Application of Multivariate Statistic and Pollution Index Techniques to Determine Beach Sand Element Distribution, East of Antalya City

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Abstract. This research was conducted on beach sands in East of Antalya city. The samples collected from 47 locations in the target area were investigated for the existence of possible heavy metal anomaly. The heavy metal contents of the samples were evaluated using categorization of Pollution Index, Enrichment Factor, Potential Ecological Risk, Toxicity Risk Index and statistical applications. Samples were distinguished in different groups of close similarities based on the statistical specifications. There was unequal distribution of elements. Ca, Cr, Fe, Ti and Pb were anomalously concentrated in some samples. Cr, Pb, and Cu showed contaminated and high risk level in some samples. The occurrence of high Cr concentration is thought to be mostly influence by natural activities while Pb and Cu are thought to be mostly due to anthropogenic influence.

1. Introduction

Besides the natural occurrence of heavy metals in soils, intensive anthropogenic activities are also recognized as sources of heavy metal pollution in beach sand [16][9]. Heavy metal anomalies are known to cause gradual but serious deterioration of water, soils and beach sand quality, which thus poses an adverse effect to the interacting biological community, together called as the ecosystem. Heavy metals have the ability to accumulate rapidly in sands that act as a sink and scavenger to them, resist degradation and are ever-present in them. Their possibility to potentially accumulate and adversely affect the biological community in frequently utilized or waste discharged areas in particular is of increasingly global concern [15][3][7]. The rapid population growth of Antalya has brought with it an increase in urbanization and touristic activities such construction of hotels and amusement center around the beach area [16]. According to [5], 25 hotels of the five star categories were constructed along this coast during the past decade. The recreational infrastructure together with the beautiful coastal beach of the city attracts tens of thousands of visitors and workers to the city each year. This increase in population in the coastal area also leads to increase in anthropogenic pressure on beaches [15][17]. The aim of this study is to determine the anomalous concentrated levels and distribution of heavy metals within the sediments using applied statistics and applied mathematics and along with the accumulation index.

2. Material and Method

Data of the 47 samples from the study area were obtained from [18]. Factor Analysis and Principal Component Analysis techniques were used to determine whether the sources of the elements were natural or anthropogenic. Cluster analysis was applied to investigate the similarities in element content of the locations, and the coexistence of the variables were determined by correlational analysis using SPSS software [1]. The interrelationship of the coexisting elements is based on the theory that, there is illustration of strong affinity between elements arising from the same source [15][8]. The qualitative approach to assess the nature and risk of pollution, were done using the application of pollution assessment index such as Pollution Index (PI), Enrichment Factor (E_f) and Potential Ecological Risk Index.

2.1. Pollution Index (PI)

The Pollution Index was applied to assess possible contamination of the beach sands. This is done by evaluating the ratio of the concentration of an element in the sample to the Maximum Permissible Concentration (MPC) of the element in the country of study as background concentration. In this case, the MPC of Turkey was used [19]. The evaluation was done using the formula below; where C is concentration of element in the sample. Refer to Table 1 for categorization of PI.

$$PI = C_{samples}/MPC_{background}$$

2.2. Enrichment Factor (E_f)

The (E_f) measure the magnitude of enrichment of a particular element to an immobile reference element in the samples, to the ration of their respective background concentration [12][4]. Fe was used as the reference immobile element. Average concentration of elements in sandstone was used for background concentration [13]. The enrichment factor was calculated using the equation:

$$EF = [C/Fe]_{sample}/[C/Fe]_{background}$$

Where [C/Fe]sample is the metal to Fe concentration ratio in the sample and [C/Fe] background is the background value of metal to Fe ratio. Enrichment factor categories are listed in Table 1.

2.3. Potential Ecological Risk Index (RI)

To evaluate the level of pollution (risk) that heavy metals are individually and/or collectively able to potential pose to the biological community within their environment of interaction, potential ecological Index was used [6]. It was calculated using the formula:

$$Ef = CF_{metal}T_f$$

$$RI = \sum E_f$$

Where (E_f) is the potential ecological risk index for single heavy metal pollution, RI is the comprehensive potential ecological risk index, which is the sum of (E_f) of the individual heavy metals; CF is an element's pollution factor calculated using sandstone background values [13]. T_f represents the biological toxic response factor of a given element, defined for each element as: As(10), Co(5), Cr(2), Cu(5), Mn(1), Ni(5), Pb(6), V(2), Zn(1) and Cd(30) [6][14][11]. Interpretations for these calculations are categorized as shown on Table 1.

Table 1. Categorization of pollution index, enrichment factor, potential ecological risk and toxicity risk index of heavy metal elements [4] [6] [11] [12] [13] [14] [19]

PI Value	PI Soil Quality	Enrichment Factor	Enrichment Level	Potential Ecological Risk Index (E_f)	Risk Level per factor	Potential toxicity Risk İndex (RI)	Risk Level
<1	Uncontaminated	<2	Uncontaminated	<40	Low	RI<150	Low grade
1<PI<3	Moderately contaminated	2-5	Moderate	40-80	Moderate	150-300	Moderate
3<PI<6	Considerably contaminated	5-20	Significant	80-160	High	300-600	Sever
6<PI<12	Highly contaminated	20-40	Very High	160-320	Higher	<600	Serious
12<PI	Extremely contaminated	>40	Extremely High	>320	Serious		

3. Results and Discussion

Results of XRF analysis of the 47 samples revealed 21 elements were recognized. Ca is the most abundant element in almost all the samples. Si dominates in sample L11 and slightly higher in L (6 and 12) as presented on Table 2 [17]. In order of abundance, Ca is followed by Si and Fe respective with Al and Mg having an almost similar concentration in the samples, as illustrated [18]. Cu, Rb, Y and Pb indicated a zero mean at a two decimal place calculation. Ca, Fe, Al, Mg, Ti, Mn, Sr, Ni, Zn, Rb, K and Ba show higher median to mean value with corresponding skewness < 0, except for Ca with skewness slightly > 0. On the other hand, Si, Na, Cr, Zr, Cu, Y, Pb, S and P show a lower median to mean values with skewness > 0 at a three decimal place evaluation. Skewness > 0 is referred to as right skewed distribution. It implies an element's concentration in most the samples is distributed on the left of its mean concentration with extremely values to the right [5]. Fe, Al, Mg, K, Cr, S, Cu, Y and Pb show a Leptokurtic distribution (Kurtosis >), which is sharper than a normal distribution, with concentration of elements concentrated around the mean and thicker tails. This indicates high probability for extreme values. The rests of the elements show a Platykurtic distribution (Kurtosis < 3), which flatter than a normal distribution with a wider peak. The less probability for extreme concentrations compared to a normal distribution, and the concentrations are spread wider around the mean (Table 2) [18].

Table 2. Simple statistical evaluation of chemical data by the SPSS 23 [18]

Sample	N	Minimum	Maximum	Mean	Median	Range	Std. Deviation	Variance	Kurtosis	Skewness
Ca	46	17.621	40.831	29.38390	29.71905	23.210	4.145415	17.184	2.868	.304
Si	46	.137	25.020	11.29301	10.79907	24.883	4.705929	22.146	2.232	.222
Fe	46	.048	4.060	2.63959	2.66685	4.012	.801662	.643	5.553	-1.946
Al	46	.042	1.835	1.39524	1.46202	1.794	.382937	.147	8.734	-2.934
Mg	46	.176	1.793	1.32890	1.42926	1.617	.386983	.150	3.047	-1.748
Na	46	.009	1.786	.60627	.46782	1.778	.361508	.131	1.674	1.123
K	46	0.000	.552	.39288	.40754	.552	.117083	.014	6.221	-2.261
Ti	46	0.000	.356	.19260	.18878	.356	.071878	.005	2.306	-.639
S	46	.001	.216	.06193	.04452	.215	.043941	.002	3.066	1.610
Mn	46	0.000	.146	.09010	.09443	.146	.030452	.001	2.316	-1.280
Sr	46	.018	.092	.06592	.07178	.073	.020920	.000	-.190	-.933
Cr	46	0.000	.581	.13487	.07314	.581	.145216	.021	3.347	1.985
Ba	46	0.000	.091	.03879	.04914	.091	.028596	.001	-1.347	-.446
P	46	.003	.169	.05312	.03445	.166	.038861	.002	.853	1.311
Zr	46	0.000	.034	.01128	.01155	.034	.009062	.000	.009	.507
Ni	46	0.000	.025	.01595	.01721	.025	.005582	.000	2.459	-1.353
Cu	46	0.000	.013	.00142	0.00000	.013	.003472	.000	3.600	2.233
Zn	46	0.000	.010	.00516	.00562	.010	.002443	.000	.643	-.812
Rb	46	0.000	.006	.00320	.00361	.006	.001571	.000	.294	-1.037
Y	46	0.000	.004	.00035	0.00000	.004	.001020	.000	5.785	2.698
PbO	46	0.000	.014	.00108	0.00000	.014	.003580	.000	8.648	3.160

According to [17], high anomalous concentrations were observed in samples L45 (A − C) for Ca while other elements showed low anomalous concentration. In samples L (6, 11-12) high anomaly is observed for Si, with Ca being low. High anomaly is observed for Cr, Ti and Fe in L (17, 30, 31-40). Pb indicates high anomaly in L (8, 24, 36-43). Zr, Ba and Sr are disseminated within their interquartile range.

4. Correlation

No significant relationship exist between Cu and Pb with any element. Strong Negative inter-correlation (r = -0.949) exist between Ca and Si, confirming the inversely proportional results of the boxplot [18]. Fe, Mg, Ti and Mn; Al and K; Sr, Mg and Mn; and Na and S, indicated a very strong correlation among themselves (r > 0.91), implying a directly proportional relationship between them. Al and K vs Fe, Si, Mg, Na, Ti, Mn, Sr, Ba, Ni, Zn and Rb show a moderate to strong significant correlation, as well as between Fe vs Sr, Cr, Zr, Ni, Zn and Rb; Mg vs Na, S, Cr, Ba, Zr, Ni and Zn; Na vs Ti, Sr and Ba; Ti vs S, Sr, Cr, Zr, Ni

and Zn; Mn vs Cr, P, Zr, Ni and Zn; Sr vs Ba, Ni and Zn; Cr vs Zr; Ni vs Zn and Rb; and Zn vs Rb (Table 3).
Pearson Correlation Coefficient Formula:

$$r = \frac{\sum \sum_{i=1}^{n} X_k X_1 \sum_{i=1}^{n} X_k \sum_{i=1}^{n} X_1}{\sqrt{\left(\sum_{i=1}^{n} X_k^2 \frac{\left(\sum_{i=1}^{n} X_k\right)^2}{n}\right)\left(\sum_{i=1}^{n} X_1^2 \frac{\left(\sum_{i=1}^{n} X_1\right)^2}{n}\right)}}$$

Table 3. Inter-correlational Relationship of Elements

	Ca	Si	Fe	Al	Mg	Na	K	Ti	S	Mn	Sr	Cr	Ba	P	Zr	Ni	Cu	Zn	Rb	Y	Pb
Ca	1																				
Si	-.949**	1																			
Fe	-.393**	.321*	1																		
Al	-.765**	.679**	.750**	1																	
Mg	-.234	.075	.845**	.751**	1																
Na	-.273	.027	.393**	.441**	.608**	1															
K	-.770**	.702**	.635**	.966**	.661**	.428**	1														
Ti	-.206	.099	.950**	.629**	.857**	.417**	.498**	1													
S	-.207	-.031	.396**	.375*	.568**	.949**	.361*	.450**	1												
Mn	-.174	.091	.925**	.651**	.866**	.377**	.530**	.918**	.369*	1											
Sr	.040	-.183	.672**	.566**	.907**	.539**	.508**	.746**	.495**	.811**	1										
Cr	.074	-.190	.655**	.145	.505**	.342*	.008	.783**	.466**	.591**	.386**	1									
Ba	-.229	.097	.270	.436**	.504**	.409**	.461**	.274	.366*	.302*	.490**	.096	1								
P	-.082	.025	.359*	.262	.383**	.131	.232	.312*	.122	.425**	.311*	.126	.193	1							
Zr	-.128	.061	.594**	.243	.400**	.194	.141	.626**	.277	.463**	.214	.760**	.025	.160	1						
Ni	-.403**	.363*	.682**	.769**	.733**	.262	.710**	.608**	.253	.693**	.585**	.189	.361*	.380**	.275	1					
Cu	-.126	.090	.037	.148	.122	-.093	.164	.003	-.130	.038	.082	-.069	.230	.045	-.057	.084	1				
Zn	-.275	.245	.670**	.511**	.530**	.295*	.481**	.601**	.278	.648**	.458**	.386**	.281	.232	.306*	.530**	-.033	1			
Rb	-.435**	.453**	.429**	.596**	.382**	.202	.658**	.333*	.227	.352*	.317*	.003	.087	.115	.040	.449**	.040	.430**	1		
Y	.120	-.189	.258	.042	.273	.142	-.090	.314*	.076	.347*	.254	.274	-.166	.146	.196	.239	.115	.112	-.077	1	
Pb	-.162	.141	.003	.066	.226	.095	.290	.012	.091	-.050	.046	-.128	.062	.091	-.242	.153	-.126	.217	.159	-.106	1

** Correlation is significant at the 0.01 level (2-tailed).
* Correlation is significant at the 0.05 level (2-tailed).

5. Hierarchical Cluster Analysis

The Pearson case analysis was used to evaluate the similarity of the chemical content in the samples. Five groups (Gp1 – Gp5) of samples with closely similar chemical content were distinguished. Gp1 (L 45 – A, B, C), Gp2 (L – 6, 12,11), Gp3 (L – 28, 42, 1, 3, 38, 9, 20, 23, 21, 17, 34, 22, 32, 33, 4, 7, 2, 13, 16, 26, 37, 39, 29, 15, 27, 31, 40, 30), Gp4 (L – 5, 8), and Gp5 (L – 18, 19, 25, 43, 24, 10, 36, 44, 14, 41). Gp1 samples are recognized to contain anomalous concentration of Ca and Gp2 samples contain anomalous Si concentration, as indicated by the boxplot analysis; Gp3 with high concentrations of Fe, Ti, Cr, Gp5 with the second highest concentrations of Si to Gp2, along with relatively higher concentrations of Ca, Mg, Sr and Cr (Figure 1). Quadratic Euclidean Dıstance, it is calculated by collecting the squares of the differences between the same variables. The distance is calculated as follows:

$$d(i, j) = (x_{i_1} - x_{j_1})^2 + (x_{i_2} - x_{j_2})^2 + \dots + \left(x_{i_p} - x_{j_p}\right)^2$$

Ward Connection Clustering Method, (Ward Linkage) Ward Link clustering method is based on the variance from the center, i.e. the deviation from the center in calculating the distance between the two clusters. It was proposed by [20]. This method is called the smallest variance method. The purpose of the ward link clustering method is to minimize the sum of the squares inside the clusters. The cluster with the same number of elements tends to be obtained and is sensitive to extreme values. In this method, the distance between j and k clusters can be found with the help of the following equation [2].

$$d_{(k,l)j} = \frac{(N_j+N_k)d_{(k,j)}+(N_j+N_l)d_{(l,j)}+N_j d_{(k,l)}}{N_j+N_k+N_l}$$

$d_{(k,l)j}$: the distance of the k and the 1st set from the cluster j to the cluster

$d_{(k,j)}$:the distance of the k-set from the j-th cluster,

$d_{(l,j)}$:the distance from the first set of group 1 to j,

$d_{(k,l)}$:the distance from the first cluster to the first cluster,

N_k :total individualism in the k,

N_l :the total individuality in the 1st cluster,

N_j :shows the total individuality of the 1st group.
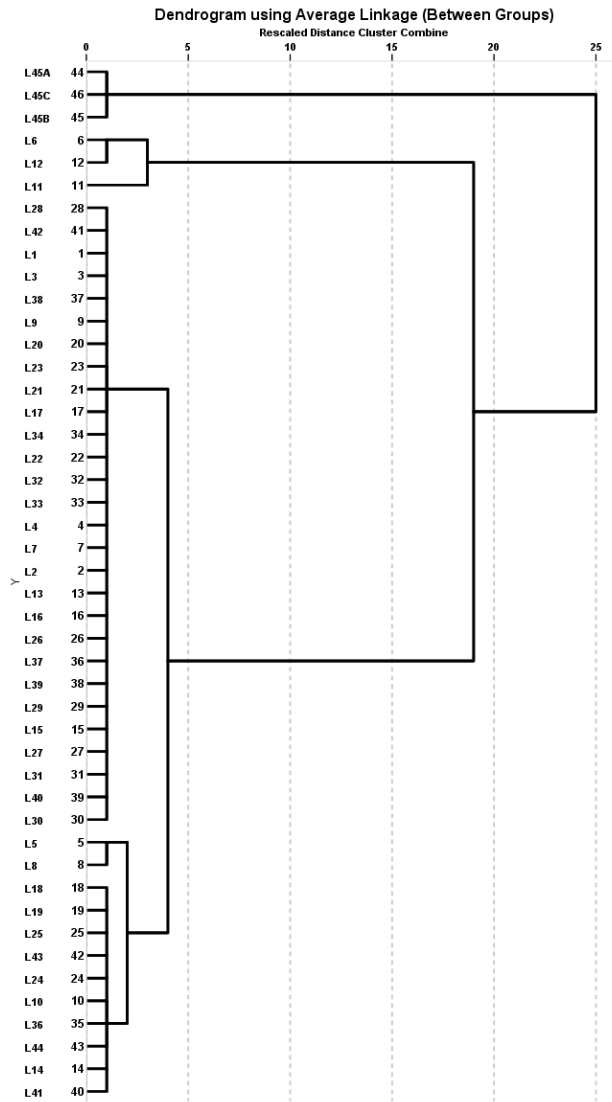
Graph 1. Categorizations of samples with closely similar chemical content

6. Principal Component Analysis

Five Principal Components extracted, explained the variances of > 91 % of the nine elements (Ca, Si, Fe, Al, Mg, K, Ti, S and Mn); 86-89 % of three elements (Na, Sr and Cr); 60-79 % of five elements (Ba, Zr, Ni, Cu and Pb); 50-59 % for two elements (Zn and Rb); and 30-35 % for two elements (P,Y) as shown on Table 4a. The five components explained 78.06 % of the total variability of the data with least Eigenvalue

> 1. Component 1, explained 41.08 % variable's variances with Fe, Al, Mg, K, Ti, Mn, Sr, Ba, P, Zr, Ni, Zn and Rb indicating their strongest loading, Component 2 explained 15.55 % with Ca, Si, Cr and Y indicating their strongest loading, Component 3 accounted for 8.42 % with highly loaded elements being Na and S. Cu and Pb that showed no significant relationship with other elements are well loaded in Component 5, which explained 5.88 % of the data's variance (Table 4a, 4b). Elements that are well loaded in component 1 are usually attributed to a natural source; those in component 2 are attributed to both natural and anthropogenic activity, and in component 3 are attributed to anthropogenic activity [10][16].

Table 4a. Loaded Components of Variable and Variability of Variable Explained[18]

			Component Matrix			
			Component			Communalities
	1	**2**	**3**	**4**	**5**	
Ca	-0.482	0.736	0.143	0.3	0.199	0.924
Si	0.348	-0.816	-0.315	-0.251	-0.111	0.962
Fe	0.926	0.134	-0.278	-0.055	0.027	0.956
Al	0.87	-0.448	-0.027	0.024	-0.051	0.961
Mg	0.928	0.191	0.143	0.173	-0.045	0.95
Na	0.593	0.127	0.629	-0.333	-0.125	0.89
K	0.795	-0.569	0.068	0.033	-0.032	0.963
Ti	0.885	0.339	-0.194	-0.054	0.045	0.94
S	0.576	0.201	0.595	-0.418	-0.095	0.91
Mn	0.883	0.284	-0.177	0.17	0.078	0.926
Sr	0.777	0.311	0.286	0.334	0.037	0.895
Cr	0.525	0.644	-0.193	-0.365	-0.065	0.866
Ba	0.472	-0.112	0.484	0.232	-0.351	0.646
P	0.392	0.085	-0.056	0.37	0.181	0.334
Zr	0.48	0.407	-0.427	-0.422	-0.182	0.789
Ni	0.787	-0.164	-0.128	0.272	0.11	0.748
Cu	0.079	-0.145	-0.103	0.501	-0.639	0.697
Zn	0.684	-0.009	-0.119	-0.014	0.3	0.572
Rb	0.528	-0.428	-0.057	-0.018	0.208	0.508
Y	0.22	0.432	-0.242	0.226	0.005	0.344
Pb	0.122	-0.333	0.294	0.049	0.629	0.611

Table 4b. Factored Component Explained

	Total Variance Explained					
Component	Initial Eigenvalues			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	8.627	41.08	41.08	8.627	41.08	41.08
2	3.265	15.549	56.629	3.265	15.549	56.629
3	1.768	8.418	65.047	1.768	8.418	65.047
4	1.496	7.126	72.173	1.496	7.126	72.173
5	1.236	5.884	78.057	1.236	5.884	78.057

7. Pollution Index

Pollution Index evaluated for heavy metals (Cr, Ni, Cu, Zn, Pb) under investigation revealed contaminated levels for Cr and NI. Extreme contamination for Cr is observed in five samples (L17, L34, L30, L29, L22), high contamination in 37 samples; considerable contamination in one sample and moderate contamination in one sample. Only two samples have not experience Cr contamination. Ni indicated considerable

contamination in four samples (L32, L25, L29, L33), moderate contamination in 40 samples and no contamination in three samples (L45A, L45B, L45C) according to the Maximum Permissible Concentration (MPC) of Tukey. Averagely, a PI value of Cr indicated contamination and Ni moderate contamination with reference to the MPC used (Table 5).

8. Enrichment Factor

Minimum, average and maximum values of E_f for each element with Fe as reference are presented on Table 5. Extremely high (in L40, L30 and L31) and very high (in L17, L15, L29, L34, L27, L22) enrichment were observed for Cr, with 33 samples indicating significant enrichment with respect to Fe. Mn (in L45B, L45A) and Pb (in L43, L24, L36, L8) also showed significant enrichment. Moderate enrichment is indicated for Mn in 43 samples, for Cr in one sample, for Ni in 18 samples and for Cu in seven samples. Crustal to minimal enrichment is observed for Zn in all the samples. Averagely, significant enrichment is observed for Cr, moderate enrichment for Mn and minimal enrichment for Ni. Potential Ecological Risk analysis per factor revealed higher - serious risk for Cr in six samples (L40, L31, L30, L17, L29, L15) and high and moderate risk in six samples (L34, L27, L22, L13, L26 and L32) and 13 samples (L2, L8, L7, L24, L21, L16, L4, L39, L37, L9, L23, L3, L20) respectively. For Cu moderate risk is observed in six samples (L32, L1, L3, L12, L9, L29) and for Pb high risk is observed in four samples (L24, L43, L36, L8). Comprehensively, three samples (L40, L31, L30) indicated severe risk level to the ecosystem and 13 samples (L17, L29, L24, L32, L34, L15, L8, L43, L22, L27, L36, L13, L26) revealed moderate risk levels. Averagely, on per factor analysis Cr indicates moderate risk and the other low risk, while comprehensive average RI is of low grade risk (Table 5).

Table 5. Summary of Contamination Risk Assessment Evaluated

	Turkey's MPC	Pollution Index			Enrichment Faktor			Potential Ecological Risk				
		Avg.	Min.	Max.	Avg.	Min.	Max.	Avg.	Min.	Max.	RI	
Mn	-	-	-	-	3.91	0.00	14.43	10.01	0.00	16.22	Avg.	132.44
Cr	100	9.01	0.00	14.60	12.15	0.00	44.44	77.07	0.00	332.00	Min	0.00
Ni	30-75	2.14	0.00	3.33	1.77	0.00	2.80	25.07	0.00	39.06	Max	379.33
Cu	50-140	0.10	0.00	0.93	0.58	0.00	4.86	7.97	0.00	72.22		
Zn	150-300	0.17	0.00	0.33	1.11	0.00	1.94	3.19	0.00	6.25		
Pb	50-300	0.04	0.00	0.47	0.57	0.00	7.79	9.13	0.00	120.00		

Most of the samples lacked considerable concentrations of Cu and Pb, this accounts for the reason these elements neither show any significant correlation with any other elements nor are well loaded together with the other elements in the samples by the PCA. The very high concentration of Ca and Si that dominates in the samples, is an influence of the rock units that is present in the region. Such rock types are usually rich in calcite and silicate minerals. Anomalous concentrations of Cr indicated contaminated levels in most of the samples. This could be accounted for by a natural process that might have deposited the weathered rock material within the beach sand. The deposited sands may also have experienced redistributed by the wave action and agents of erosion active along the coast. There is possibly only a little anthropogenic influence on the Cr concentration in the sand. Mn, Pb, Ni and Cu indicated some level of enrichment in the sands, which is really not usually reliable, as enrichment assessment varies for a particular element depending on the reference element used in the evaluation. PER suggested some ecological risk could be associated to the Pb and Cu contents, which are probably due to anthropogenic influence. However, only Cr indicates some levels of pollution with regards MPC used.

9. Acknowledgements

10. Conclusion

There was uneven distribution of the elements within the samples. Samples can divide in 5 groups of closely similar chemical content. Gp1 samples are characterized with anomalous concentration of Ca and Gp2 with anomalous Si concentration; Gp3 possess high concentrations of Fe, Ti, Cr and Gp5 with second highest concentrations of Si to Gp2, along with relatively higher concentrations of Ca, Mg, Sr, Cr. In all the samples but for the L6, L11 and L12 samples, Ca had the highest concentration. The high concentrations of Ca and Si in the samples are due to the influence of the rock types occurring in the area. Most of the samples lacked considerable concentrations of Cu and Pb, which are not significantly correlated with any element and hence indicating a likely anthropogenic source contribution with contaminated levels of enrichment and some high ecological risk level; yet below the national PI level. Cr concentration in most samples indicated some levels of contamination. High concentration of Cr is likely due to the influence of the rock materials occurring around the area and with little influence from anthropogenic activities. Summarily, most of the heavy metal except Pb and Cu are thought to be from a natural source according to multivariate statistics and accumulation index calculations.

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