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Environmental Assessment of Al-Hammar Marsh Sediments, Southern Iraq

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Abstract

Concentrations and distribution of major, minor, and trace elements were studied in thirteen sediment samples from Al-Hammar Marsh.

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) were used to process the data and identify the possible sources of elemental constituents in sediment samples.Results of chemical analysis revealed that Major element mean concentrations were in the order of Ca> Si> K> Mg> and minor elements were in the order of Al> Fe>S>Cl> Ti> P>Mn> Sr> N and trace elements were in the order of Cr> Ni> Zr>V>Zn> Cu>Br> Co>Pb >Mo>As>U> Se> Cd.

Mainly increasing of Salinity in Marsh water and sediments led to increasing of Mg, S, Ca, Br, Cl concentrations in Al-Hammar Marsh Sediments.

Multivariate statistical techniques PCA and AHCA revealed that V, Zn, As, Se, Mo, Pb, Co, Fe, Ni, and Cu were most probably derived from fertilizers and petroleum extraction wastes in and near the study site. U (at St_1) and Sr came from fertilizers and for U might be from military weapon. Br, Cd, Cl, Ca, S, P and N indicated anthropogenic source (fertilizers, animal waste, and domestic sewage). While Mg, Cr, Mn were mainly associated with anthropogenic activities (fertilizers and animal wastes). On the other hand Al, Si, Ti, K، and Zr were primarily of natural sourcing from erosion of parent rocks. Enrichment Factor gave compatible results with PCA and AHCA findings and revealed that Al-Hammar Marsh sediments were highly contaminated by S, Mg, Cl, Ca, P, Br, Se, Mo, Ni, Co, Cu, and Sr. and it were minimally contaminated by Zn, V, U, Cr (excluding S_3), As, Fe, Mn, and N.

Keywords: Sediments, Multivariate statistical techniques, pollution analysis, Al-Hammar Marsh.

التقييم البيئي لرواسب هور الحمّار، جنوب العراق

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الخلاصة

تركيز وتوزيع العناصر الرئيسية والثانوية والشحيحة قد درست في ثلاثة عشر عينة من رواسب هور الحمّار. قد تم تطبيق تقنيات Agglomerative Hierarchal Cluster والتحليل العنقودي Principal Components analysis التحليل الاحصائي المتعدد المتغيرات تحليل التلوث (عن طريق حساب معامل

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الاغناء) قد استخدمت من اجل معالجة المعلومات وتعيين المصادر المحتملة وكذلكAnalysis للعناصر الكيميائية المكونة للرواسب.

وفيما يخص نتائج التحليل الكيميائي كشفت ان معدلات التركيز للعناصر الرئيسية كانت موزعة بالترتيب التالي في الرواسبCa> Si> K> Mg> اما تركيز العناصر الثانوية كانت موزعة بالترتيب التالي Al>Fe>S>Cl>Ti>P>Mn>Sr>N توزيع العناصر الشحيحة كانت بالترتيب التالي Cr> Ni>. Zr>V>Zn> Cu>Br> Co>Pb >Mo>As>U> Se> Cd كشفت عن ان المغنسيوم والكروم والمنغنيز كانت مشتقة من مصادرPCA وAHCA تقنيات التحليل الاحصائي المتعدد المتغيرات غير طبيعية اي من الانشطة البشرية والتي هي الاسمدة ومخلفات الحيوانات. اما عناصر البروم والكادميوم والكلورايد والكالسيوم والكبريت والفسفور والنايتروجين فان مصدرها هو الانشطة البشرية وتتمثل بالاسمدة ومخلفات الصرف الصحي ومخلفات ألحيوانات بينما فيما يخص الفانديوم والخارصين والزرنيخ والسيلينيوم والمولوبيدنيوم والرصاص والكوبالت والحديد والنيكل والنحاس فان المصدر المحتمل لهذه العناصر هو الاسمدة ومخلفات الاستخراج النفطي في وبالقرب من منطقة الدراسة. اليورانيوم والسترانتيوم مصدرهما الاسمدة اما اليورانيوم ربما يكون مصدره ايضا من الاسلحة الحربية. من الجانب الاخر فان الالمنيوم والسيلكون والتيتانيوم والبوتاسيوم والزركون كان مصدرهم طبيعي من تعرية المواد الجيولوجية.

وبينت ان رواسب هور الحمّار كانت (PCA) و (AHCA) كانت النتائج المستحصلة من معامل الاغناء متوافقة مع نتائج التحليل الاحصائي

ملوثة تلوثا كبيرا بالمغنسيوم والمنغنيز والكلورايد والكالسيوم والفسفور والبروم والسلينيوم والمولوبودنيوم والنيكل والكوبالت والنحاس والسترانتيوم . اما فيما يخص عناصر الخارصين والفانيديوم واليورانيوم والكروميوم والزرنيخ والتيتانيوم والمنغنيز والكروم والنايتروجين فقد كانت الرواسب ملوثة تلوثا واطئا بها.

1. Introduction

Marshes are important for economic, social and biodiversity values characterized by frequency of water flows and quality, accumulation of nutrients and organic matter and the production of commercially important vegetation and fish. They were the permanent habitat for millions of birds and a flyway for millions more migrating between Siberia and Africa [1].

The study of sediments plays an important role for their longer residence time, and the role is called "the record of history" [2]. Marsh sediments are normally the final pathway of both natural and anthropogenic components produced or derived to the environment As such, it is important to study these components systematically (i.e. their distribution, levels, and sources) [3] .

Sediment quality is a good indicator of pollution in the water column, where it tends to concentrate the inorganic (heavy metals) and other organic pollutants. Some kinds of toxic sediments kill benthic organisms, reducing the food available to larger aquatic organisms such as fish. Some contaminants in the sediment are taken up and magnified by benthic organisms in a process called bioaccumulation [4]. Moreover contaminants in sediments, depending on the sorption characteristics, can eventually be partly or totally released back into the water column threatening the aquatic life as well [5].

While some studies have addressed the water quality and environmental status of Al- Hammar Marsh, few studies addressed comprehensive study for elemental constituents in sediments, sediments quality, and sources of pollutants these study was study of Abdullah (1982) was conducted on the Sedimentology, petrography, geochemistry and hydrochemistry of the recent sediments for Al-Hammar Marsh in southern Iraq [6]. The study concluded that the chemistry of Al-Hammar Marsh sediments is affected by the geological formations and sediments exposed in the river coarse. Manii study (2009) was conducted on the mineralogy and geochemistry of soils and sediments in addition to study of marsh water and groundwater in study area [8]. The sediment characteristics, mineralogy and heavy metal content served as a background for future restoration activities [8]. Therefore, it is important here to study elements (distribution, levels, and sources) in sediments of Al- Hammar Marsh in order to evaluate their environmental impacts, their adverse effects on aquatic life, and mitigate and manage the contaminants input into marsh.

2. Study Sites

The study area is located in the southern of Iraq between latitudes (30 º 33´- 30º 58´N) and longitudes (46 º 24´ - 47 º 39´ E) (Figure - 1) Al-Hammar Marsh is the largest Marsh on the right side of Euphrates River before it joins Tigris River at Al-Qurna to form Shutt Al-Arab [9]. Sediment samples were collected from 13 sites along Al- Hammar Marsh during January, 2014 (table -1, Figure -1).

Table 1- Location of the sediment samples collected from Al-Hammar Marsh.

Sediment samples	Site names	Coordinates		Province
		N	E	
St $_1$	Suk Al Shuyukh	30°53'49.38"	46°29'47.87"	Thiqar
St $_2$	Al Sinaf	30°48'5.24"	46°35'3.87"	Thiqar
St $_3$	Hor Abu tina	30°50'42.55"	46°58'37.14"	Thiqar
St $_5$	Al-Chibayish	30°56'48.73"	46°46'1.99"	Thiqar
St $_7$	Qrmat Ali	30°35'43.87"	47°41'51.25"	Basra
St $_9$	Al-Shafi	30°49'26.51"	47°29'46.61"	Basra
St $_{10}$	Al-Mashab	30°38'39.11"	47°41'6.39"	Basra
St $_{11}$	Kirmashia	30°49'8.03"	46°37'1.36"	Thiqar
St $_{12}$	Al-Barga	30°42'6.99"	47°35'3.43"	Basra
*S $_2$	Al-Hartha	30°38'24.79"	47°42'35.32"	Basra
*S $_3$	Rumillah Oil field	30°41'0.66"	47° 7'27.70"	Basra
*S $_{3B}$	Al-Hartha	30°40'44.72"	47°36'24.34"	Basra
*S $_6$	Al-Hartha	30°36'43.88"	47°40'1.31"	Basra

*Dry sediments

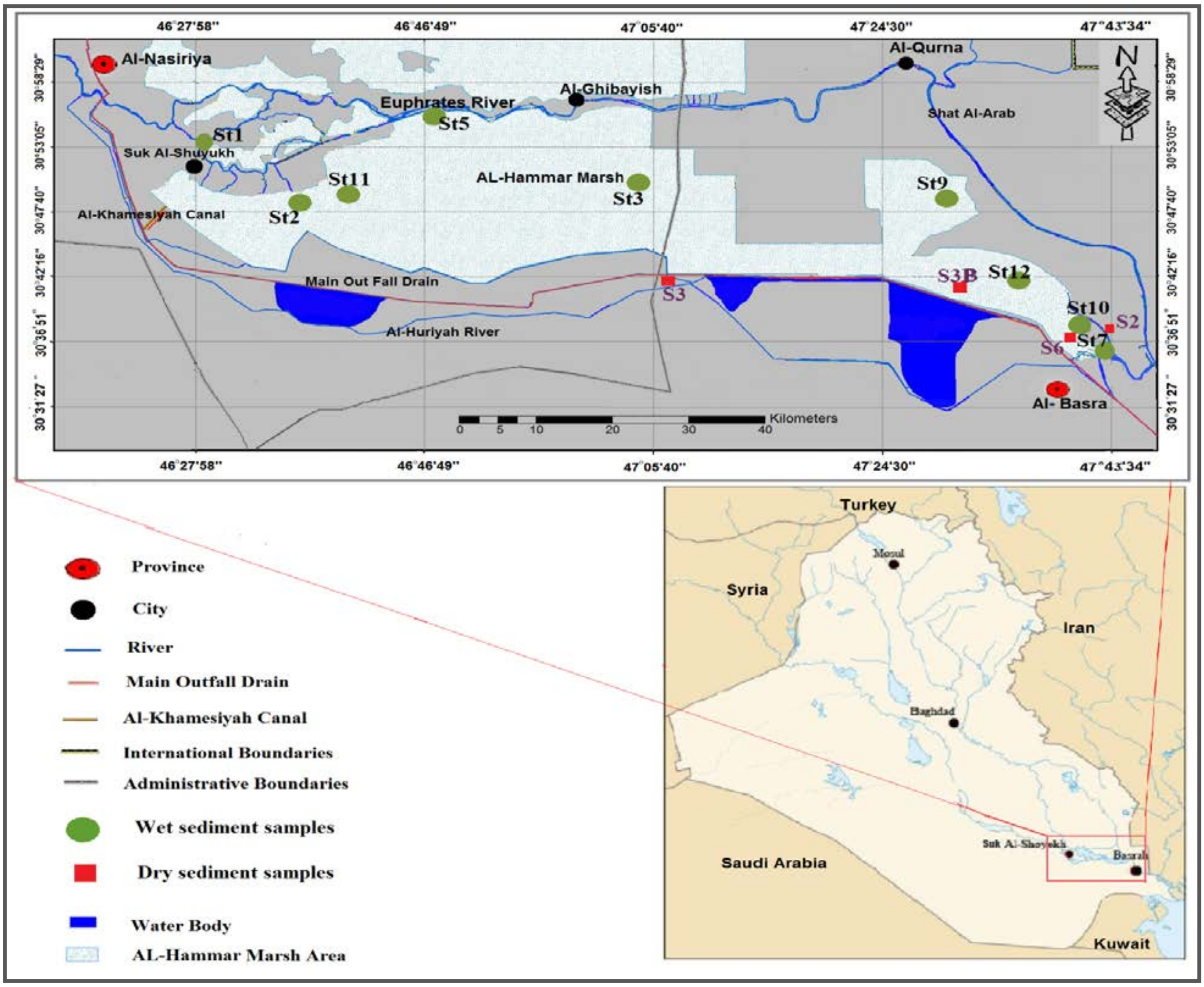


Figure 1- Map of study area with sampling stations after CRIM (2013).

3. Methods

3.1 Organic Matter and Element Analysis

Organic matters (OM) were determined by the most common procedure involves reduction of potassium dichromate (K_2CrO_7) by OC compound and subsequent determination of the unreduced dichromate by oxidation –reduction titration with ferrous ammonium sulfate [10]. 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) [11] as shown in table -2.

Concentrations of major, minor, and trace elements (Ca, Si, Mg, Al, P, S, Cl, K, Ti, V, Cr, Co, Mn, Fe, Ni, Cu, Zn, Se, Cd, As, Br, Sr, Zr, N, Zr, Mo, Pb, and U) in thirteen sediment samples were measured by X-Ray Fluorescence (XRF) device, samples were seived in 2mm seive then grinded well to be powder of 0.063 µm in size prior to test , 4 g for each sediment sample was required for this test .

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, minor, and trace elements.

Principal component analysis (PCA) technique was applied to infer the hypothetical source of heavy metals (natural or anthropogenic). Factor analysis was performed by varimax rotation.

Varimax rotation was employed because orthogonal rotation minimizes the number of variables with a high loading on each component and therefore facilitates the interpretation of Factor analysis results [12]. This technique clusters variables into groups such that variables belonging to one group are highly correlated with one another and assuming that highly correlated compounds come from the same source [10].

Factor loadings values of > 0.75, between 0.75 – 0.5 and between 0.5 – 0.3 are classified as strong, moderate and weak respectively based on their absolute values [13].

Agglomerative Hierarchal Cluster Analysis (AHCA) classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables. AHCA is often coupled with PCA to check results and to group individual parameters and variables [14]. The purpose of AHCA is to discover a system of organizing observations where a number of variables share observed properties. A dendrogram is the most commonly used method of summarizing hierarchical clustering [15]. In the current study, AHCA was used to evaluate the sources similarities of heavy metals in sediment samples.

3.3Pollution 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 [16].

The formula to calculate EF is

$$EF= (C_X/C_y)_S/(C_x/C_y)_{RS}$$

Where C_X is the measured concentration of the examined metal in sediment sample (mg/kg), and C_y is concentration of immobile element in the sample (Zr here), and $(C_X/C)_{RS}$ is the concentration of element X to immobile element ratio in the selected reference sample [17]. The immobile element is often taken to be Al [18,19], Li, Sc, Zr [20].

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 [20]. Total elemental concentrations (ppm) in the world soil according to Vinogradov (1959) [21] (table 2) is considered to calculate EF. 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 [22, 23, 24].

4 Results and discussion

4.1 Organic Matter and Element Analysis

Organic Matter (OM) ranged from 4.05 % to 5.3 % with mean value 4.55 %, while TOC ranged from 2.349 % to 3.07 % with mean value of 2.66 % (Table 2). These results concord with Aqrawi study (1997) [25] which assumed that in most of the brackish-water lakes and marshes, the TOC of the organic-rich layer is <5%. Major element mean concentrations were in the order of Ca> Si> K> Mg> and minor elements were in the order of Al> Fe>S> Cl> Ti> P>Mn> Sr> N and trace elements were in the order of Cr> Ni> Zr>V>Zn> Cu>Br> Co>Pb >Mo>As>U> Se> Cd (Table -2, Figures -2, -3, and -4).

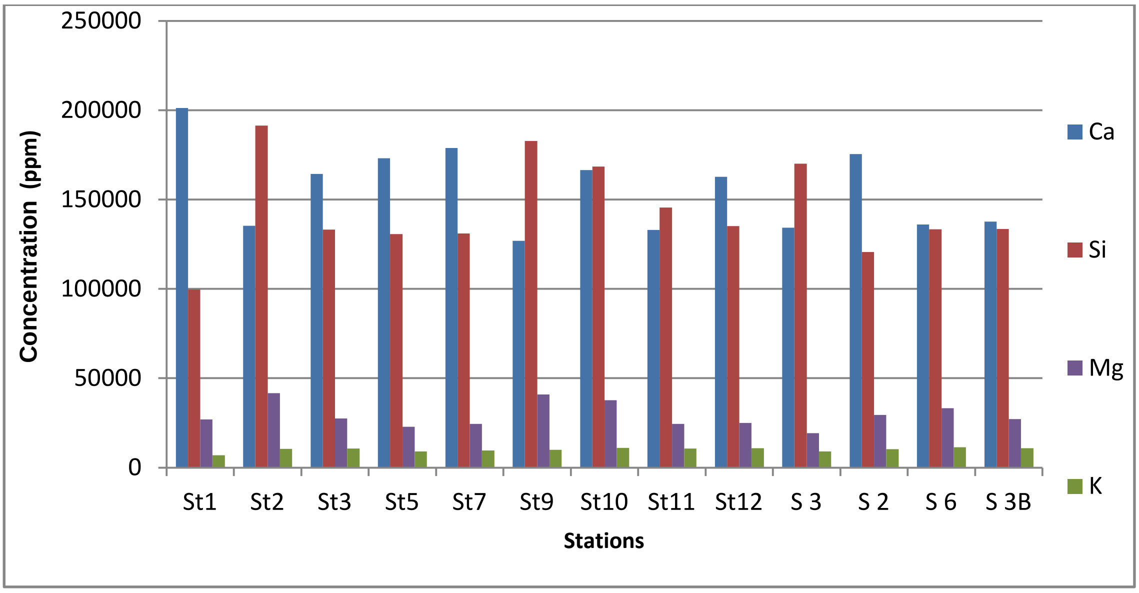


Figure 2- Distributions of major elements in sediments.

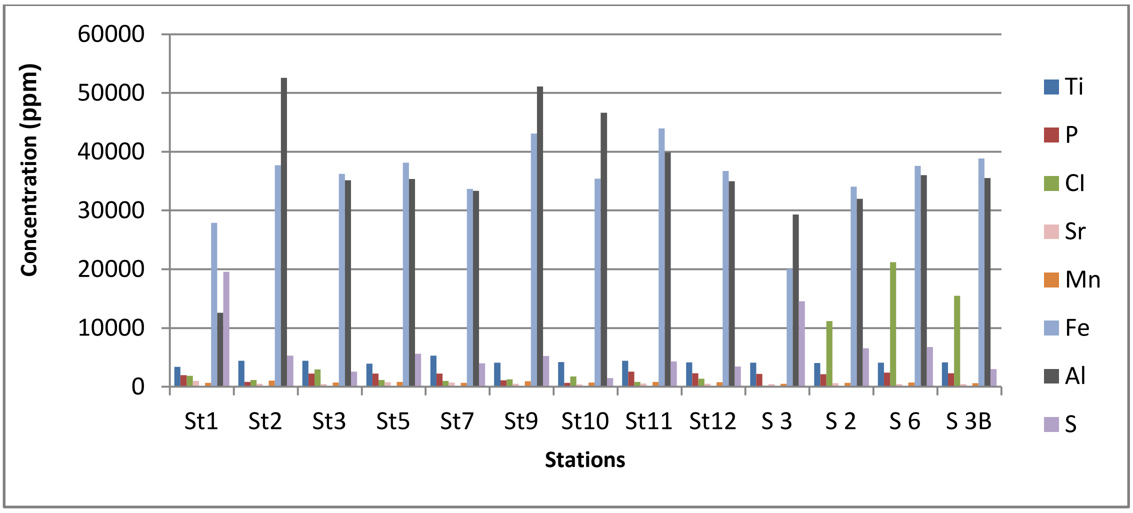
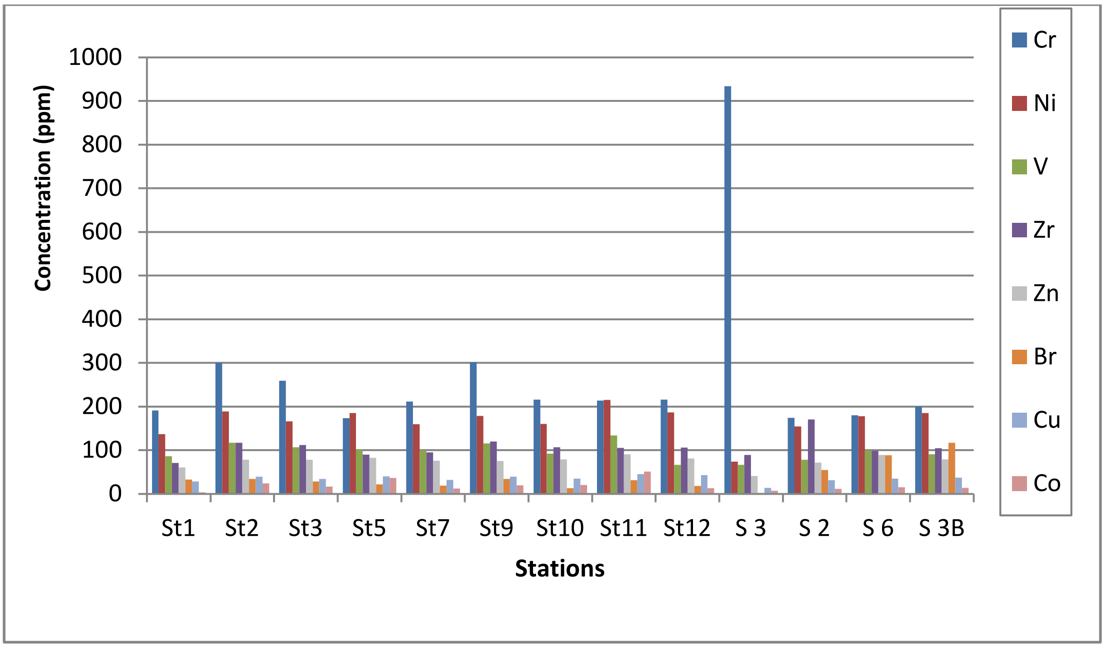


Figure 3- Distributions of minor elements in sediments.



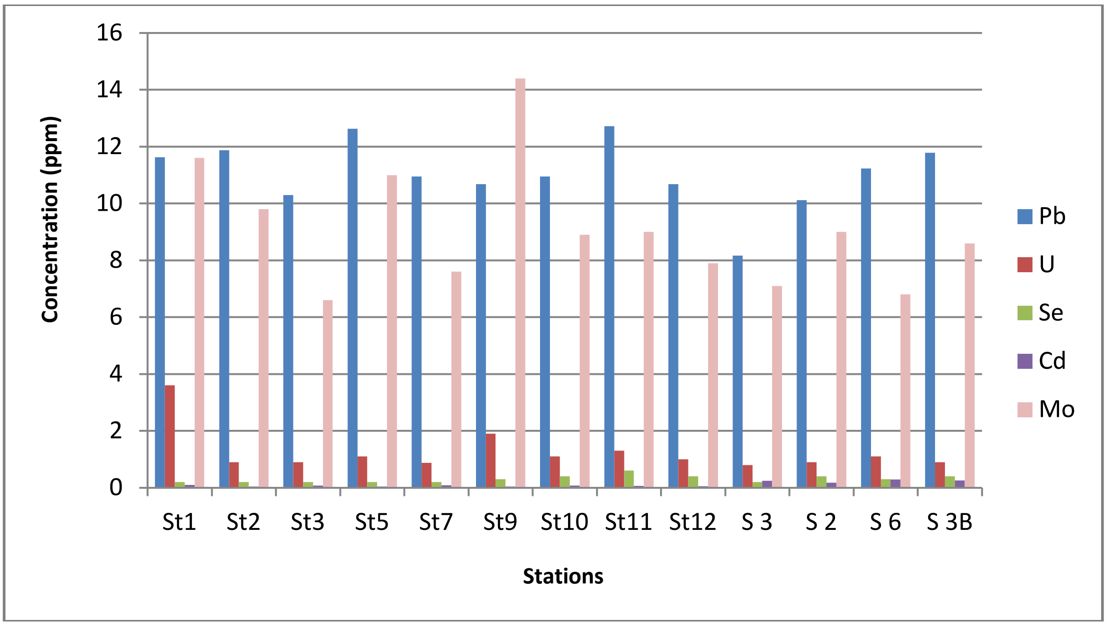


Figure 4 - Distributions of trace elements in sediments.

Table 2- Results of chemical analysis for Al-Hammar Marsh sediments with water pH and Total elemental concentrations in the world soil according to Vinogradov (1959).

Elements	Unit	St_1	St_2	St_3	St_5	St_7	St_9	St_{10}	St_{11}	St_{12}	$*S_2$	$*S_3$	$*S_6$	$*S_{3B}$	Mean	Vinogradov, 1959
Ca	ppm	201190	135311	164403	173052	178914	126948	166476	133024	162759	175482	134239	136026	137598	155802	13700
Si	ppm	99751.2	191445	133146	130762	131043	182842	168537	145629	135203	120664	170126	133427	133520	144315	330000
Fe	ppm	27883.9	37705.5	36229.5	38153.2	33655.1	43099	35432	43938.4	36719.1	34025.9	20077	37565.6	38845.8	35640.8	38000
Mg	ppm	26887.8	41592.3	27593.5	22786.3	24517.5	41001.2	37744.3	24427	24915.6	29457.2	19185.8	33220.8	27092.9	29263.2	6300
S	ppm	19583.5	5302.36	2599.12	5646.78	4016.82	5250.3	1464.56	4341.21	3426.11	6575.89	14573.5	6788.15	3007.21	6351.96	850
Al	ppm	12617.6	52590.6	35115.1	35354.1	33352.7	51082.3	46610.2	39894.2	34988.1	31966.1	29304.1	35998.9	35496.2	36490	71300
K	ppm	6981.32	10535.5	10651.7	8999.58	9663.76	9987.55	11025.3	10610.2	10809.5	10278.1	9124.12	11465.3	10792.9	10071.1	13600
Ti	ppm	3395.68	4427.46	4434.65	3958.03	5324.34	4110.31	4219.42	4416.66	4154.08	4019.18	4084.53	4092.33	4169.07	4215.83	4600
P	ppm	1994.76	828.28	2255.29	2268.8	2245.25	1098.41	661.14	2564.26	2314.2	2160.59	2197.69	2408.47	2282.35	1944.58	800
CI	ppm	1883	1155	2932	1150	972.6	1294	1782	833.2	1385	11180	188.4	21180	15460	4722.71	450
Sr	ppm	976.6	520.21	470.91	804.16	717.23	505.33	420.26	543.21	513.28	587.69	453.58	462.2	446.81	570.88	850
Mn	ppm	649.96	1028.66	741.36	842.76	694.04	962.82	705.81	840.43	760.26	681.87	526.57	702.09	636.79	751.8	300
Cr	ppm	190.68	300.29	258.89	173.58	211.28	301.66	215.65	213.81	216.06	173.71	933.91	179.94	199.92	274.57	200
Ni	ppm	136.89	189.06	165.8	184.89	159.59	178.77	160.07	214.91	186.23	154.33	73.86	177.98	184.98	166.72	40
V	ppm	86.26	117.07	106.99	101.39	99.71	115.39	91.87	133.88	66.1	77.86	66.66	100.27	90.75	96.48	100
Zr	ppm	70.99	117.26	111.79	90.17	94.98	119.71	106.9	105.34	105.94	170.57	88.98	98.31	104.46	106.57	300
Zn	ppm	60.42	78.01	77.85	82.75	76.24	74.8	78.65	90.78	80.74	71.5	40.57	88.86	78.97	75.4	50
N	ppm	36	32	35	34	30	28	24	31	29	38	35	40	41	33.31	20
Br	ppm	32.9	34.3	28.2	21.5	18.9	33.8	12.8	30.9	18.1	54.89	1.7	88.6	117.2	37.98	5
Cu	ppm	28.04	39.22	34.43	39.78	31.95	39.54	34.99	45.21	43.22	30.92	13.26	35.15	36.83	34.81	20
Pb	ppm	11.63	11.88	10.3	12.63	10.95	10.68	10.95	12.72	10.68	10.12	8.17	11.23	11.79	11.06	17
Mo	ppm	11.6	9.8	6.6	11	7.6	14.4	8.9	9	7.9	9	7.1	6.8	8.6	9.1	2
As	ppm	3.79	4.73	3.29	3.6	2.88	4.81	3.26	5.79	0.46	2.12	2.42	3.03	9.8	3.85	5
U	ppm	3.6	0.9	0.9	1.1	0.87	1.9	1.1	1.3	1	<1	< 0.10	1.1	<1	1.38	1.8
Co	ppm	3	23.75	16.83	36.57	12.27	19.74	20.13	50.65	12.66	11.17	7	15.1	13.76	18.66	8
Se	ppm	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.6	0.4	<0.5	<0.5	<0.5	<0.5	0.3	0.001
Cd	ppm	0.1	0.04	0.07	0.04	0.09	0.04	0.08	0.06	0.05	0.18	0.24	0.29	0.26	0.12	**0.35
O.M	%	4.59	4.05	4.56	4.615	4.125	4.345	4.165	4.625	4.68	5.1	5.3	4.65	4.95	4.55	
TOC	%	2.662	2.349	2.645	2.676	2.392	2.52	2.415	2.682	2.714	2.958	3.074	2.697	2.871	2.66	

*Dry sediments.

** Cd natural abundance in world soil [26].

4.2 Principal Components Analysis (PCA)

By applying PCA on chemical analysis results (Table -2) three factor components with eigenvalues greater than 1 were extracted which explained 94.765 % of the data variation (Table -3). The factor loadings of the different variables are presented in Table -4.

In detail, the first factor (F1), which has strong factor loading of K(0.96), Zn (0.89), Ti (0.82), Fe(0.77), Ni(0.76), and moderate factor loading of Cu(0.71),Co (0.57), Se(0.7), Zr (0.66), and Si (0.551) accounts for 36.074% of variance. F1 could be better explained as anthropogenic source. This source considered agriculture activities and wastes from oil extraction, excluding Si, and Zr which derived from natural deposited. F2, which has strong factor loadings of Mg (0.94), Al (0.74), Cr (0.86), Mn (0.77), V (0.56), and Si (0.79), accounts for 28.022% of the variance. Si came from erosion of crustal material, while Mg, Cr, and Mn which considered as anthropogenic source derived from agriculture runoff from farm lands.

F3 which has strong factor loading of Br (0.96), Cd (0.80), Cl (0.79), and moderate factor loading of N (0.73) and TOC% (0.58), As (0.664) accounts for 15.435% of the variance.PC3 source can be considered anthropogenic. Fertilizers, human sewage and livestock manure are known to be a significant source of these elements [27].

The last one is F4 and it has strong factor loading of Pb (0.97) and moderate of Co (0.72), V (0.61), Ni (0.603), Cu (0.561) and As (0.60) accounts for 15.234% of the variance these element have same source which was fertilizers and waste from oil extraction processes.

Table 3- Total variance explained four components selected.

Initial Eigenvalues			Rotation Sums of Squared Loadings		
Eigenvalue	**Percent**	**Cum Percent**	**Variance**	**Percent**	**Cum Percent**
15.3138	52.806	52.806	10.4614	36.074	36.074
6.3676	21.957	74.763	8.1264	28.022	64.096
3.1791	10.962	85.726	4.4761	15.435	79.531
2.6213	9.039	94.765	4.4179	15.234	94.765

Table 4- PCA loadings of major, minor and trace elements on varimax rotated principal components.

		Components		
Elements	**F 1**	**F 2**	**F 3**	**F 4**
Mg	0.089	0.9461	0.35	-0.655
Al	0.010	0.747	0.098	-0.089
Si	0.551	0.791	-0.209	0.153
P	-0.091	-0.939	0.260	0.116
S	-0.972	-0.172	0.083	-0.047
CI	0.118	-0.463	0.797	-0.296
K	0.970	0.124	0.186	-0.038
Ca	-0.756	-0.510	-0.204	-0.342
V	0.434	0.561	-0.217	0.610
Cd	-0.003	-0.513	0.802	-0.278
Cr	0.345	0.861	-0.311	0.063
Mn	0.350	0.772	-0.361	0.348
Fe	0.771	0.399	-0.023	0.481
Co	0.576	0.184	-0.308	0.720
Ni	0.762	0.203	-0.056	0.603
Cu	0.716	0.284	-0.246	0.561
Zn	0.897	-0.059	0.026	0.420
As	0.083	0.325	0.664	0.602
Se	0.700	-0.020	-0.176	0.498
Br	0.052	-0.192	0.967	-0.012
Sr	-0.923	-0.294	-0.199	0.064
Mo	-0.533	0.070	-0.215	0.283
Pb	-0.089	0.007	-0.058	0.976
U	-0.975	-0.060	0.109	0.027
Ti	0.820	0.099	-0.334	-0.021
Zr	0.661	0.269	0.225	-0.432
PH	-0.008	-0.911	0.064	-0.310
TOC%	-0.209	-0.741	0.582	-0.053
N	-0.318	-0.557	0.730	-0.122

4.3 Cluster analysis

Agglomerative Hierarchal Cluster Analysis (AHCA) applying Ward's method was performed on the results of element concentrations in sediment samples of Al-Hammar Marsh (Table -2).
The results are illustrated in the dendrogram (Figure -5).
AHCA highlighted 4 specific element response patterns (R1, R2, R3, and R4).

The distance cluster represents the degree of association between elements, where clusters with smaller or shorter distances between them are more similar to each other than clusters with larger or longer distances between. From the dendrogram cluster R1 has the shortest distance (6.98) and highest similarity to cluster R2, whereas cluster R3 is the least similar and has the greatest distance to R1 (19.33) (Figure -5).

Elements clustering in R1 (Mg, Al, Si, Cr, Mn, K, Ti, and Zr) that dominate in the F 2 indicate to natural and anthropogenic sources. Al, Si, Ti, K and Zr are lithophile elements according to Goldschmidt's classification of geochemical elements [28]. Lithophile elements are those showing an affinity for silicate phases and are concentrated in the silicate portion (crust and mantle) of the earth [28]. Concentration results of Mg, Cr, and Mn show increasing by these elements in Al-Hammar Marsh sediments comparing with the natural abundance in world soil [21] Mg main source is increasing of Sabkha phenomenon in southern of Iraq. Beside that for the Mg, Cr, and Mn it may come from fertilizers. Fertilizers are known to be a significant source of these elements [29 , 27].

V, Fe, Ni, Cu, Co, Zn, Se, As, Pb, and Mo clustered in R2 (dominating in the F1and F4) indicating same source, which can be derived from agricultural activities and petroleum production, and these trace metals are released from fertilizers and from oil refineries [30, 31]. Bowen (1979) referred that high cobalt concentration usually also have high arsenic and, nickel concentrations [32].

P, TOC%, N, Cl, Cd, and Br clustered in R3 (dominating in the F3) indicate anthropogenic sources. Mainly are fertilizers according to Hooda (2010) [33]. Municipal effluents may increase P, TOC%, N concentrations [34]. Nitrate-N, ammonium-N, and phosphate-P are the three most common contaminants derived from unregulated animal waste disposal practices. These three chemicals are usually found at concentrations ranging from 1,000 to 50,000 mg kg_1 (elemental form) in animal wastes [34]. Increasing in Br and Cl was due to with high salinity in sediments of marsh and also from agricultural sourcing [35, 36] .

S, Ca, Sr, and U clustered in R4. High concentrations of S and Ca in Al-Hammar Marsh sediments came from natural and anthropogenic sourses. Natural source was due to increasing of evaporation and salinity in water and sediments of Al-Hammar Marsh and anthropogenic sources were from Fertilizers and manure (buffalo wastes) according to Cunningham et al. (2007) [37]. Most animal wastes are high in TDS (Na, Cl, Ca, Mg, K, and soluble N [34].While U (at St_1) and Sr represent radioactive contaminants [34] and Sr is geochemically similar to calcium and substitutes for Ca in many Ca-bearing minerals, including sulphates (gypsum), carbonates and feldspars (38). The source of U and Sr may be fertilizers and for U might be military weapon has contributed to rising it concentrations as well.

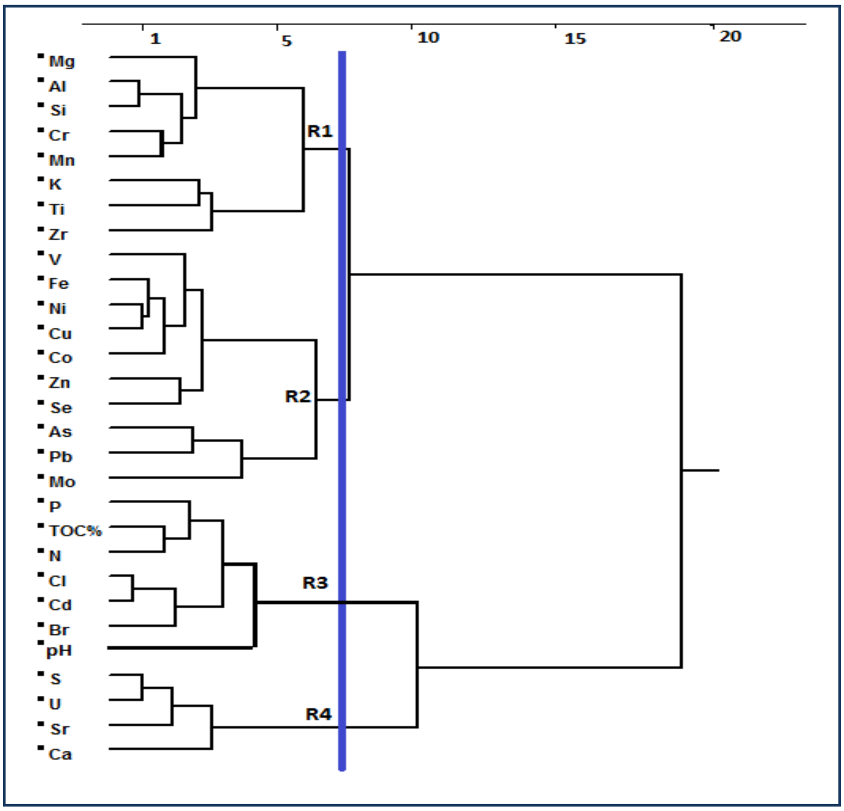


Figure 5- Dendrogram of elements measured using Ward method.

4.4 Pollution Analysis

The result of EF calculations for Al-Hammar Marsh sediment samples are shown in table 5.

EF value for Se shows extremely high enrichment which has mean EF value of 1033.35 so depending on this value Al-Hammar Marsh sediments highly polluted by Se and the sources of Se considered anthropogenic sources.

EF values for S, Ca, and Br show a very high enrichment which have mean EF values of 18.82, 33.54, and 21.58 respectively. This enrichment indicates anthropogenic remarkable source for S, Ca, Br. Elements Mg, P, Cl, Mo, Cu, Sr, Co, and Ni have mean EF values of 13.33, 7.19, 15.94, 13.33, 12.03, 5.73, 6.67, and 5.01 respectively, thus, Al-Hammar Marsh sediments are polluted in these elements, and they are mainly of anthropogenic sources. Elements Al, Si, Cr, Mn, K, Ti V, N, Fe, U, Zn, As, and Pb have mean EF values of 1.45, 1.27, 4.1, 2.55, 2.13, 2.67, 2.81, 2.68, 2.69, 3.35, 4.36, 2.25, and 1.91 respectively, therefore, Al-Hammar Marsh sediments are unpolluted in these elements.

Table 5 - Results of Enrichment Factor for sediment samples.

Elements	**EF_1**	**EF_2**	**EF_3**	**EF_5**	**EF_7**	**EF_9**	**EF_{10}**	**EF_{11}**	**EF_{12}**	**EF_{S2}**	**EF_{S3}**	**EF_{S6}**	**EF_{SB3}**	**Mean**
Al	0.75	1.9	1.3	1.6	1.5	1.8	1.8	1.6	1.4	0.79	1.39	1.54	1.43	1.45
As	3.2	2.4	1.8	2.4	1.8	2.4	1.8	3.3	0.3	0.75	1.63	1.85	5.63	2.25
Br	27.81	17.6	15.1	14.3	11.9	16.9	7.2	17.6	10.3	19.31	1.15	54.07	67.32	21.58
Ca	62.06	25.3	32.2	42	41.2	23.2	34.1	27.7	33.6	22.53	33.04	30.3	28.85	33.54
Co	1.58	7.6	5.6	15.2	4.8	6.2	7.1	18	4.5	2.46	2.95	5.76	4.94	6.67
Cr	4.03	3.8	3.5	2.9	3.3	3.8	3	3	3.1	1.53	15.74	2.75	2.87	4.1
Cu	5.92	5	4.6	6.6	5	5	4.9	6.4	6.1	2.72	2.24	5.36	5.29	5.01
Fe	3.1	2.5	2.6	3.3	2.8	2.8	2.6	3.3	2.7	1.57	1.78	3.02	2.94	2.69
K	2.17	2	2.1	2.2	2.2	1.8	2.3	2.2	2.3	1.33	2.26	2.57	2.28	2.13
Mg	18.04	16.9	11.8	12	12.3	16.3	16.8	11	11.2	8.22	10.27	16.09	12.35	13.33
Mn	3.23	3.1	2.3	3.3	2.6	2.8	2.3	2.8	2.5	1.41	2.09	2.52	2.15	2.55
Mo	24.51	12.5	8.9	18.3	12	18	12.5	12.8	11.2	7.92	11.97	10.38	12.35	13.33
Ni	14.46	12.1	11.1	15.4	12.6	11.2	11.2	15.3	13.2	6.79	6.23	13.58	13.28	12.03
P	10.54	2.6	7.6	9.4	8.9	3.4	2.3	9.1	8.2	4.75	9.26	9.19	8.19	7.19
Pb	2.89	1.8	1.6	2.5	2	1.6	1.8	2.1	1.8	1.05	1.62	2.02	1.99	1.91
S	31.34	16	8.2	22.1	14.9	15.5	4.8	14.5	11.4	13.61	57.81	24.37	10.16	18.82
Se	845.19	511.7	536.7	665.4	631.7	751.8	1122.5	1708.8	1132.7	<879.4	<1685.7	<1525.7	<1436.0	1033.35
Si	1.28	1.5	1.1	1.3	1.3	1.4	1.4	1.3	1.2	0.64	1.74	1.23	1.16	1.27
Sr	13.76	4.4	4.2	8.9	7.6	4.2	3.9	5.2	4.8	3.45	5.1	4.7	4.28	5.73
Ti	3.12	2.5	2.6	2.9	3.7	2.2	2.6	2.7	2.6	1.54	2.99	2.71	2.6	2.67
V	3.65	3	2.9	3.4	3.1	2.9	2.6	3.8	1.9	1.37	2.25	3.06	2.61	2.81
Zn	5.11	4	4.2	5.5	4.8	3.7	4.4	5.2	4.6	2.52	2.74	5.42	4.54	4.36
Zr	1	1	1	1	1	1	1	1	1	1	1	1	1	1
U	11.7	1.9	2.8	1.9	2.1	4.1	2.4	2.8	2.4	<2.20	<0.2	2.58	2.21	3.35
CI	9.73	3.61	9.62	4.68	3.75	3.96	6.11	2.9	4.79	24.3	0.78	78.99	54.27	15.94
N	4.18	2.25	2.58	3.11	2.61	1.93	1.85	2.43	2.26	1.84	3.24	3.36	3.24	2.68
Cd	1.16	0.28	0.52	0.37	0.78	0.28	0.62	0.47	0.39	0.87	2.23	2.43	2.05	0.96

5. Conclusions

1. TOC in marsh sediments was <5 %, Low TOC level in this study was due to high salinity of marsh water which was 6841.58 mg/L.
2. Major element mean concentrations were in the order of Ca> Si> K> Mg> and minor elements were in the order of Al> Fe> S> Cl> Ti> P>Mn> Sr> N and trace elements were in the order of Cr> Ni> Zr>V>Zn> Cu>Br> Co>Pb >Mo>As>U> Se> Cd.
3. Increasing in Mg, S, Ca, Br, Cl concentrations in Al-Hammar Marsh Sediments were due to natural and anthropogenic sources. Increasing of Salinity in Marsh water and sediments is natural source which considered the main source. Agricultural activities and domestic sewage are considered anthropogenic sources for these elements.
4. Multivariate statistical techniques such as Principal Component Analysis (PCA) and Agglomerative Hierarchal Cluster Analysis (AHCA) revealed that Mg, Cr, Mn were mainly

associated with anthropogenic activities. Mainly agricultural activities (fertilizers and animal wastes) considered as a source for these elements. Br, Cd, Cl, Ca, S, P and N indicate anthropogenic source it is clear from fertilizers and domestic sewage, animal waste. While V, Zn, As, Se, Mo, Pb, Co, Fe, Ni, Zn, and Cu came from anthropogenic source. Most probably were derived from fertilizers and petroleum extraction. U (at St_1) and Sr came from fertilizers and for U (at St_1) might be associated with military weapon. On the other hand Al, Si, Ti, K. and Zr are lithophile elements were derived from original materials and therefore interpreted as from natural sources.

5. EF results (mean value) revealed that Al-Hammar Marsh sediments were highly contaminated by S, Mg, Cl, Ca, P, Br, Se, Mo, Ni, Co, Cu, and Sr and minimally contaminated by Zn, V, U (excluding St_1 which was highly contaminated by U), Cr (excluding S_3), As, Fe, Mn, and N.

6. EF results show the most polluted station (in most elements) was St_1 (located in inlet of Al-Hammar marsh Suk Al- Shuyukh) comparing with other stations. This may due to filtration and bioremediation processes which activate in Al-Hammar marsh.

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