The influential factors on the geochemistry of chemical elements in recent sediments of the Tigris River, Iraq

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Abstract

This study is concerned with the factors that control the chemistry of the recent sediments of the river Tigris extending from Turkish-Iraqi border to Qayyarah town south of Mosul city, covering about 230 km of the river course. Chemical analysis of recent sediment samples of the Tigris River was performed using X-ray fluorescence. Statistical analysis of the chemical analysis data was carried out to determine the influential factors on the geochemistry of major and trace elements in the sediments.

The results showed that many factors may control the composition of these sediments including the composition of the clastic rocks exposed along the course of the river. Other factors include the geochemical behavior of the elements concerned, intensity of the chemical weathering and sediment sorting. The results also showed that some elements including P, Mo, Ni, Zn and Pb are probably affected by anthropogenic activities.

Keywords: Influential factors, geochemistry, recent sediments, Tigris river**.**

Introduction

The chemical composition of river sediments generally depends on a number of factors including composition of basin rocks, structural and geomorphological status of the river basin, climate that controls type of weathering processes, hydrological characteristics of the river and density of vegetation within the basin[12,17-19]. Among all the above, the lithology seems to be the most effective factor in controlling the sediment geochemistry[16]. In addition, human activities may sometimes have a clear effect on the chemistry of river sediments[2,14]. River sediments also contain and retain many environmental pollutants[8]. Thus, sediments can become sources of pollution when environmental conditions change.

The current research aims to identify the factors controlling the major and trace elements composition in the recent sediments of the Tigris River within the area extending from Faysh Khabur north of Dohuk to Qayyarah south of Mosul (Fig.1).

Geology of the Tigris Riverbed: The Tigris River originates from the highlands of south and south-eastern Turkey, a very complex area of nape zone[15]. The river then proceeds to the south-east passing through various rock types of basalt, clastic and carbonate rocks in Diyarbakir areas, the Mardin Mountains and the Raman Hills[20].

When the river enters the Iraqi lands, it passes through the molasse deposits of Muqdadiya and Injana formations. Then, it continues to run through the Fat'ha formation (alternating beds of limestone, gypsum and siltstones) and river deposits, which appear along the river course.

Although the main course of the Tigris River passes through few formations; the river basin inside Iraq includes tributaries in northern and eastern Iraq (Fig. 1) where many formations are exposed, these are mainly composed of carbonate, evaporites, marl, clay and sandstone rocks as well as the Quaternary deposits represented by river terraces, flood plain deposits, slope deposits and flood fans.

Field and Laboratory Work: A total of 10 samples of surface sediments (0–10 cm) were collected from the Tigris Riverbed at ten locations along the course of the river from the Turkish-Iraqi border to the Qayyarah town, covering approximately 230 km of the river course within Iraq (Fig. 1). Sampling was conducted during low-flow conditions, about 1kg of fine grained sediment (sand and finer grain-sized) samples were directly collected by hand from each of the sampling sites.

The samples were placed in polythene bags and transferred to the laboratory where they were oven dried at 60°C. Bulk sample chemical analysis using X-ray fluorescence (Turboquant Powders Method) was conducted at the Freiberg University-Hydrogeology Institute where the samples were analyzed for their content of major, minor and trace elements (Table 1).

Chemical elements data (Table 1) was treated statistically using SPSS version 19. Correlation analysis was applied to determine the relationship between the elements under investigation. Multi variables statistical techniques such as factor and cluster analysis were used to combine a large number of initial data, so they can be easily interpreted to obtain geochemical information and to identify potential factors or sources that affect geochemistry of the sediments.

Factor analysis is a common statistical technique used in dealing with chemical raw data, for deriving from a number of given variables a smaller number of different, more useful variables[6]. Factor analysis was performed using principal component analysis method and based on normalized varimax rotated matrix.

Hierarchical cluster analysis (Word's Method) was used to observe the interconnectivity between the chemical elements and the possibility of dividing into convergent groups expressing similar geochemical behavior or indicating that they are affected by certain factors unrelated to the geochemical behavior of the elements.

This statistical technique helps to divide the data of a number of variables into specific groups and present the results in a simplified manner by the convergence of elements and groups of elements[9,11]. All the statistical analyses were done using SPSS version 19.

Results and Discussion

Table 1 shows the contents of the main, secondary and trace elements of the current samples analyzed using X-ray fluorescence. Table 2 provides a comparison of the chemical composition between the recent sediments of Tigris River (current samples) and the upper and middle Miocene clastic rocks exposed within the basin and course of Tigris River[4].

Table 1
Major and trace elements composition of the samples
(Concentrations of major oxides (%) and trace elements (ppm))

(wt%)	Sample No.									
	1	2	3	4	5	6	7	8	9	10
SiO_2	35.71	40.58	36.11	35.19	33.29	28.90	30.19	41.98	38.25	40.95
TiO_2	0.84	0.93	0.73	0.66	0.63	0.60	0.63	0.84	0.77	0.82
Al_2O_3	9.82	11.36	9.98	9.37	8.88	7.57	8.14	13.40	10.01	11.32
Fe_2O_3	5.66	5.77	4.94	5.50	4.35	3.67	4.33	7.84	4.82	5.98
MgO	7.69	8.50	5.64	7.25	5.01	4.40	4.26	9.21	6.25	6.43
CaO	19.50	14.45	21.55	21.53	26.60	29.55	28.12	14.09	18.30	18.61
Na_2O	1.10	1.84	1.40	1.55	1.50	0.98	1.41	2.02	1.76	2.01
K_2O	1.20	1.41	1.27	1.21	0.99	0.87	1.08	1.78	1.26	1.39
P_2O_5	0.19	0.19	0.15	0.24	0.12	0.13	0.13	0.19	0.16	0.19
S	0.14	0.10	0.10	0.09	0.14	0.09	0.07	0.05	0.20	0.07
Cl	0.02	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.03	0.01
(ppm)										
V	90.00	89.00	94.00	90.00	86.00	79.00	95.00	158.00	93.20	125.0
Cr	454.1	385.6	222.3	373.3	320.4	176.2	277.4	235.9	356.2	245.9
Mn	820.6	786.7	540.0	623.2	492.5	516.5	502.6	1025.0	706.4	810.1
Co	9.90	28.90	7.00	16.20	5.00	2.55	3.00	32.30	13.70	14.30
Ni	191.70	189.90	149.60	258.00	152.40	109.20	141.70	291.40	150.80	197.00
Cu	35.10	33.50	33.50	40.80	30.50	26.00	23.90	58.10	29.20	40.40
Zn	79.50	74.40	73.60	116.30	59.60	55.30	59.30	113.30	78.20	95.90
Ga	12.70	14.00	12.60	12.60	11.60	10.50	9.70	16.60	12.00	14.30
As	4.90	5.10	5.20	5.10	4.50	3.70	5.40	9.30	6.00	8.10
Br	6.90	3.80	4.50	5.60	6.20	7.70	7.20	4.80	7.50	8.50
Rb	43.50	47.70	50.20	46.40	41.80	37.00	46.70	67.90	46.10	51.80
Sr	323.90	244.10	246.50	333.90	336.40	321.00	285.70	243.30	364.80	261.30
Y	18.80	21.00	18.80	16.20	15.10	14.20	15.70	22.90	18.30	19.10
Zr	156.50	138.90	132.50	106.50	114.30	117.50	125.00	119.30	131.30	120.90
Nb	9.30	10.20	8.00	7.10	7.00	6.50	6.20	10.30	7.40	8.90
Mo	10.20	9.20	7.70	10.70	8.00	10.20	7.90	9.20	7.90	7.70
Sn	3.40	<3	<3	<3	<3	7.20	<3	<3	<3	<3
Sb	<3	<3	<3	<3	<3	11.00	<3	5.70	<3	<3
I	<3	<3	<3	6.00	8.40	10.30	2.60	<3	<3	<3
Cs	<4	12.10	<4	<4	<4	<4	<4	<4	<4	<4
Ba	184.30	213.90	156.70	161.70	185.30	191.90	166.20	266.40	239.80	203.70
La	<2	68.30	<2	<2	15.70	82.60	<2	<2	<2	29.40
Ce	<2	82.00	<2	<2	<2	<2	<2	<2	<2	<2
Hf	3.10	1.40	2.10	<2	<2	<2	<2	1.90	2.00	1.90
Ta	60.60	60.10	61.00	57.90	61.30	60.50	68.50	64.30	62.20	60.30
Pb	9.90	9.10	13.20	18.10	13.10	9.90	10.50	17.00	11.10	14.10
Th	4.40	5.20	5.80	5.00	4.70	5.60	5.10	7.00	4.50	6.20

Table 2 shows that the average concentrations of chemical elements of the current study samples are generally within the range of middle and upper Miocene rocks, this suggests that the clastic rocks of these formations contribute significantly to the composition of the recent sediments of the Tigris River, in particular that these rocks are widely exposed in the Tigris River course and basin.

The range of SiO_2 content in the study samples is between 28.9% and 41.98% with an average of 36.12%. Quartz and chert are contributing phases of SiO_2 content. However, the strong correlation between SiO_2 and Al_2O_3, Fe_2O_3, MgO, Na_2O and K_2O (Table 3) indicates the possible presence of other clastic phases such as feldspar, biotite and muscovite minerals. However, the strong positive correlation between SiO_2 and Al_2O_3 (0.9) and K_2O (0.9) indicates the presence of clay minerals.

Clay minerals may have the greatest influence on the overall geochemical properties of the sediments under study. This is supported by the strong correlation between the major components of clay minerals (SiO_2, Al_2O_3) and trace elements (V, Mn, Co, Ni, Cu, Zn, Ga, As, Rb, Th, Y, Nb, Ba). The strong correlation between TiO_2 and silica can be attributed to the presence of rutile within the crystals of the fine-size quartz and mica minerals[21].

In addition to some other minerals such as titanium magnetite and ilmenite[5], this is strengthened by the strong correlation coefficient between titanium and iron and aluminum. It seems that the correlation coefficients between the main elements also reflect the poor sorting of sediments. This is supported by the lack of sorting between quartz and other mineral components which may indicate an immature chemical weathering of the source rocks[7].

This is also evident from the results of the Hierarchical Cluster Analysis (Fig. 2) which shows the grouping of the elements (SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O, V, Mn, Co, Cu, Ga, Rb, Y and Nb) within one space. This supports what was mentioned earlier about the immature chemical weathering of the source rocks and the absence of a good sorting of sediments. This reflects the control of quartz, clay minerals and non-carbonate clastic material on the concentrations of the elements of this group.

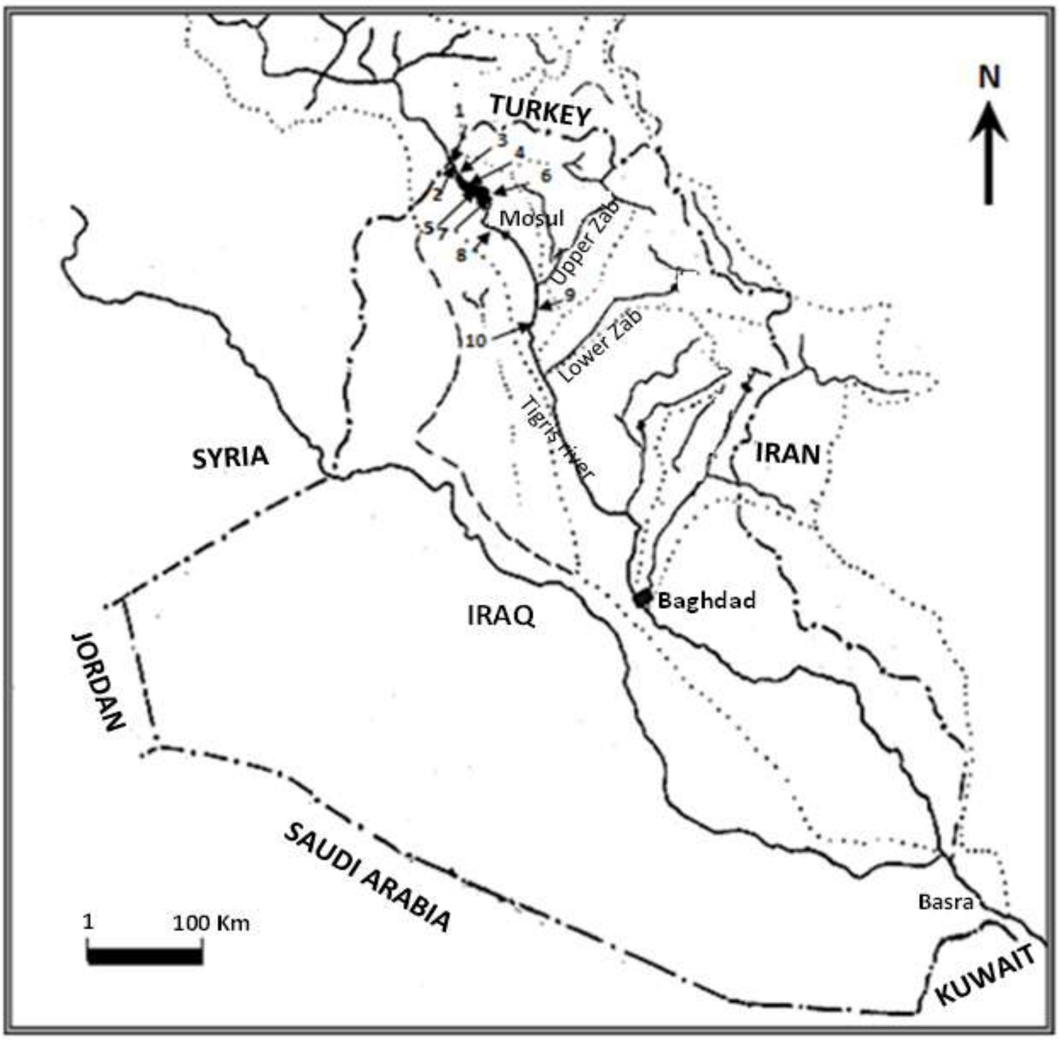

Figure 1: Map of Tigris river basin and its tributaries showing the sampling sites (1- 10)

Table 2
Comparison of chemical composition of the Tigris sediment of the present study with the clastic rocks of the Fat'ha and Injana formation

Oxides (wt%)	**Current study**		**Fat'ha Fm.**		**Injana Fm.**	
	Range %	**Average %**	**Range %**	**Average %**	**Range %**	**Average %**
SiO_2	28.9-41.98	36.115	32.72-48.95	42.74	34.88-54.27	44.26
TiO_2	0.6-0.93	0.745	0.31-0.73	0.46	0.21-0.47	0.35
Al_2O_3	7.57-13.4	9.985	5.79-13.88	10.81	3.96-14.1	10.89
Fe_2O_3	3.67-7.84	5.286	2.71-7.17	4.83	2.48-5.8	3.73
MgO	4.26-9.21	6.464	2.63-8.28	4.77	1.93-7.05	3.38
CaO	14.09-29.55	21.23	9.13-21.6	14.6	12.62-25.15	15.56
Na_2O	0.98-2.02	1.557	1.94-2.2	2.02	1.89-2.38	2.09
K_2O	0.87-1.78	1.246	1.68-4.07	3.7	2.23-3.77	3.09
P_2O_5	0.12-0.24	0.169	0.11-0.27	0.21	0.1-0.24	0.15
Trace Elements (ppm)						
Ni	109-291.4	183.17	220-395	320	91-177	113
Co	2.55-32.3	13.285	20-80	44	4-20	14
Cu	23.9-58.1	35.1	13-14	14	12-13	12
Zn	23.9-58.1	80.5	60-135	86	35-60	46
Mn	793-1025	682	512-1326	786	529-1006	764
Cr	176.2-454.1	304	267-907	499	67-233	130
V	79-158	99.9	84-126	103	60-90	72
Sr	243.3-364.8	296.1	325-425	372	200-349	305
Zr	106.5-156.5	126.3	66-220	122	85-134	120
Rb	37-67.9	47.9	25-54	41	69-75	72
Y	14.2-22.9	18	25-37	32	18-22	20

The strong negative correlation between calcium and other major elements indicates that calcium is present in the carbonate phase. The increase in the carbonate content in the sediments leads to a decrease in the percentage of other clastic material. This is reflected in the Dendrogram (Fig. 2) which shows the separation of calcium, bromine and strontium in a completely independent group indicating their presence within the carbonate phase.

This is also supported by the positive correlation between strontium, bromine and calcium and the negative correlation of these three elements with the major elements of clay minerals and other non-carbonate minerals. The negative correlation between calcium and magnesium suggests that magnesium is not present as a major or a minor component in the carbonate phases.

The tree diagram of the elements (Fig. 2) shows that they are distributed into four main groups. The first Cr, Zr and Hf are characterized by low mobility in weathering environments and are often found in some highly resistant minerals. The second which is in contrast to the first group, includes elements (Ca, Br, Sr) characterized by high mobility during the weathering and metamorphism processes. Such elements are therefore enriched in carbonate sedimentary rocks and their aggregation in a single group indicates their presence in the carbonate phase. The third consists of wide range of elements that have accumulated due to the combined effects of the geochemical behavior of the elements and the weathering processes and sediment environment in terms of the degree of sorting and maturity of the sediments.

This group includes the elements of clay minerals released in the weathering environments and elements of the ferromagnetic minerals and trace elements which their geochemical properties allow to enter in the ferromagnetic minerals, or it may be adsorbed on clay minerals and iron oxides[3]. The fourth group includes Pb, P_2O_5, Ni and Zn, these elements seem not to be very similar in geochemical behavior in order to be in one group, their grouping in the same group may be resulted from anthropogenic factors.

Factor analysis: Factor analysis was performed on chemical data using principal component analysis method and based on normalized varimax rotated matrix. It revealed that there are three main factors affecting the concentration of the elements. These factors account for more than 91% of variance. The first represents 60.1% of the variance, the second 16.33% and the third 14.93% of the total variance (Table 4).

Table 3
Correlation coefficients of the main, secondary and trace elements of the Tigris recent sediments in the present study

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	P_2O_5	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As	Br	Rb	Sr	Y	Zr	Nb	Mo	Ba	Pb	Th
SiO_2	1																										
TiO_2	0.86	1																									
Al_2O_3	0.95	0.81	1																								
Fe_2O_3	0.84	0.72	0.94	1																							
MgO	0.82	0.83	0.85	0.89	1																						
CaO	-0.96	-0.92	-0.92	-0.85	-0.91	1																					
K_2O	0.9	0.76	0.97	0.95	0.84	-0.9	1																				
P_2O_5	0.59	0.52	0.52	0.65	0.76	-0.66	0.54	1																			
V	0.66	0.44	0.82	0.85	0.55	-0.57	0.85	0.29	1																		
Cr	0.2	0.4	0.06	0.13	0.43	-0.35	0.03	0.49	-0.31	1																	
Mn	0.83	0.83	0.9	0.92	0.89	-0.87	0.87	0.6	0.76	0.22	1																
Co	0.85	0.77	0.89	0.87	0.92	-0.9	0.89	0.62	0.63	0.21	0.83	1															
Ni	0.65	0.46	0.75	0.9	0.83	-0.68	0.78	0.79	0.7	0.23	0.74	0.78	1														
Cu	0.72	0.49	0.85	0.94	0.79	-0.69	0.85	0.61	0.86	-0.05	0.8	0.77	0.92	1													
Zn	0.66	0.4	0.68	0.81	0.73	-0.65	0.73	0.87	0.65	0.15	0.67	0.68	0.93	0.86	1												
Ga	0.91	0.76	0.97	0.94	0.87	-0.88	0.92	0.59	0.8	0.04	0.89	0.87	0.8	0.91	0.74	1											
As	0.75	0.51	0.84	0.83	0.54	-0.64	0.86	0.35	0.97	-0.22	0.77	0.64	0.67	0.8	0.67	0.78	1										
Br	-0.35	-0.35	-0.43	-0.4	-0.53	0.45	-0.45	-0.25	-0.1	-0.15	-0.19	-0.57	-0.4	-0.36	-0.23	-0.43	-0.02	1									
Rb	0.72	0.51	0.88	0.89	0.64	-0.68	0.93	0.36	0.94	-0.21	0.74	0.74	0.75	0.86	0.68	0.82	0.91	-0.39	1								
Sr	-0.46	-0.49	-0.59	-0.53	-0.36	0.42	-0.61	-0.08	-0.54	0.38	-0.38	-0.47	-0.29	-0.43	-0.19	-0.55	-0.49	0.5	-0.63	1							
Y	0.9	0.9	0.95	0.89	0.85	-0.94	0.95	0.47	0.71	0.14	0.88	0.86	0.63	0.73	0.55	0.89	0.73	-0.5	0.82	-0.63	1						
Zr	0.19	0.6	0.14	0.09	0.28	-0.35	0.11	0.05	-0.16	0.51	0.3	0.06	-0.18	-0.17	-0.25	0.06	-0.12	-0.09	-0.09	-0.11	0.39	1					
Nb	0.85	0.94	0.89	0.84	0.89	-0.89	0.82	0.51	0.58	0.25	0.88	0.83	0.61	0.69	0.48	0.89	0.57	-0.47	0.64	-0.6	0.93	0.46	1				
Mo	-0.17	0	-0.1	0.12	0.36	-0.02	-0.08	0.51	-0.17	0.31	0.18	0.18	0.35	0.21	0.31	0.07	-0.28	-0.14	-0.18	0.23	-0.08	0	0.11	1			
Ba	0.64	0.54	0.7	0.6	0.56	-0.63	0.66	0.13	0.65	-0.05	0.75	0.69	0.39	0.54	0.33	0.64	0.66	-0.05	0.58	-0.13	0.64	0.04	0.56	-0.06	1		
Pb	0.33	-0.1	0.4	0.53	0.32	-0.23	0.45	0.51	0.56	-0.17	0.25	0.34	0.75	0.74	0.81	0.49	0.53	-0.2	0.58	-0.1	0.19	-0.65	0.08	0.12	0.08	1	
Th	0.41	0.21	0.6	0.59	0.29	-0.3	0.62	0.09	0.81	-0.72	0.45	0.45	0.44	0.68	0.43	0.63	0.72	-0.19	0.75	-0.74	0.5	-0.34	0.41	-0.11	0.39	0.48	1

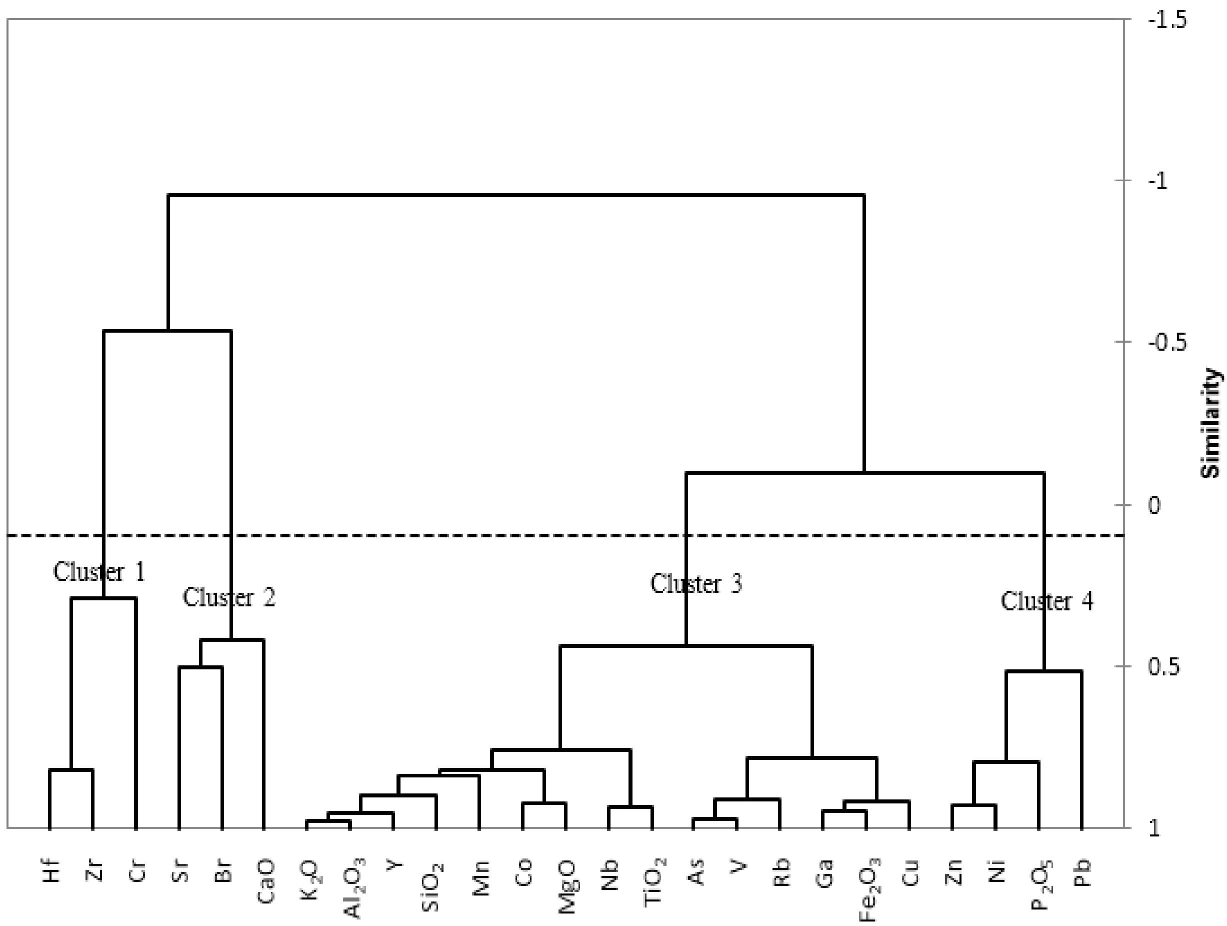

Figure 2: Dendrogram showing clustering of elements

The first factor: This factor is a dipole factor, the first pole is the positive loading of the following elements (SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O, TiO_2, V, Mn, Co, Ni, Cu, Zn, As, Rb, Y, Nb). It appears from figure 3 that this factor strongly affects the concentrations of SiO_2, Al_2O_3, Fe_2O_3, MgO, K_2O and TiO_2, which are the main components of clay minerals and the associated fine grained fragments of mafic minerals and quartz; therefore, it represents the combined contribution of clay minerals and accompanied clastic materials.

The positive loading of the trace elements on this factor indicates the absorption of these elements by clay minerals and iron oxides, or entering into the crystalline structure of some of the mafic minerals. The second pole of this factor is the negative loading of calcium oxide (CaO), which indicates negative relationship between carbonates content and other clastic components.

The second factor: This factor shows the positive loading of Zr, Cr and TiO_2, it is also involved in influencing the content of SiO_2, MgO, Nb and Y but to a lesser degree than the effect of the first factor (Fig. 3). It is noted that the elements loaded to this factor are those that exist within the resistant heavy minerals such as chromite, zircon and rutile and that the source of these minerals is the igneous rocks[7] which derived from northeastern Iraq and southern Turkey[3].

The third factor: This factor shows positive loading of P_2O_5, Mo, Zn, Ni and MgO. This factor does not individually affect the loaded elements (Fig. 4), but shares other factors in influencing the content of these elements. It seems that all these elements are not compatible in geochemical behavior and that the collection of these elements may be due to unnatural factor especially as they are widely used in industry and agriculture[10].

The presence of phosphorus may indicate phosphate fertilizer as an important source of this element[1]. As this factor mainly affects the concentration of P_2O_5 and Mo, this refers to agricultural activities, especially since P_2O_5, Mo, Zn, MgO are widely used in the agricultural fertilizer industry.

Conclusion

1. The results indicate that the clastic rocks exposed along the course and basin of the Tigris river constitute the most important sources of the river recent sediments.

2. Correlation coefficients between the major elements and also the cluster analysis results indicate poor sorting of the sediments by lack of sorting between quartz and other mineral components which may indicate an immature weathering of the source rocks.

Table 4
Factor loadings, total variance, eigenvalue, cumulative total variances and communalities of the main factors affecting concentrations of the elements in the Tigris River sediments

Elements	Factor 1	Factor 2	Factor 3	Communalities
SiO_2	0.848	0.405	0.093	0.892
TiO_2	0.624	0.757	0.103	0.972
Al_2O_3	0.951	0.281	0.076	0.989
Fe_2O_3	0.926	0.167	0.299	0.974
MgO	0.713	0.448	0.518	0.978
CaO	-0.777	-0.539	-0.235	0.949
K_2O	0.958	0.212	0.103	0.974
P_2O_5	0.433	0.189	0.803	0.868
V	0.947	-0.188	-0.073	0.937
Cr	-0.174	0.651	0.543	0.749
Mn	0.828	0.373	0.258	0.892
Co	0.803	0.296	0.338	0.847
Ni	0.761	-0.073	0.611	0.958
Cu	0.895	-0.115	0.364	0.946
Zn	0.718	-0.153	0.615	0.917
Ga	0.921	0.204	0.219	0.938
As	0.944	-0.109	-0.098	0.913
Rb	0.961	-0.080	-0.029	0.930
Y	0.861	0.481	0.025	0.973
Zr	-0.076	0.902	-0.111	0.832
Nb	0.739	0.587	0.158	0.916
Mo	-0.164	0.005	0.853	0.755
Eigen values	15.046	2.836	2.218	
Total variance(%)	60.103	16.334	14.926	
Cumulative(%)	60.103	76.437	91.363	

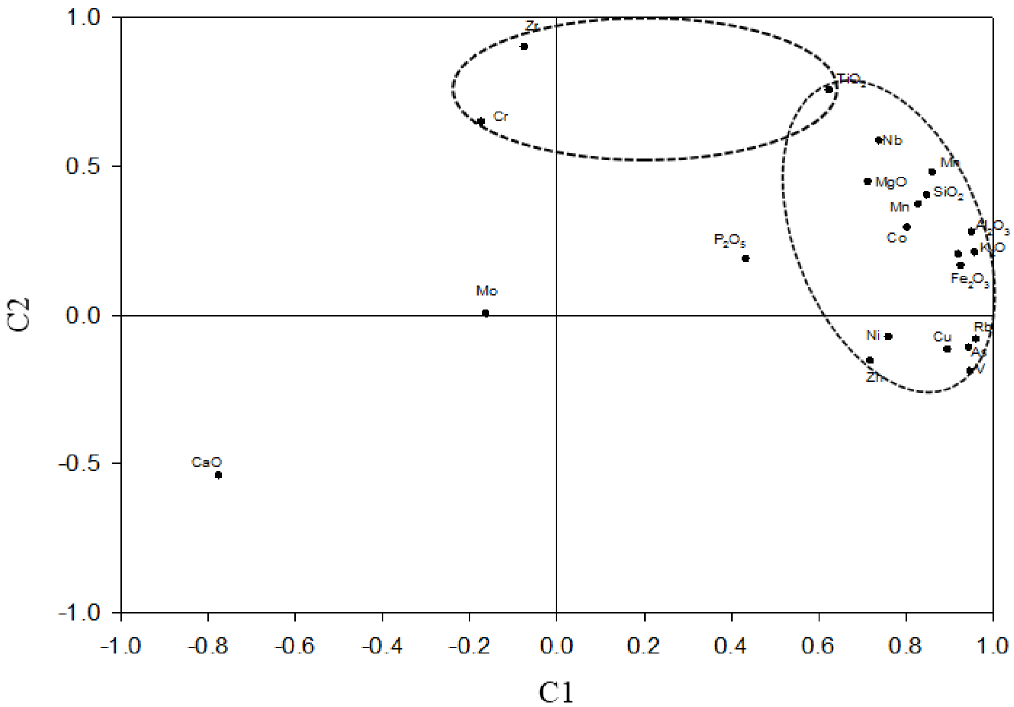

Figure 3: graphical representation of loadings of the first and second components after rotation

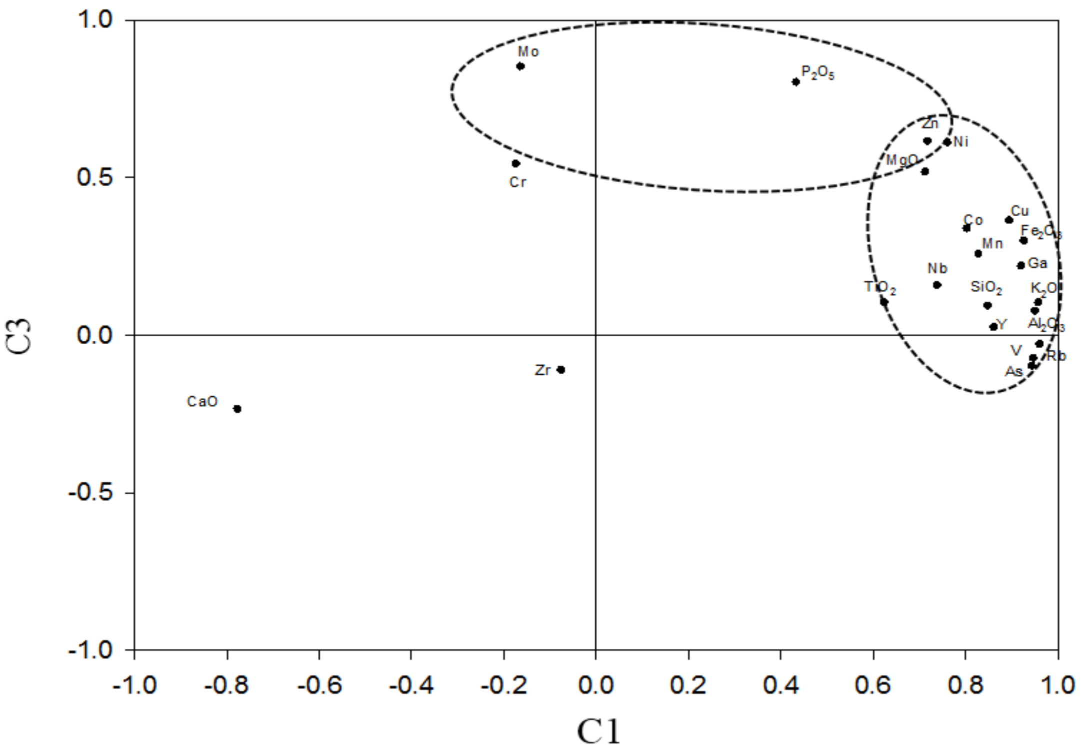

Figure 4: Graphical representation of loadings of the first and third components after rotation

3. The results of the cluster and factor analysis showed that the chemical elements in the Tigris recent sediments are present in four groups, depending on the geochemical behavior of these elements in the weathering environments and the degree of sorting and maturity of the sediments, in addition to the potential impact of human activities on certain elements such as phosphorus, zinc, nickel and lead.

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