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Multivariate Statistical Evaluation of Major and Trace Elements in Shatt Al-Arab Sediments, Southern Iraq

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Abstract

River sediments are normally the final pathway of both natural and anthropogenic components derived or produced to the environment. As such, it is important to study these components systematically (i.e. their distribution, levels, and sources). Multivariate statistical techniques such as Principal Component Analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA) as well as pollution analysis such as Enrichment Factor (EF) analysis were used to analyze the data and identify possible sources of sediment's components in Shatt Al-Arab at Basra Governorate. The results of PCA and AHCA were compatible, defining four groups of elements; each group has a specific sourcing (a) Mg, Mo, and As show a general enrichment having mean EF values of 8.34, 12.41, and 7.01 respectively, indicating that Shatt Al-Arab is polluted in these metals, and they are mainly of anthropogenic sources; (b) P, Cl, V, Br, Th, Cu, and Ba have mean EF values of 4.18, 3.52, 1.31, 18.85, 1.67, 2.44, and 0.54 respectively indicating that Shatt Al-Arab is unpolluted in Cl, V, Th, Cu, and Ba; minimally polluted in P, and significantly polluted with Br; (c) Al, Ni, Rb, Nb, Ga, Ti, Y, Mn, and Fe have the lowest mean EF of 1.29, 1.50, 1.07, 0.67, 1.60, 1.67, 0.91, 1.43, and 1.40 respectively; therefore, Shatt Al-Arab can be considered unpolluted in these elements; (d) Pb, Sr, Cr, Zn, and U have mean EF of 0.74, 2.38, 2.78, 2.92, and 0.80 respectively indicating that Shatt Al-Arab is unpolluted in these elements. Hence, AHCA and PCA findings are compatible with EF analysis, strongly confirming the suggested sources of elements.

Keywords: Pollution, Sediments, Multivariate Analysis, Pollution Index, Shatt Al-Arab, Basra

1. Introduction

With the rapid industrialization and economic development, pollutants are continuing to be introduced to rivers via several pathways, including irrigation, runoff, atmospheric deposition, and point sources, where pollutants are produced as a result of metal mining, refining, and refinishing by products (Qingjie et al., 2008). River sediments are usually regarded as the ultimate sink for nutrients and heavy metals discharged into the environment (Banat et al., 2005). Contaminated sediments can threaten life in the benthic environment, exposing organisms to hazardous concentrations of toxic chemicals. Some contaminants in the sediment are taken up by benthic organisms in a process called bioaccumulation. When larger animals feed on these contaminated organisms, the toxins are taken into their bodies, moving up the food chain in increasing concentrations in a process known as biomagnification (Begum et al, 2009). Moreover contaminants in sediments, depending on the sorption characteristics, can eventually be partly or totally released back into the water column (Jonsson et al., 2003) threatening the aquatic life as well.

With the development of ecological geochemistry survey and exploration geochemistry survey, a great deal of data related to contaminant concentrations in water sediments has been obtained which can be used to assess the quality of ecological geochemistry environment. In past years, tremendous efforts have been made to characterize the loading and distribution of pollutants in sediments (Pettine, 1994; Neumann,1998; Weisz, 2000; Camusso, 2002; Arambarri, 2003;Akcay, 2003; and Glasby, 2004). These studies have improved our understanding of contamination in river ecosystems over the world.

While some studies have addressed the water quality status of Shatt Al-Arab, few or no studies have addressed the sediment quality in the river. Therefore, it is important to study the river's benthic environment systematically (i.e. contaminants distribution, level, and sourcing) in order to manage the contaminants input into the river so that their concentrations in the sediment do not reach toxic values. Hence, the elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Pb, Th, and U) were measured and analyzed using multivariate statistical techniques such as Principal Component Analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA), and Enrichment Factor (EF) analysis. Specific research questions addressed here are: How the major and trace elements are distributed in Shatt Al-Arab sediments? What are the levels of these elements in Shatt Al-Arab sediments? And what are the possible sources of contamination (if any)?

2. Study Sites

Sediment samples were collected during May, 2010 from 8 sites. Samples 1, 2, 3, and 4 were collected from irrigation canals called Al-Hababa, Abu-Mgera, Khoz, and Gekor respectively, all these irrigation canals branch from Shatt Al-Arab and pass through cultivated farmlands carrying huge amount of agricultural runoff wastes toward Shatt Al-Arab. Samples 5, 6, 7, and 8 that collected from different locations at Shatt Al-Arab namely at

Al-Najebia power station, at Daker island, before Al-Taleamy Hospital, and after Al-Taleamy Hospital respectively (Figure 1).

3. Methods

3.1 Organic Matter and Element Analysis

Semi-quantitative loss on ignition (LOI) method has been used to determine the organic matter content. The LOI method is based on the removal of all organic matter followed by determination of sample weight loss. 5.000 g of dried sediment sample (into a ceramic crucible with known weight (W1)) was placed in a standard drying oven set at105 ˚C for 2 h then placed in a desiccator and weighed (W2). Samples then placed in a furnace preset at 440˚C and combusted for 2 h and weighed (W3). Total Organic Matter content (TOM %) is calculated as:

$$TOM\ \% = [(W2-W3)/(W2-W1)] \times 100$$

Since LOI method determines the organic matter content in the soil or sediment, it is necessary to convert the organic matter content to total organic carbon content. Traditionally, for soils, a conversion factor of 1.724 has been used to convert organic matter to organic carbon based on the assumption that organic matter contains 58% organic carbon (i.e. g organic matter/1.724 = g organic carbon) (Schumacher, 2002).

Bench XRF Spectrometer/ SPECTRO XEPOS-2006 was used to analyze the sediment samples. Powder of size 0.063 µm and 5.0 g of each sample was used to be analyzed in the XRF Spectrometer to determine the element concentrations. Concentrations of Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ba, Pb, Th, and U were measured.

3.2 Statistical Analysis

Multivariate statistical techniques such as Principal Component Analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA) were performed using JMP 8.0 (SAS System) to determine the sources of major and trace elements. The major aim of the PCA is data reduction to better describe the relationship among the variables. PCA with VARIMAX rotation was applied to the water quality data set to form a correlation matrix for different variables and assist in the identification of sources of various pollutants. The principal components are defined simply as linear combinations of the measurements and contain both common and unique variance (DeCoster, 1998). Eigen values in PCA indicate the significance of the components. The component with the highest Eigen value is taken to be the most significant. Eigen value should be one or greater for proper considerations during PCA (Nair et al., 2010). Factor loadings values of > 0.75, between 0.75 – 0.5 and between 0.5 – 0.3 are classified as strong, moderate and weak based on their absolute values (Nair et al., 2010). We conducted AHCA by constructing a dendrogram that displayed the cohesiveness and correlations among the variables (Yongming et al., 2006). Clustering begins by finding the two samples that are most similar, based on the distance matrix, and merging them into a single group. This procedure of combining two samples and merging their characteristics is repeated until all the samples have been joined into a single large cluster (Kaufman and Rousseeuw, 1990).

3.3 Pollution Analysis

Pollution indices such as Enrichment Factor (EF) are powerful tools for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and the public (Caeiro et al., 2005). In order to evaluate if the content of a chemical element in the sediments derives from natural or anthropogenic sources, enrichment factor was calculated for all studied sediment samples using zirconium (Zr) as a reference element. The enrichment factor is the relative abundance of a chemical element in a sediment sample compared to the bedrock. Zirconium is generally considered as mainly originated from natural lithogenic sources (rock weathering of mineral zircon) and has no significant anthropogenic source. It has widely been used in geochemical studies of mineral weathering as a ‘conservative’ lithogenic element, against which relative enrichments has been compared (Blaser et al., 2000).The enrichment factors (EF) was calculated according to:

$$EF = (M / Zr)_{sediment} / (M / Zr)_{earth's\ crust}$$

Where (M) is total elemental concentration (mg/kg) and (Zr) is total concentration of Zr (mg/kg) measured in sediment sample/earth’s crust, respectively. Total elemental concentration (mg/kg) in the earth’s crust is: Mg = 9000, Al = 72000, P = 430, Cl = 450, Ti = 4400, V = 135, Cr = 100, Mn = 950, Fe = 50000, Ni = 190, Cu = 55, Zn = 79, Ga = 15, As = 1.8, Br = 2.5, Rb = 90, Sr = 375, Y = 33, Zr = 165, Nb = 20, Mo = 1.1, Ba = 650, Pb = 55, Th = 6, and U = 1.8 (Krauskoff and Bird, 1995). EF < 2 shows deficiency to low enrichment and can be considered in the range of natural variability. 2 < EF < 5 shows low enrichment (i.e. some enrichment caused by anthropogenic input). 5 < EF < 20 is a clear indication of human influence (significant enrichment caused by anthropogenic inputs). EF 20 to 40 is very high enrichment and EF > 40 is extremely high enrichment (Golchert, 1991; Hernandez et al., 2003; Fong et al., 2008).

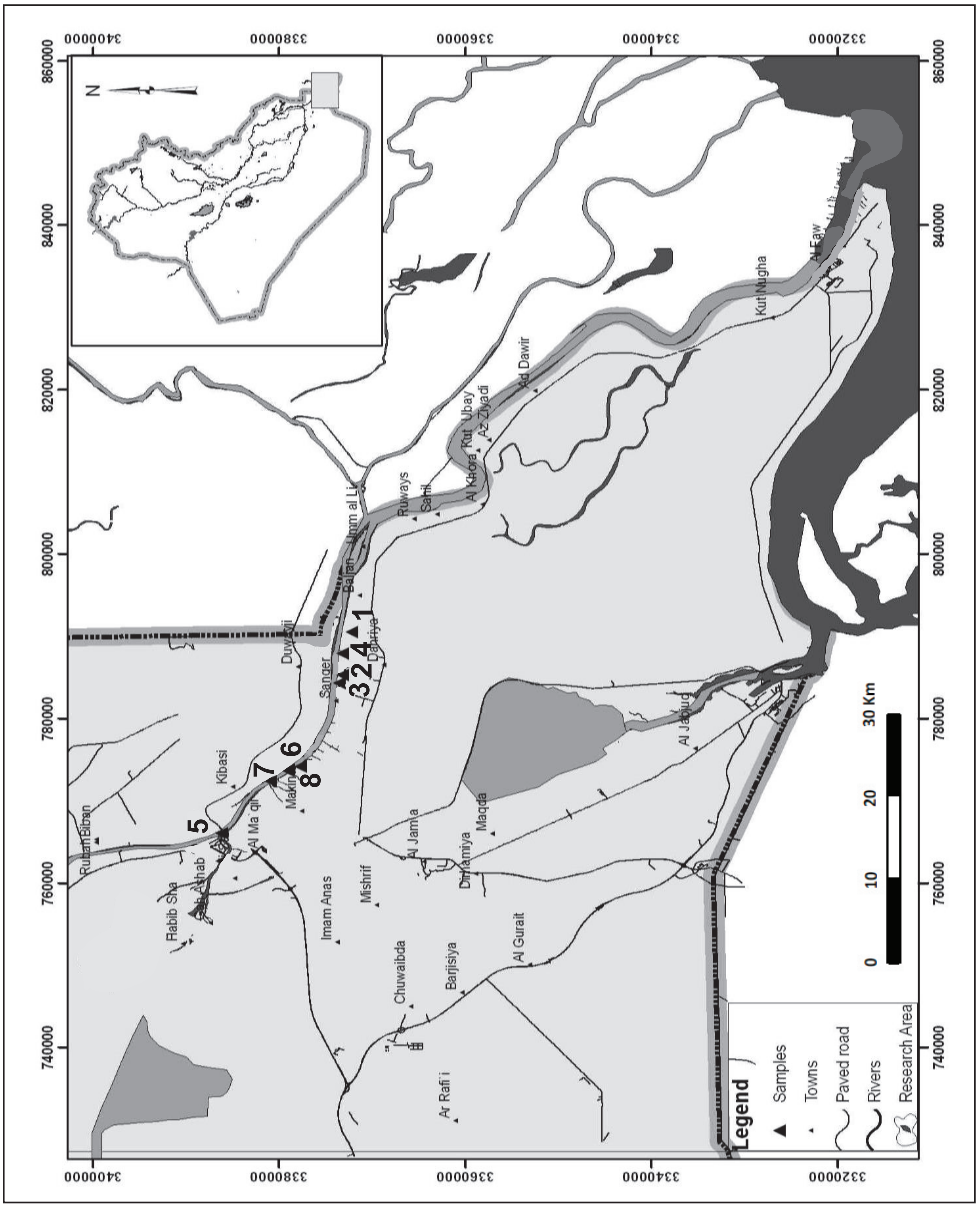

Figure 1. Study Sites

4. Results and Discussion

4.1 Organic Matter and Element Analysis

Table 1 shows the TOM (g), TOC (g), and TOC % for sediment samples at our study sites. TOM ranges from 0.19 g (site 1) to 0.30 g (site 5) with an average of 0.25 g. TOC ranges from 0.11 g (site 1) to 0.17 g (site 5) with an average of 0.14 g. TOC % ranges from 2.15 % (site 1) to 3.42 % (site 5) with an average of 2.85 %. Sediments at all sites have low TOC % which is expected for an arid region. Sediments in the current study might have higher concentrations of carbon being derived from inorganic carbonates than from organic carbon sources. Element mean concentrations were in the order Si > Ca > Al> Mg > Fe > K> S > Ti > P > Cl > Mn > Sr > Ba > Ni > Cr > Zn > V > Zr > Cu > Rb > Br > Pb > Y > Ga > Mo >Nb > As > Th > U (Table 2). Among the heavy metals Br, As, and Mo are of high concentrations in sediments. In general, concentrations of all elements measured in sediment samples were higher than those in water samples for the same sites found by Al-Tawash et al. (2013, in press). Saeed and Shaker (2008) and Dube et al. (2001) stated that sediments are normally the final pathway of both natural and anthropogenic components produced or derived to the environment. Sediments tend to adsorb and concentrate the heavy metals and other organic pollutants and that can explain the higher element levels in Shatt Al-Arab sediment samples compared to water samples.

Table1. Total Organic Matter content (% TOM), (TOM), Total Organic Carbon (TOC), and % TOC

Site No.	Site Name	TOM %	TOM (g/5g)	TOC (g/5g)	TOC %
1	Al-Habab irrigation canal	3.80	0.19	0.11	2.15
2	Abu Mgera irrigation canal	5.80	0.29	0.16	3.19
3	Khoz irrigation canal	4.00	0.20	0.11	2.28
4	Gekor irrigation canal	4.80	0.24	0.14	2.80
5	Shatt Al-Arab at Najebia power station	6.00	0.30	0.17	3.42
6	Shatt Al-Arab at Daker Jazera	5.40	0.27	0.16	3.16
7	Shatt Al-Arab before Taleamy hospital	5.00	0.25	0.15	3.00
8	Shatt Al-Arab after Taleamy hospital	4.80	0.24	0.14	2.80
	Mean	4.95	0.25	0.14	2.85

4.2 Statistical Analysis

The percentage of variance by different components extracted is displayed in Table 3 and the factor loadings of the different variables are presented in Table 4. Four principal components (PC1, PC2, PC3, and PC4) were obtained. Applying PCA on the water quality parameters displayed a cumulative variance of 85.52 % (Table 3). PC1 accounts for 37.58 % of the total variance and is dominated by the strong factor loadings for Al (0.88), Y (0.98), Nb (0.82), Rb (0.82), Mn (0.92), Ni (0.93), Fe (0.86), and Ti (0.95), other elements demonstrate relatively low factor loadings in this case indicating their independency within this group (Table 4). PC2 accounts for 17.99 % of the variance (Table 3) and is dominated by S, Pb, and Sr having factor loadings of 0.90, 0.76, and 0.59 respectively (Table 4). PC3 accounts for 17.38 % of the variance (Table 3) and is dominated by Mg, Mo, K, and Si having factor loadings of 0.53 and 0.70, 0.82, and 0.80 respectively (Table 4). PC4 accounts for 9.85 % of the variance (Table 3) and is dominated by Ba, P, Cu, and V having factor loadings of 0.44 and 0.60, 0.86, and 0.49 respectively (Table 4).

AHCA highlighted 4 specific element response patterns (R1, R2, R3, and R4, Figure 2). The degree of relationship between clusters is represented by the distance of the centroid of one cluster to another, where clusters with smaller or shorter distances between them are more similar to each other than clusters with larger or longer distances between. Here, cluster R1 has the shortest distance (9.9), and highest similarity to cluster R2, whereas cluster R4 is the least similar and has the greatest distance to R1 (17.3) (Figure 2). Elements clustering in R1 (Mg, Mo, Si, K, and As) that dominate in the PC3 indicate towards the anthropogenic influence on the sediments with respect to the described elements. Fertilizers are known to be a significant source of these elements (Weiner 2000). Four sites out of eight sites in the current study represent irrigation canals that pass through some of the most cultivated belts and receive agricultural return flow and that can explain the relatively high concentrations of these elements in these four sites. P, Cl, water pH, V, TOC %, Br, Th, Cu, Zr, and Ba that clustered in R2 (dominating in the PC2) are associated with both anthropogenic and natural sourcing. P, TOC %, and Br might be of agricultural sourcing (Reimann and de Caritat 1998; Kabata and Pendias 2001) and therefore they have relatively high concentration at irrigation sites. Zr, Cl, Ba, Cu, V, and Th are of natural sourcing as they enter the aquatic environment mainly by weathering of natural deposits (Weiner 2000, Bradl, 2005). Water pH clustered with this group as it affects the dissolution, precipitation and adsorption of these elements in sediments (Bam et al, 2011). Cluster R3, includes Al, Ni, Rb, Nb, Ga, Ti, Y, Mn, and Fe (dominating in the PC1) are lithophile elements according to Goldschmidt's classification of geochemical elements (Mason and Moore, 1982). Lithophile elements are those showing an affinity for silicate phases and are concentrated in the silicate portion (crust and mantle) of the earth (Mason and Moore, 1982). Therefore, elements clustered in R3 can be considered of natural sources. Elements in cluster R4 that include S, Pb, Sr, Ca, Cr, Zn, and U (dominating in the PC4) are mainly of natural sourcing. Ca and Sr are associated with weathering of silicate bearing minerals for example, calcium-rich component of the plagioclase feldspars, pyroxenes, anorthite and amphiboles found in the study area (Alloway, 1995; Ganyaglo et al., 2010). Zn, S, and Pb may be the result of weathering of natural deposits (e.g. galena and sphalerite), similarly, Cr and U can result from erosion of natural deposits (Weiner, 2000).

Hence, Agglomerative Hierarchal Cluster Analysis (AHCA) is in close agreement with the findings of Principal Component Analysis (PCA), in other words, elements grouped in a specific cluster (AHCA) dominate in a specific component (PCA) which indicates their common source.

Table 2. Concentrations of 29 elements (mg/kg) and water pH measured in sediment samples

Site No.	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni
1	44240	44300	166400	601	1502	365	10780	163500	3611	84	127	632	32400	135
2	37860	48560	167600	845	7849	657	10920	155500	3681	94	143	600	36290	148
3	36210	43190	154300	899	5678	620	9564	164400	3751	84	167	583	32860	134
4	36010	43330	158200	1061	7359	1264	10390	166700	3573	86	134	628	32660	125
5	39030	50400	163900	959	4063	990	10880	150100	3795	91	136	774	36450	154
6	37890	50460	162900	921	5605	1386	10860	149800	3888	101	144	734	36500	154
7	37510	49960	164400	1054	3617	619	10900	145400	3907	87	142	821	37810	158
8	37700	50070	162800	1005	3953	592	10880	147000	3851	93	142	773	40780	159
Mean	38306	47534	162563	918	4953	812	10647	155300	3757	90	142	693	35718	145

Site No.	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb	Th	U	Water pH
1	60.8	77	11.7	7.1	9.0	48.0	418	14.5	82.4	6.7	9.3	137	14.6	4.7	0.4	7.69
2	63.5	124	12.8	5.9	41.3	49.2	496	14.8	77.7	6.6	7.8	128	31.5	5.4	0.5	7.73
3	70.8	177	11.9	5.4	16.8	44.4	486	14.9	85.8	6.1	5.6	144	23.4	4.8	0.9	7.42
4	79.2	142	10.6	6.0	28.6	46.2	534	14.4	82.4	6.3	7.9	132	25.3	5.2	0.9	7.94
5	63.7	101	13.0	6.7	25.7	51.4	429	15.7	84.8	6.9	6.2	122	16.1	4.9	0.9	7.87
6	50.8	105	13.0	8.0	21.0	50.9	427	16.3	88.0	7.7	5.9	182	18.6	5.3	0.3	7.73
7	60.7	110	13.3	6.5	23.2	51.3	414	16.5	85.1	7.1	5.9	253	16.8	5.6	0.9	7.86
8	92.6	110	11.9	6.4	26.0	50.5	424	15.9	88.4	7.2	6.9	354	17.7	5.0	0.6	7.71
Mean	67.8	118	12.3	6.5	24.0	49.0	454	15.4	84.3	6.8	6.9	182	20.5	5.1	0.7	7.74

Table 3. Total variance explained (4 components selected)

	Initial Eigenvalues			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	12.75	41.12	41.12	11.65	37.58	37.58
2	6.52	21.04	62.16	5.58	17.99	55.57
3	4.66	15.02	77.18	5.39	17.38	72.95
4	2.59	8.34	85.52	3.90	12.57	85.52

4.3 Pollution analysis

The result of EF calculations are shown in Table 5. EF values for Mg, Mo, and As (clustered in R and dominated in the PC3) show a general enrichment having a mean EF value of 8.34, 12.41, and 7.01 respectively (Figure 3), thus, Shatt Al-Arab is polluted in these metals, and they are mainly of anthropogenic sources; P, Cl, V, Br, Th, Cu, and Ba (clustered in R2 and dominated in the PC2) have mean enrichment factor values of 4.18, 3.52, 1.31, 18.85, 1.67, 2.44, and 0.54 respectively (Figure 3), indicating that Shatt Al-Arab is unpolluted in Cl, V, Th, Cu, and Ba; minimally polluted in P; and significantly polluted with Br. Al, Ni, Rb, Nb, Ga, Ti, Y, Mn, and Fe (clustered in R3 and dominated in PC1) have the lowest mean enrichment factor of 1.29, 1.50, 1.07, 0.67, 1.60, 1.67, 0.91, 1.43, and 1.40 respectively (Figure 3); therefore, Shatt Al-Arab can be considered unpolluted in these elements. Pb, Sr, Cr, Zn, and U (clustered in R4 and dominated in PC4) have mean enrichment factor of 0.74, 2.38, 2.78, 2.92, and 0.80 respectively (Figure 3); therefore, Shatt Al-Arab is unpolluted in these elements. It is noteworthy that pollution analysis is in good agreement with both AHCA and PCA* analyses in determining the elemental sourcing (i.e. natural or anthropogenic).

5. Conclusions

- Sediments can be used as sensitive indicators for monitoring pollutants in aquatic environments.
- Major and trace elements in Shatt Al-Arab sediments are the result of both anthropogenic and natural sources.
- Multivariate statistical techniques such as Principal Component Analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA) that were performed to analyze the data and identify the possible sources of the studied elements revealed that As, Mg, Mo, Br, and P were mainly associated to anthropogenic activities, such as, fertilizers. On the other hand, the rest of elements were controlled by original materials and therefore interpreted as of natural sources.
- Pollution analysis such as Enrichment Factor (EF) can be used along with multivariate statistical analyses (i.e. AHCA and PCA) to support the element sourcing findings. EF that was used to assess whether the concentrations observed represent background or contaminated levels gave compatible results with PCA and AHCA findings.
- It is concluded that Shatt Al-Arab is moderately to highly polluted for some of the studied elements. The spatial extent of pollution was examined, and it was found that the most polluted areas are located in the cultivated farmlands.
- Finally and noteworthy, the study presents the first analysis ever that examined the molybdenum and arsenic content in sediments in Iraq. Both heavy metals (i.e. Mo and As) have elevated levels.

* AHCA is already in close agreement with PCA

Table 4. Rotated Component Matrix[a]

	Component			
	1	2	3	4
Mg	-.165	-.683	.530	-.454
Al	.879	.259	.271	-.211
S	-.301	.900	-.239	.079
Ba	.702	-.213	.052	.434
Y	.975	.047	-.096	-.106
Zr	.676	-.378	-.435	.117
pH	.197	.350	.711	.203
% TOC	.534	.710	.269	-.127
Th	.378	.686	.168	-.013
U	-.032	.120	-.280	.715
P	.471	.530	-.196	.601
Mo	-.631	-.240	.695	-.042
K	.495	.120	.822	-.249
Pb	-.514	.760	-.138	.070
Nb	.821	-.013	.241	-.402
Rb	.817	.108	.501	-.232
As	.447	-.220	.304	-.650
Sr	-.714	.586	-.197	.302
Ga	.678	.189	-.008	-.496
Br	.042	.890	.255	.186
Zn	-.343	.365	-.769	.388
Mn	.923	-.089	.240	.131
Ni	.929	.095	.157	-.128
Cu	-.048	-.071	.019	.862
Fe	.861	.164	.200	.188
V	.543	.480	.082	-.485
Cr	.039	.149	-.935	.059
Ca	-.954	-.127	-.187	.062
Ti	.946	.016	-.282	-.102
Cl	.118	.563	-.117	-.159
Si	.239	.018	.805	-.422

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.
[a]. Rotation converged in 6 iterations.

Table 5. Enrichment Factor (EF) for studied elements

Site No.	Mg	Al	P	Cl	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Nb	Mo	Ba	Pb	Th	U
1	9.84	1.23	2.80	1.62	1.64	1.25	2.54	1.33	1.30	1.42	2.24	1.94	1.56	7.83	7.19	1.07	2.23	0.88	0.67	16.92	0.42	0.53	1.57	0.45
2	8.93	1.43	4.18	3.10	1.77	1.48	3.03	1.34	1.54	1.65	2.48	3.34	1.81	6.90	34.97	1.16	2.81	0.95	0.70	15.05	0.42	1.22	1.91	0.71
3	7.74	1.15	4.03	2.65	1.64	1.20	3.22	1.18	1.26	1.36	2.50	4.30	1.53	5.72	12.88	0.95	2.50	0.87	0.59	9.79	0.42	0.82	1.54	1.07
4	8.01	1.21	4.95	5.62	1.62	1.28	2.69	1.32	1.31	1.32	2.91	3.58	1.42	6.62	22.83	1.03	2.85	0.87	0.63	14.37	0.41	0.92	1.73	1.11
5	8.44	1.36	4.35	4.28	1.68	1.31	2.65	1.58	1.42	1.58	2.28	2.47	1.69	7.18	19.94	1.11	2.23	0.93	0.67	10.96	0.37	0.57	1.59	1.08
6	7.89	1.32	4.02	5.77	1.65	1.40	2.70	1.45	1.37	1.52	1.75	2.48	1.63	8.26	15.70	1.06	2.14	0.93	0.72	10.05	0.52	0.63	1.65	0.31
7	8.08	1.35	4.76	2.66	1.72	1.25	2.74	1.67	1.47	1.62	2.16	2.68	1.72	6.94	17.94	1.11	2.14	0.97	0.69	10.39	0.75	0.59	1.81	1.08
8	7.82	1.30	4.37	2.45	1.63	1.29	2.64	1.52	1.52	1.57	3.17	2.60	1.48	6.58	19.35	1.05	2.11	0.90	0.67	11.70	1.02	0.60	1.55	0.62
Mean	8.34	1.29	4.18	3.52	1.67	1.31	2.78	1.43	1.40	1.50	2.44	2.92	1.60	7.01	18.85	1.07	2.38	0.91	0.67	12.41	0.54	0.74	1.67	0.80

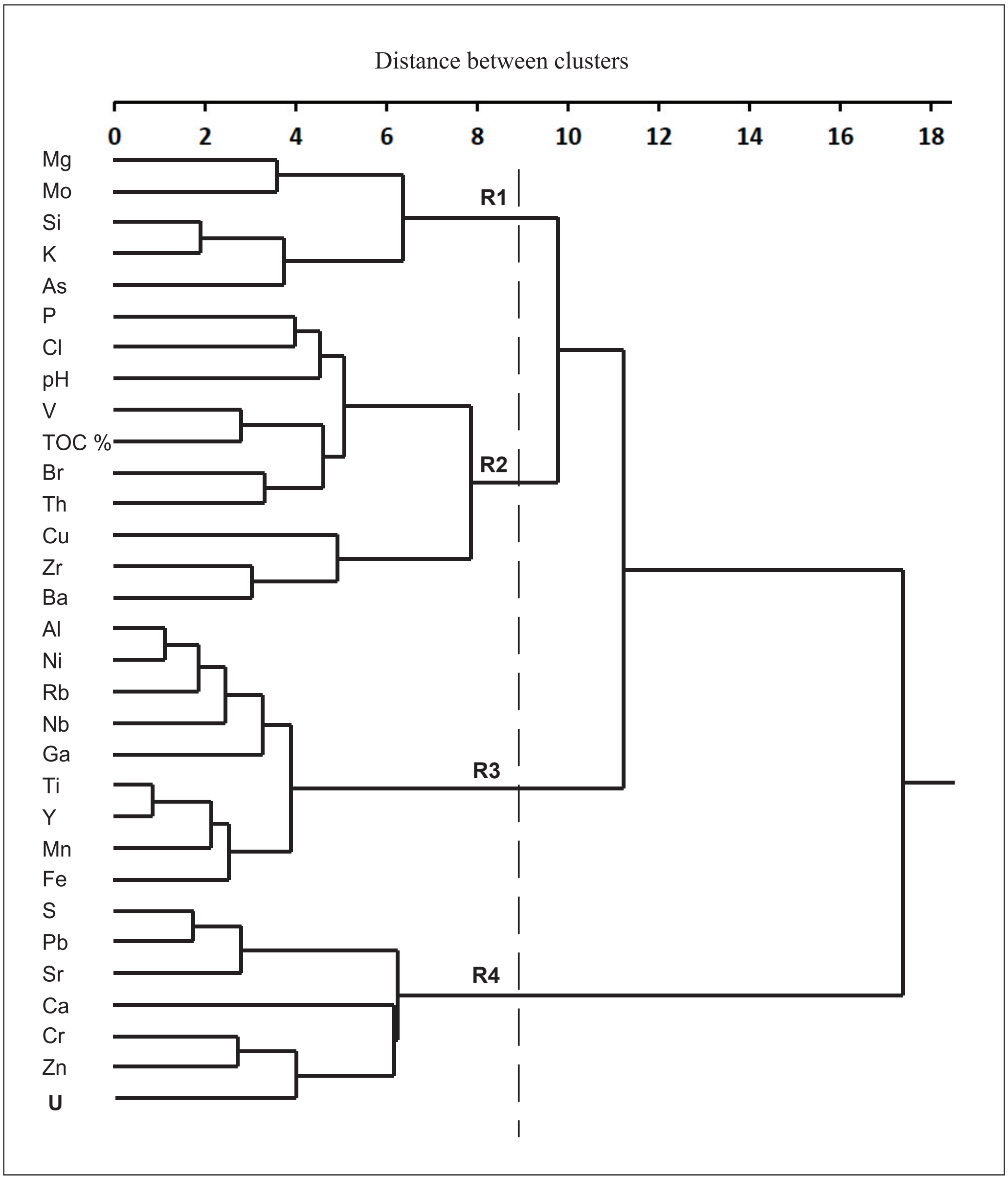

Figure 2. Dendrogram of elements measured and pH using Ward method

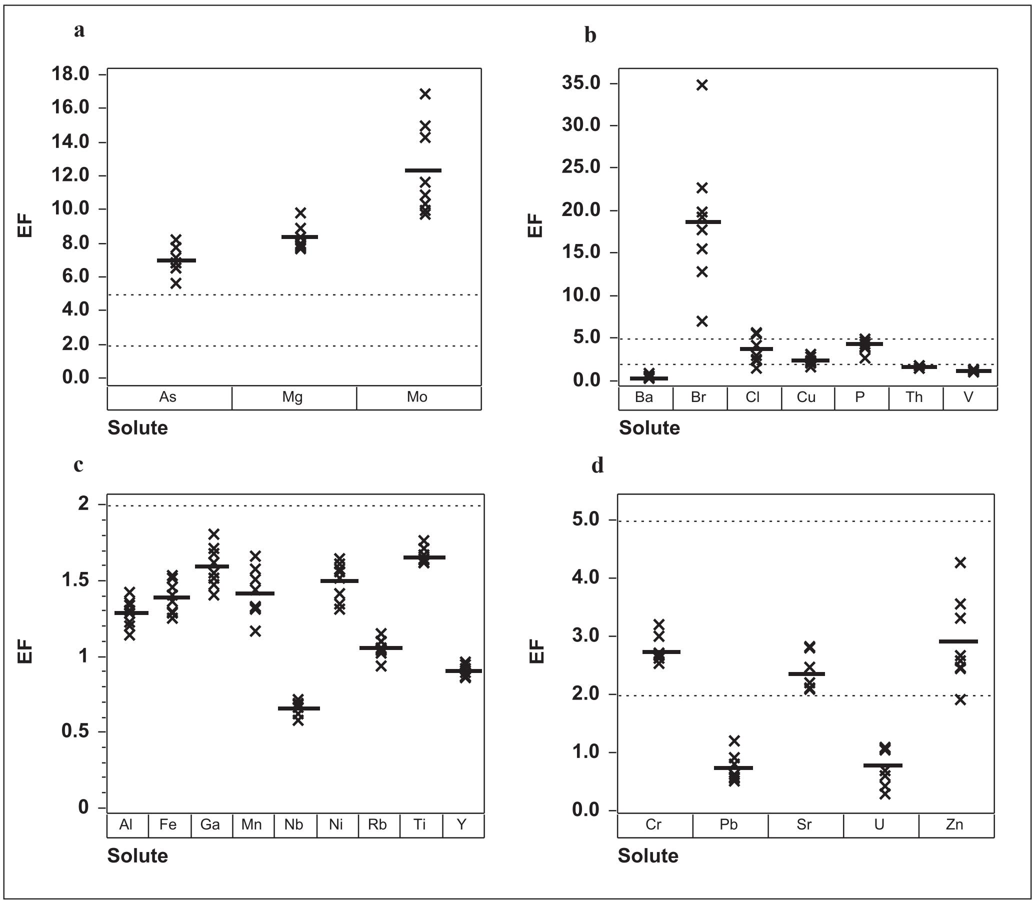

Figure 3. Enrichment Factor (EF) for elements where plots a, b, c, and d represent clusters 1, 2, 3, and 4 respectively. The middle horizontal thick lines represent the mean EF while the dotted horizontal thin lines represent EF of 2 and 5. EF of 2 is a threshold between natural and possible anthropogenic element sourcing while EF of 5 represents a threshold between possible anthropogenic and significant anthropogenic element sourcing

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