Mn		Ni	
	W	S	W	S	W	S	W	S	W	S	W	S
S 1	12,88± 4,88	20,87± 7,77	8,47± 4,55	11,57± 4,40	43,19± 22,43	60,82± 4,51	541,01± 88,62	510,00± 73,33	3161,63± 908,15	4237,17± 306,90	50,18± 7,98	70,23± 15,42
S 2	11,71± 3,34	18,26 ± 5,52	6,67± 2,37	11,23± 0,67	35,50± 12,81	54,55± 10,79	528,20± 63,97	526,94± 68,64	3162,74± 718,56	4203,36± 458,20	45,70± 4,78	67,52± 13,82
S 3	10,63± 1,43	16,19± 3,76	6,19± 0,20	10,18± 2,53	27,32± 6,79	47,66 ± 14,57	509,98± 59,28	626,19± 57,05	3180,93± 664,88	4265,47± 551,58	44,86± 11,95	65,39± 11,78
S 4	10,12± 1,65	17,74± 4,83	4,46± 1,44	9,68±1 ,23	26,13± 5,05	37,99± 3,27	541,13± 7,58	670,24± 55,60	3462,37± 502,73	4323,56± 411,41	36,48± 2,69	61,72± 16,36
S 5	10,72± 2,42	15,71± 1,02	3,71± 0,46	8,58±1 ,88	24,91± 3,20	32,84± 4,61	606,95± 32,90	701,89± 43,71	3597,37± 528,55	4517,26± 395,43	45,52± 14,32	59,25± 1,61
Averag e±SD	11,21± 2,60	17,75± 4,69	5,90± 2,67	10,25± 2,39	31,41± 12,60	46,77± 12,96	545,45± 59,36	607,05± 94,21	3313,00± 605,26	4309,36± 382,97	44,55± 9,18	64,82± 11,67

Result of our study clearly show that; generally, Mn and Zn accumulation in sediment relatively higher than other workspace while Cr, Ni, Pb (excepting winter for Ortaköy), Cu (excepting winter for Geyik Dam, Ortaköy and Sarıçay stream) accumulation was lower than other studies (Table 4).

Table 4: Comparison of metlas in sediment (μg/g) with different other studies in Aegean part of Turkey

Location	Season	Station	Cr	Pb	Cu	Zn	Mn	Ni
Present study	Winter	General	11,21	5,90	31,41	545,45	3313,00	44,55
	Summer		17,75	10,32	46,77	607,05	4309,36	64,82
Gediz River [a]	Average	General	200	128	140	160	510	106
Büyük Menderes River [a]	Average	General	165	54	137	120	388	315
Geyik Dam [b]	Winter	General	92	31.30	11	32	174	320
	Summer		239	28	120	104	190	104
Ortaköy [b]	Winter	General	15	0.70	7	39	150	390
	Summer		240	28	110	102	230	102
Sarıçay Stream [b]	Winter	General	45	15.20	18	18	320	180
	Summer		1308	29	128	304	2613	304
Gediz River [c]	Average.	Nif Stream	53	14.50	72.10	94.90	-	47
		İstanbul Bridge	218.90	5.50	53.70	60.70	-	44.20
		Karaçay	134.5	18	96.50	357.30	-	69.40
		Muradiye Bridge	891.01	8.48	91.21	279.69	-	68.14
		Menemen	647.50	11.97	89.82	155.46	-	52.59
Küçük Menderes River [d]	Average	General	5.04-69.25	7.00-8.00	6.90-58.35	16.20-227.40	152.1-439.2	13.39-68.25
Sarıçay Stream [e]	Average	General	38.24	32.56	47.12	123.6	265.98	32.01
World surface rock average			71	16	32	127	720	49

a: Akcay [4], b: Tuna [5], c : Öner and Çelik [28], d: Basaran [29], e: Öğlü [8]

Correlation matrix

Spearman's rank correlation analysis was applied to test the relationship among the metals analyzed and showed table 5 and 6. The correlation matrix for water showed that Cr and Zn were highly correlated with Mn and Ni showing a strong positive association (Cr-Mn= 0.573, Cr-Ni= =0.530, Zn-Mn= 0.838, Zn-Ni= 0.867; p<0.001). Only Pb was negatively correlated with all metals except Cu but correlation was not significantly important (table 5).

The high correlation obtained between Cr, Ni, Pb, Cu and Cr in sediments of Sarıçay Stream suggests not a common pollution source of these metals. Zn is only metals show negative correlation with other metals (except Mn).

Table 5: Spearman's rank correlation matrices of metal concentration in water

	Cr	Pb	Cu	Zn	Mn	Ni
Cr (n=30)	1,000					
Pb	0,332	1,000				
Cu	0,210	0,455*	1,000			
Zn	0,329	-0,313	-0,128	1,000		
Mn	0,573**	-0,162	0,018	0,838**	1,000	
Ni	0,530**	-0,056	-0,073	0,867**	0,800**	1,000

Table 6: Spearman's rank correlation matrices of metal concentration in sediment

	Cr	Pb	Cu	Zn	Mn	Ni
Cr	1,000					
Pb	0,742**	1,000				
Cu	0,732**	0,842**	1,000			
Zn	-0,005	-0,029	-0,228	1,000		
Mn	0,276	0,240	0,194	0,676**	1,000	
Ni	0,578**	0,534**	0,422*	0,333	0,679**	1,000

Assessment of metal pollution in sediment of sarıçay stream

The CF for all metals were the descending order of Mn>Zn>Cu>Ni>Pb>Cr. The mean CF values of Mn, Zn, Cu, Ni, Pb and Cr were 4.6, 4.3, 1, 0.9, 0.4 and 0.2 during winter and 6.0, 4.8, 1.5, 1.3, 0.6, 0.3 during summer (Fig. 2). The value of contamination factor (CF) on winter for Cr, Pb and Ni metals showed low degree of contamination (CF < 1), whereas Mn and Zn showed considerably degree (3≤CF< 6). CF values on summer similar with winter but Mn showed very high degree (CF≥6) on summer.

The assessment of pollution load index (PLI) values of metals in sediment are showed in Figure 3 which were ranged from 0.18 to 0.21 during winter and 1.43–1.80 during summer, it is supporting that the sediment of the studied stream was not contaminated on winter but contaminated on summer (The PLI value > 1 is polluted whereas

< 1 indicates no pollution). However, the higher PLI values on summer indicated that Mn and Zn are the major contributors to the sediment pollution. Higher PLI values on summer were calculated in sampling sites from S 1 to S 5, which increasing the PLI values from river side to the sea side. The highest PLI values were observed in sampling sites 5 of nearest location to the sea where collected of domestic, industrial and agricultural waste comes from other stations. However, higher values of PLI in sites 5 on summer should get more attention especially in the management of landscaping for agricultural and industrial development in this site.

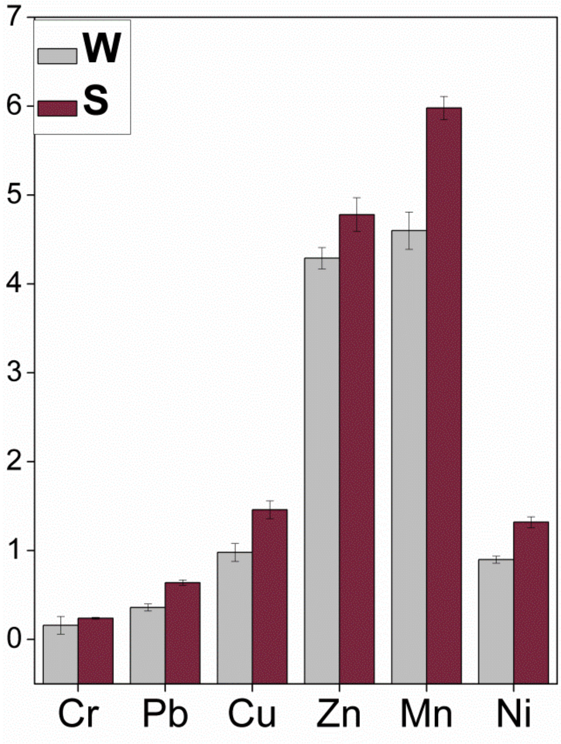

Fig 2: Contamination factor (CF) of metals in sediment of Sarıçay Stream

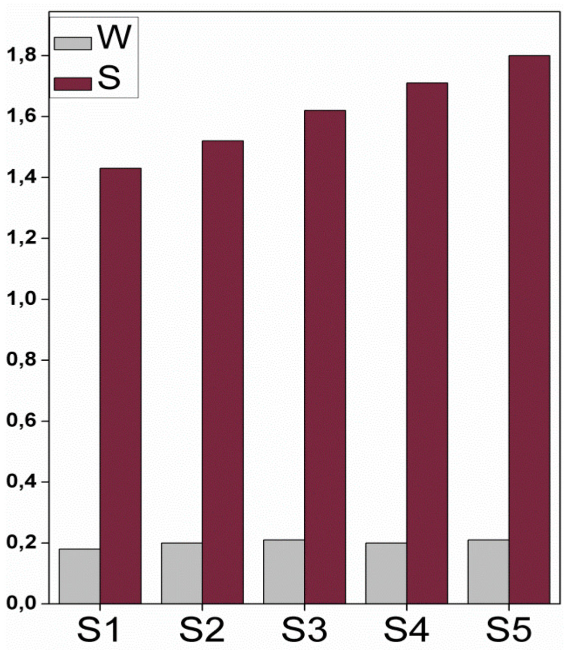

Fig 3: Pollution load index (PLI) value in sediment of Sarıçay Stream

The geoaccumulation factor (*I*geo) values of the studied metals were presented on Figure 4. Overall, the *I*geo for all metals were the descending order of Mn>Zn>Cu>Ni>Pb>Cr. Among the sites, the mean of *I*geo values for Cr, Pb, Cu and Ni were 0.1, 0.24, 0.65, 0.6 during winter and 1.6, 0.42, 0.97, 0.88 during summer respectively indicating unpolluted status of the sediment whereas *I*geo values for Mn (3.06-3.99 for winter and summer respectively) and Zn (3.18) during summer indicates heavily contaminated status. On the other hand *I*geo value for Zn (2.86) on winter indicates moderately to heavily contaminate of sediment. Mn and Zn are known as essential elements for aquatic organism; however, it is unknown whether high accumulation of these metals in Sarıçay stream may exert lethal effects to aquatic organism in the near future.

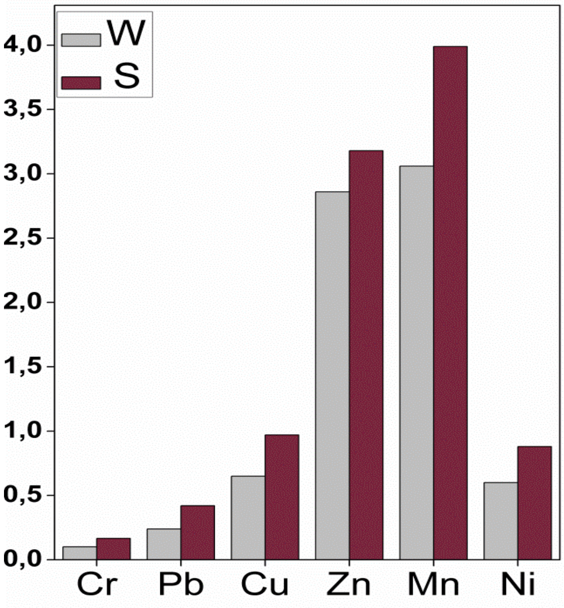

Fig 4: Geoaccumulation index (*I*geo) value of metals in sediment of Sarıçay Stream

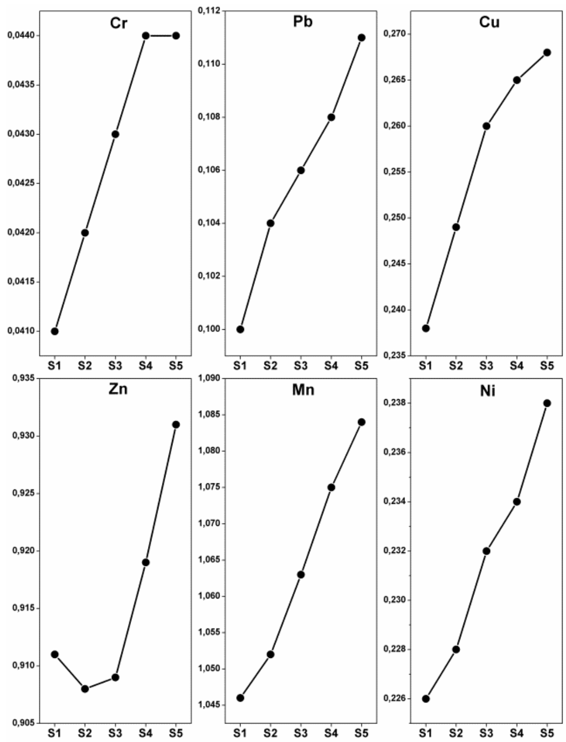

Fig 5: Enrichment ratio (ER) values for heavy metals in sediments of sampling sites, Sarıçay stream

Enrichment factor (ER) is a normalization technique widely used to categorize the metal fractions that is associated with sediments [18]. Figure 5 showed the mean ER values of the metals studied. The mean ER values of Cr, Pb, Cu, Zn, Mn and Ni were 0.04, 0.10, 0.25, 0.91, 1.06 and 0.23 respectively. ER values for Cr, Pb, Cu, Zn and Ni at all station were <1 indicated no enrichment of these metals. ER values for Mn showed minor enrichment in all stations.

The reason of higher ER values of Mn and Zn than other metals can explain Sarıçay stream affected by the intense fertilizers and pesticides used for agricultural activity.

CONCLUSION

1.Result of our study clearly show that; generally, Mn and Zn accumulation in sediment relatively higher than other workspace while Cr, Ni, Pb and Cu accumulation was lower than other studies. Furthermore, higher geoaccumulation factor (*I*geo), pollution load index (PLI) and contamination factor (CF) values on summer indicated that Mn and Zn are the major contributors to the sediment pollution.

2. Mn and Zn showed higher ER values when compared to the other metals. This indicated that agricultural inputs were probably the major contributor for the enrichment of metals in sediments of the studied stream.

3. Correlation analyses showed that there was a close relationship Cr, Ni, Pb, Cu and Cr in sediments. Alternatively, negative correlations were noted among Zn and other metals in sediment. The correlation matrix for water showed that Cr and Zn were highly correlated with Mn and Ni showing a strong positive association. These result demonstrated that Mn, Zn and Ni common source or they were able to interact to cause common pollution.

4. Metal concentrations assessment in the present study were comparable to other regions of the Aegean part and based on the calculated indices it can be classified as unpolluted to moderately polluted stream environment.

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REFERENCES

[1] XX Long; XE Yang; WZ Ni, *J Appl Ecol*., **2002**, 13,757–762.
[2] CK Jain, *Water Research.*, **2004**, 38, 569–578.
[3] K Novotry; A Turzikova; J. Komarek, *Fresenius Journal of Analytical Chemistry*., **2000,** 366, 209–212.
[4] H Akcay; A Oguz; C Karapire, *Water Research*., **2003,** 37, 813–822.
[5] AL Tuna; F Yilmaz; A Demirak; N Ozdemir, *Environ Monit Assess.,* **2007**, 125, 47–57.
[6] M Senze; MG Kowalska; P Pokorny., W Dobicki, R Polechoński, *Poland. Pol. J. Environ. Stud*., **2015,** 24(5), 2167-2175.
[7] O Dalman; A Demirak; A Balci, *Food Chemistry Environ Monit Assess*., **2006**, 125, 47–57,
[8] B Oglu; B Yorulmaz; TO Genc; F Yilmaz, Carpathian Journal of Earth and Environmental Sciences., **2015,** 10, (2), 85 – 94.
[9] A Baba, *Water Air and Soil Pollution*., **2003**, 144, 3–18,
[10] Usepa. Methods for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual. EPA-823-B-01-002. Office of Water, **2001**, Washington, DC,
[11] B Sures; H Taraschewski; C Haug, *Analytica Chimica* Acta., **1995,** 311, 135-139.
[12] DC Tomilson; DJ Wilson; CR Harris; DW Jeffrey, *Helgol. Wiss. Meeresunlter.*, **1980,** 33, 566–575.
[13] KK Turekian; KH Wedepohl, *Geol. Soc. Am. Bull.,* **1961,** 72, 175–192.
[14] K Loska; J Cebula; J Pelczar; D Wiechuła; J Kwapulinski, *Water Air Soil Pollut*., **1997**, 93, 347–365,
[15] G Muller, *Umschau*., **1979,** 79, 778-783.
[16] P Rath; UC Panda; D Bhatta; BN Sahoo, *J Geol. Soc. Ind*., **2005,** 65, 487-492.
[17] AS Likuku;, KB Mmolawa; GK Gaboutloeloe, *Environment and Ecology Research*., **2013**, 1(2), 32-40.
[18] MDS Islama; MDK Ahmedc; M Raknuzzaman; MDH Al Mamun; MK Islame, *Ecological Indicators*., **2015,** 48, 282–291.
[19] RL Rudnick; S Gao, Composition of the continental crust. In: Holland, H.D., Turekian, K.K. (Eds.), Treatise on Geochemistry, vol. 3. Elsevier, Amsterdam, Netherlands, **2003**, 1–64.
[20] GB Yu; Y Liu; S Yu; SC Wu; AOW Leung; XS Luo; B Xu; HB Li; MH Wong, *Chemosphere*., **2011,** 85, 1080–1087.
[21] MA Rahman; H Ishiga, *Environ. Monit. Assess*., **2012**, 184, 5755–5771.
[22] SA Simex; GR Helz, *Environmental Geology*, **1981**, 3, 315- 323.
[23] A Franco-Uria; C Lopez-Mateo; E Roca; ML Fernandez-Marcos, *J. Hazard. Mater*., **2009,** 165, 1008–1015.
[24] JA Baptista Neto; BJ Smith; JJ Mcallister, *Environ. Pollut*., **2000**, 109(1), 1-9.
[25] AP Mucha; MTSD Vasconcelos; AA Bordalo, *Environ. Pollut*. **2003**, 121(2), 169-180.
[25] JM Martin; M Meybeck, *Marine Chemistry*. **1979**, **7**(3), 173-206.
[26] GF Bırch; MA Olmos, *J. Mar. Sci*., **2008**, 65, 1407–1413.

[27] Usepa, Screening Level Ecological Risks Assessment Protocol for Hazardous Waste Combustion Facilities. Appendix E: Toxicity Reference Values. EPA 530-D99-001C, vol. 3. **1999**. http://www.epa.gov/epaoswer/hazwaste/combust/ eco-risk/voume3/a ppx-e.pdf.
[28] O Oner; A Celik, *Ekoloji*., **2011**, 20, 78, 48-52.
[29] AK Basaran, *Journal of Animal and Veterinary Advances*., **2011**, 10(24), 3274-3280.