

Assessment of Pollution by Heavy Metals in Surface Sediments at Wadi Al-Wala, Jordan

Abstract

The concentration levels of Cd, Fe, Cu, Mn, Pb, and Zn in sediment samples from Wadi Al-Wala were determined in order to assess the level of contamination. Sixteen sediment samples were collected during the period from 2016. The highest concentrations of Zn, Cu and Cd originate mainly from anthropogenic sources such as discharge of agricultural materials residuals and the weathering of surrounding rock formations. Sediment contamination assessment was carried out using the pollution indicators such as enrichment factor (EF), pollution load index (PLI), and geo-accumulation index (Igeo). The Results of Igeo analyses of Wadi Al-Wala sediments proved that concentrations of Mn, Cu, Pb, and Fe are safe and these elements are practically unchanged by anthropogenic influences, while the concentration of Zn and Cd exceeded the average value. PLI analysis proved that Wadi Al-Wala is moving towards a probable environmental pollution with regard to heavy metals (Zn and Cd), while. The results of EF showed high concentrations of Zn, Cu and Cd in the study area. Correlation coefficients analysis showed varying relation between the different parameters depending on the input sources of each metal. In order to protect the sediments from further contamination, monitoring and management of the heavy metal anthropogenic discharges is suggested.

Key words: Wadi Al-Wala, Sediments, Heavy metals, Pollution Assessment, Jordan.

1. Introduction

Environmental pollution is a problem in modern societies. Out of the various kinds of pollution, high contamination of aquatic systems with toxic heavy metals is of major concern since these elements are not biodegradable and their elevated uptake by crops may also affect food quality and safety. Heavy metals enter these aquatic systems mainly through natural inputs such as weathering and erosion of rocks and anthropogenic sources including urban, industrial and agricultural activities, terrestrial runoff and sewage disposal [1]. Heavy metals discharged into aquatic systems may be immobilized within stream sediments by main processes such as adsorption, flocculation and co-precipitation. Therefore, sediments in aquatic environments serve as a pool that can retain metals or release metals to the water column by various processes of remobilization [2, 3, 4]. Several processes lead to the association of heavy metals with solid phases, such as direct absorption by fine-grained inorganic particles of clays; adsorption of hydrous ferric and manganic oxides which may in turn be associated with clays; adsorption on or complication with natural organic substances, or associated with inorganic particles, and direct precipitation as new solid phases [5]. Numerous studies have demonstrated that the concentrations of metals in sediments can be sensitive indicators of contaminants in aquatic systems [6,7,8,9,10]. Many approaches have been applied in order to assess the severity of

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sediment contamination and to understand the natural and anthropogenic inputs in the river system.

The main objective of this study was characterization of selected heavy metals concentration (Copper, Zinc, Cadmium, Manganese, Iron, Arsenic and Lead) in the Surface's sediments for distribution and concentrations in sediments from Wadi Al-Wala area. Also, it aims to assess sediments pollution potentiality by heavy metal using Geo-accumulation (Igeo), Pollution Load index (PLI) and Enrichment Factor (EF) and Pearson's correlation coefficients for different parameters. This assessment will help in providing a better perspective about the contamination amount and sources in the study area, which in turn will help in understanding the mechanisms driving and controlling this contamination. This study also aims to assess the various sources of contamination to have a prospect regarding the possible prevention of this contamination.

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2. Study Area

2.1 Geographical Location

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The study area is located in the middle part of Jordan, Wadi Al-Wala lies between latitudes (30°20' and 31°50'N and between longitudes (35°12' E and 36°38'E), it occupies an area of about 2050 km² (Fig. 1). The study is a part of Al-Wala basin in the middle parts of Jordan; the total area of the basin is 1900 km². The basin has a flat topography in the east and steep slopes in the west. Altitude of the study area varies from 321 m below sea level at the eastern shoreline of the Dead Sea (lowest point on earth) to 997 m in the eastern parts of the study area. The basin is dominated by an arid Mediterranean climate with relatively cold winters and hot summers. The mean monthly air temperature ranges from 6°C in January up to 22°C in August, with a mean annual air temperature of 15.0°C. With exception to northwestern parts. The mean annual rainfall is 100 - 200 mm, occurring mainly during winter season (October-April). The mean annual potential evaporation ranges from 1600 mm in the western parts to 2000 mm in the east and 2200 mm at the outlet near the Dead Sea. In terms of land use, about 47% of the basin is used as open rangelands. Agricultural activity is also taking place in the basin where rain-fed cultivation of wheat and barley is practiced in 38% of the basin. Irrigated areas form 3% of the total area of the basin, while 7% of the basin is urban[11].

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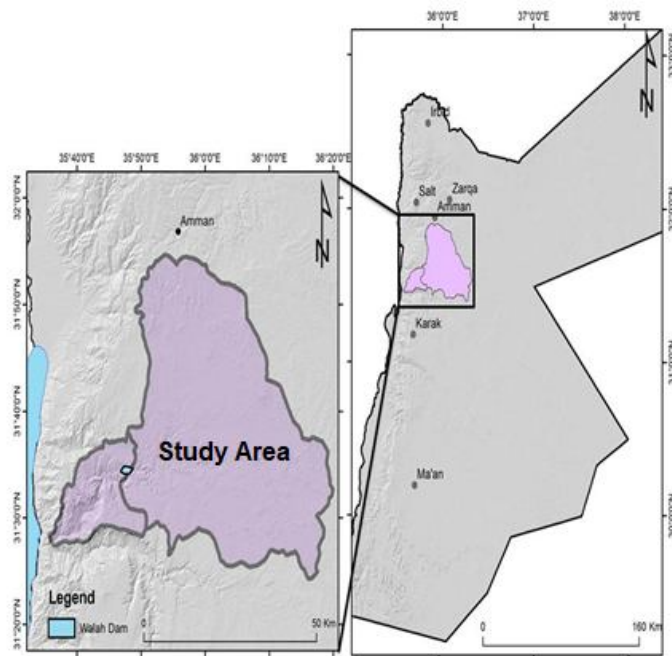


Fig.1: Location map of the study area

2.2 Geological Setting

The area study covered by upper cretaceous group Belqa and Ajlun (Fig.2). The groups are mainly dominated by cretaceous carbonate rocks that outcrop in most of the study area [12]. The oldest rock that outcrops in the study area is the upper Wadi as Sir Limestone (WSL) formation, deposited in an agitated marine environment, from the Turonian age. The lower part is composed of marl, marly limestone, coquina, Micrite, sand and dolomitic with Chert nodules that has an average thickness of 62 m. The upper part is composed of limestone, dolomitic limestone and fossiliferous limestone with an average thickness of about 4.5 m [12].

An abrupt change in sedimentation resulting from an extensive Coniacian marine transgression marks the base of Belqa group where a predominantly chalky unit of Wadi Umm Ghudran (WG) formation of Coniacian-Santonian age overlies Ajlun group. This formation consists of Mujib Chalk, brecciated dolomitic limestone, and Dhiban Chalk with fish teeth outcropping all over the basin area. The formations of Belqa group include Al Hisa Phosphorite formation (AHP), (Campanian age), which consists of dark grayish Chert, marly limestone and phosphate, and the Muwaqqar Chalk Marl formation (MCM) (Maastrichtian age), which consists of marl and chalk with chalky and micritic limestone concretions. Also it includes Madaba Calcareous Breccia (MCB) (Eocene age), which consists of brecciated and partly conglomeratic clasts of phosphate, limestone, chert and chalk in a mudstone matrix located on hills, slopes and along some Wadi in Madaba area.

The geology of the study area has some unique formations that include basaltic flows of Pleistocene, as volcanic tuffs restricted to the upper courses of Wadi Al Haidan. Quaternary Superficial Deposits (Pleistocene age) of Fluvial and Lacustrine Gravels (PI) cover most of

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the wades of the basin, particularly in the east. Aridic soils are dominating the lower rainfall zones, while dark brown Mediterranean soils are dominating the high rainfall zones.

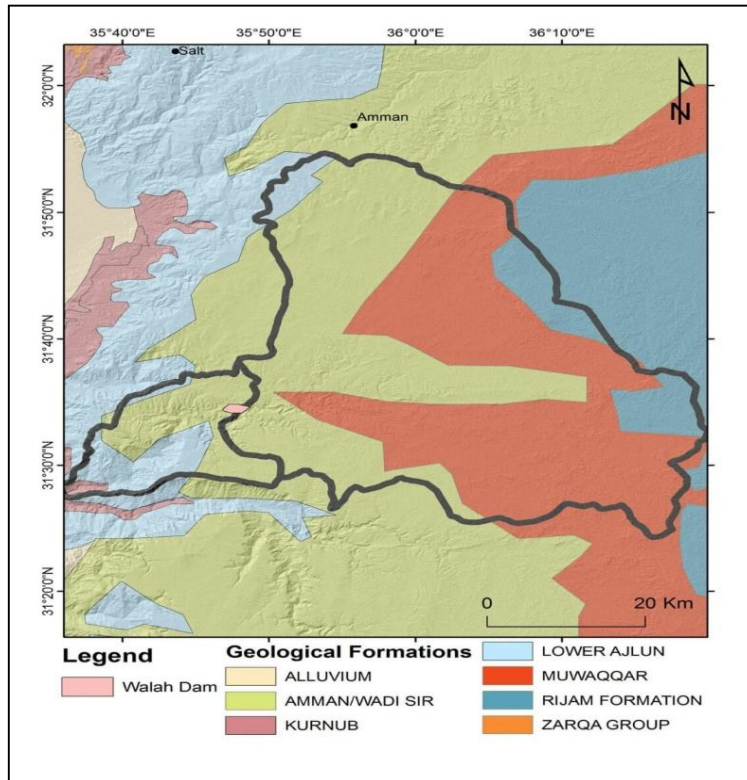


Fig. 2: Geological Map of the study area

3. Sampling and Analytical Techniques

Sixteen Stream sediment samples were collected along the main valley of Wadi Al Wala. Samples were collected at depths of 0-20 cm during. Samples were collected in a manner to cover the whole stream sediment in the study area (Fig. 3). Large stones and debris were first removed. Then, sediment samples were air-dried and put in stainless steel sieve to remove very large particles to have a homogenous sample. Afterward, samples were transferred to labeled, pre-washed, polyethylene bags to be transported to the laboratory for further sample preparation and analysis.

3.1 Extraction

The samples were prepared and delictdried in the oven at 55°C for 2 hours. All dried samples were sieved; particles <63 μm (0.05-mm) in size were chosen to be analyzed as this size is

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proven to be the best size for analysis for arid and semi-arid regions[13]. The extraction method is used in pollution studies to determine the heavy metal contents and the best extraction results were obtained with Ammonium-Acetate-EDTA Extraction. 20 gm. air-dry soil samples were placed in a 300 ml Erlenmeyer flask, with adding 100 ml extracting solution. Then, it was shaken mechanically for 30 minutes. After shaking, suspension materials were filtered and the filtrate was collected in a polyethylene flask.

3.2 Percentage of Carbonate

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To determine the carbonate (CO_3^{2-}) content of the sample study using titration method for [14]. The Sample preparation by using (2.5 gm.) from the powdered sample and then 100 ml of 1.N. of HCl were added to the sample while keeping the beaker undisturbed for about 20 minutes, after that, it was stirred with a glass rod. After 20 minutes, the solution was filtered and the clear solution was collected in a new beaker. After that Titration of the blank by using 20 ml of 1.N. HCl were taken by a pipette, and put it in conical volumetric flask, then, 4 or 5 drops of bromophenol blue indicator were added, and then, the solution turned to yellow color. At the end point of the titration, the color of the solution in the conical volumetric flask turned blue. At this step, the reading on the burette and the amount of NaOH used in the solution were recorded. This procedure was repeated for blank titration three times and the average blank value was calculated. Titration of the samples study, using 20 ml of the sample solution from the first step were taken and put it in the conical volumetric flask. Then, it was titrated with NaOH in the burette, with the addition of 4 or 5 drops of the bromophenol blue indicator.

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At the end point of the titration the color of the sample solution in the conical volumetric flask turned blue. At this step, the reading on the volumetric flask (burette) and the amount of NaOH used in the sample solution have been noted. This is the test of titration value. This procedure for sample solution titration repeated three times and the average test value was calculated.

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$$\text{Carbonate percent} = 10 * (\text{Blank value} - \text{Test value}) \dots\dots\dots \text{equation 1}$$

3.3 percent of Organic Matter (OM)

The percentage of organic matter (OM) were determine by using Ashing method (Lose On Ignition [15]. The Procedure is:

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- 1- Clean a dried crucible at 105°C for 2 hours have been weighted and labeled
- 2- 2g of sample placed in the crucible then sample and crucible weighted.
- 3- Crucibles placed with sample in muffle furnace at 500°C for two hours.
- 4- The crucible and samples are weighted after heating.
- 5- The amount of (OM) calculated by subtracted the weight in step (4) from the weight in step (2). Combustion at 550° C converts Organic Matter (OM) to CO_2 according to the reaction $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$.

$$\% \text{OM} = (\text{weight sample before Ashing} - \text{weight sample after Ashing}) / (\text{weight sample before Ashing}) * 100 \dots\dots\dots \text{equation 2}$$

All the sample study preparation in the Laboratory of the Faculty of Earth and Environmental Sciences. The heavy metals analysis was done using Atomic Absorption Spectrophotometer at Jordan University. The chemical analysis of the studied samples is listed in Table 1.

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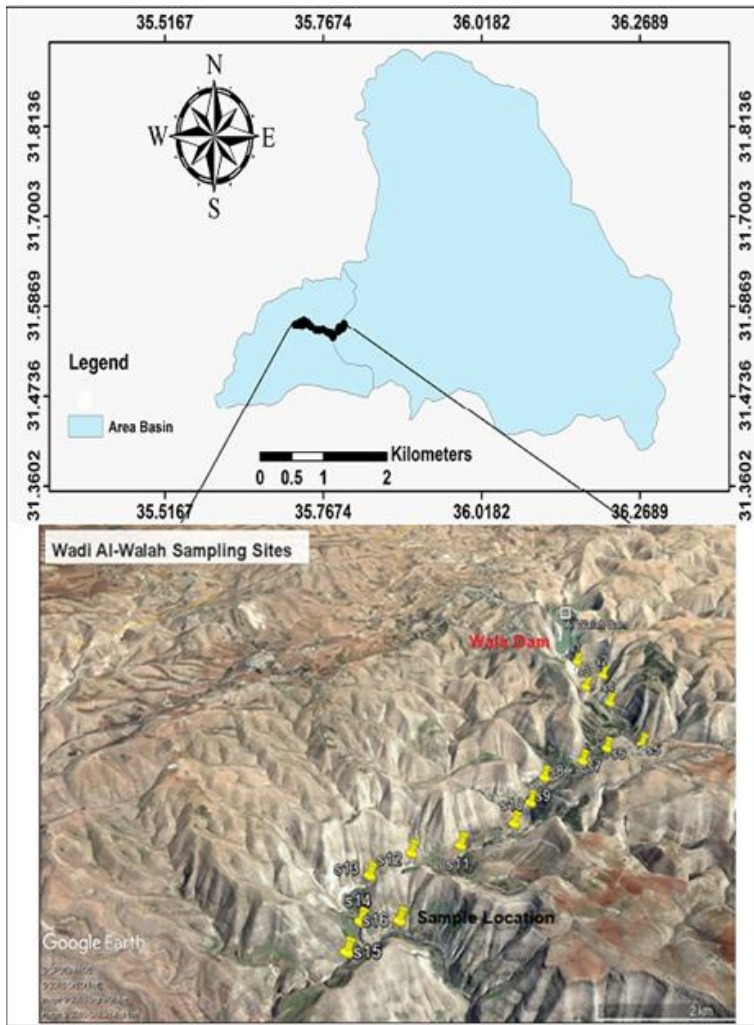


Fig. 3: sample location map

Table 1: Concentrations of Heavy Metals (Mg/l), CO₃ (WT%) and percent of organic matter (OM) for the Studied Samples

Sample No.	Mg/l						Wt %	%
	Cd	Fe	Zn	Cu	Pb	Mn	CO ₃	OM
1	0.404	7.25	4.092	0.744	0.203	12.592	50	0.541
2	0.446	7.35	1.248	0.087	0.291	15.768	60	0.806
3	0.833	3.05	3.194	0.211	0.459	22.142	20	0.612
4	0.606	8.147	9.316	0.2435	0.128	6.911	25	0.501
5	0.310	6.91	8.681	0.587	0.152	35.649	20	0.503
6	0.167	4.856	2.792	0.089	0.703	4.309	23	0.634
7	0.127	31.483	1.311	0.854	0.168	34.105	57	0.591
8	0.114	3.891	0.696	0.124	0.144	33.816	38	0.699
9	0.064	3.386	0.229	0.023	1.097	21.325	27	0.739
10	0.123	3.26	0.264	0.042	0.209	30.587	16	0.787
11	0.182	3.72	0.699	0.057	0.199	14.854	48	0.345
12	0.166	4.718	1.445	0.067	0.198	25.045	32	0.485
13	0.089	2.335	1.345	0.075	0.211	19.234	45	0.510
14	0.348	6.07	4.326	0.113	0.205	20.741	47	0.512
15	0.084	2.85	0.240	0.078	0.229	26.252	54	0.464
16	0.093	1.65	0.441	0.073	0.207	9.668	55	0.407
maximum	0.833	31.483	9.316	0.854	1.097	35.649	60	0.806
minimum	0.064	1.65	0.229	0.023	0.128	4.309	16	0.345
Average	0.260	6.308	2.520	0.217	0.300	20.812	38.563	0.571

4. Sediment Contamination Assessment

To determine the level of heavy metals contamination in the surface sediments samples for the study area, there is many calculation methods have been proposed. These method is Enrichment Factor (EF), Pollution load index and Geoaccumulation index (Igeo)[16,17]. The Enrichment factor (EF) was used to compare the metals originating from anthropogenic activities to those of natural origins, and to determine the degree of contamination and the possible anthropogenic impact on the sediments of Wadi Al-Wala area. The EF analysis was first presented by [18] to evaluate trace element concentration as follows in equation 3:

$$EF = (M/Fe) \text{ sample} / (M/Fe) \text{ background} \dots\dots\dots \text{equation 3}$$

Where, M/Fe sample is the ratio of metal and Fe concentration in the sample, M/Fe background is the ratio of metal and F concentration of a background (The geochemical normalization of heavy metal data was employed for conservative elements such as Fe, Al and Si. According to [19 and 20](2003), Fe was used to normalize heavy metal contaminants. In this study, Fe was used as a conservative tracer to differentiate natural components from anthropogenic ones. The

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background concentrations of the heavy metal study are taken from [21]. The classification of pollution degree based on the enrichment ratio methodology was divided into a five-category system [22]; If (EF < 2), this implies a depletion to minimal enrichment suggestive of no or minimal pollution. If EF is within the range of 2–5, this indicates a moderate enrichment, suggestive of a moderate pollution. If EF is within the range of 5–20, it means a significant enrichment, suggestive of a significant pollution. If EF is within the range of 20–40, it means a very high enrichment, indicative of a very strong pollution, and if (EF > 40), it means an extreme enrichment, indicative of an extreme pollution signal.

The pollution index (PI) and Pollution load index (PLI) were used to assess heavy metal pollution in the soil, sediments, and dust. The pollution index (PI) was defined by the following equation4:

$$PI = C_n / B_n \dots\dots\dots \text{equation4}$$

where C_n and B_n are the measured and background concentrations of metal n, respectively, in the surface sediment samples. PI is classified by [23] (as follows: PI ≤ 1 indicates a low level of pollution; 1 < PI ≤ 3 indicates a middle level of pollution, and PI > 3 a high level of pollution. The pollution Load Index (PLI) for each sample was calculated following the method by [24 and 25]. It was defined by the following equation5:

$$PLI = \sqrt[n]{CF_1 + CF_2 + CF_3 + \dots + CF_n} \dots\dots\dots \text{equation5}$$

Where; n is the number of metals (six in the present study) and CF is the contamination factor. The contamination factor (CF) can be calculated from the following relation: is calculated from the following relationship in equation 6:

$$CF = \frac{(C_n) \text{Concentration of the heavy metal in the soil sample}}{(B_n) \text{Background concentration of the same metal}} \dots\dots\dots \text{equation6}$$

where C_n is the measured concentration of a heavy metal in the surface sediments, and B_n is the background value. According to, [23, 26 and 27], the PLI value (PLI ≤ 1) indicates a low level of pollution, while 1 < PLI ≤ 2 indicates a middle level of pollution and PLI > 2 a high level pollution. Where; the background value is in average shale [21].

The Geoaccumulation index (I_{geo}) was used by [28 and 29] to assess heavy metal pollution. The I_{geo} was used to assess metal contamination in urban soils by comparing current and pre-industrial values [29, 30]. In this study, the geoaccumulation index (I_{geo}) was used to determine the extent of heavy metal pollution in Wadi Al-Wala surface sediments. The following equations are used in the calculation by equation 7 [31]:

$$I_{geo} = \log_2 (C_n / 1.5 B_n) \dots\dots\dots \text{equation7}$$

Where C_n is the concentration of the element 'n', and B_n is the geochemical background value of the element n, and 1.5 is the background matrix correction factor due to lithogenic effects. The geochemical background value in average shale is used to calculate I_{geo} [21]. The geoaccumulation index (I_{geo}) scale consists of seven grades from 0 to 6, ranging from unpolluted to highly polluted [31, 23]. The Geoaccumulation index value class designation of sediment quality is as follows:

- I_{geo} < 0 unpolluted environments
- 0 < I_{geo} ≤ 1 unpolluted-to-moderately polluted
- 1 < I_{geo} ≤ 2 moderately polluted
- 2 < I_{geo} ≤ 3 moderately-to-strongly polluted
- 3 < I_{geo} ≤ 4 strongly polluted
- 4 < I_{geo} ≤ 5 strongly to- extremely- polluted, and

Igeo >5 extremely polluted

5. Result and Discussion

5.1 Heavy Metal Distribution

The chemical concentrations of the heavy metals determined for the study sample are listed in Table 1. The variable concentration of heavy metal distributions along Wadi Al Wala area has shown in Fig.3. The high level of Cu, Mn, Pb, Cd, Cr and Ni was found along the Wadi Al-Wala.

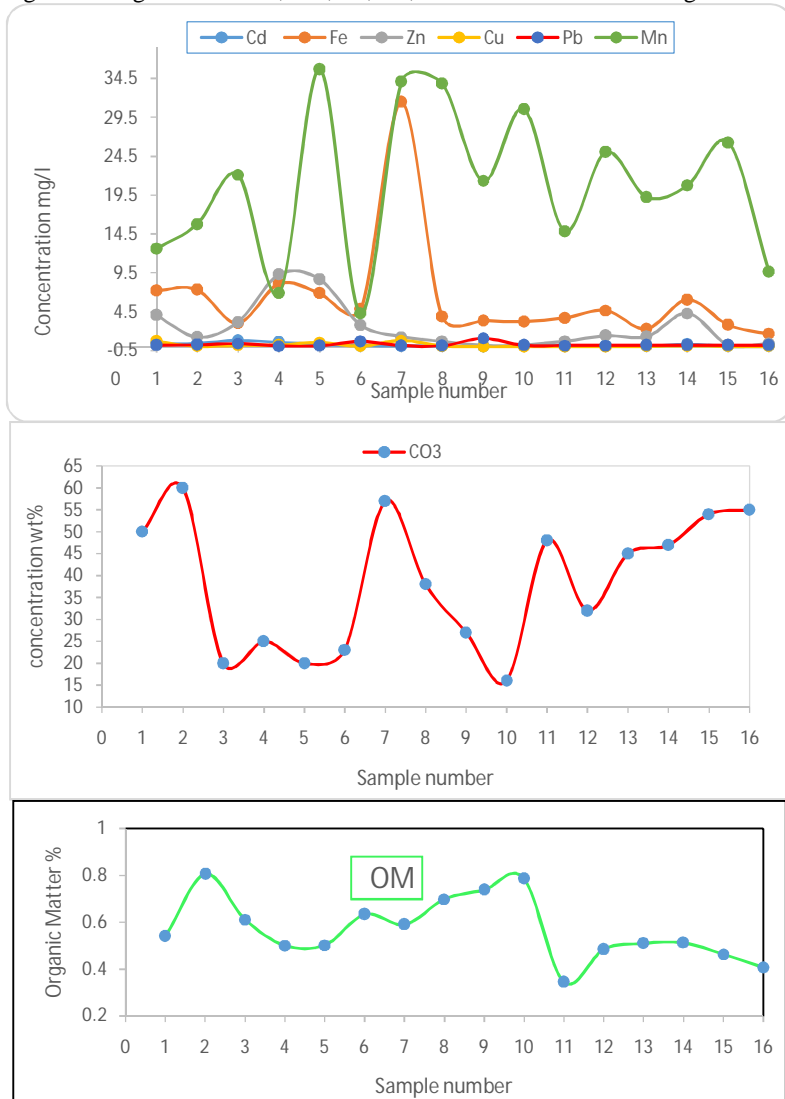


Fig.:3 Distribution of metal concentration (ppm) for Cd, Fe, Zn, Cu, Pb, and Mn and percentage of organic matter (OM%) and CaO wt% for the surfaces sediment samples from Wadi Al-Wala area.

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5.1.1 Statistical Analysis

The statistical correlation analysis can be used as a way to indicate correlation between any two variables to indicate the strength of relationship between these variables. High correlation between Fe with Cu ($r = 0.74$) and Cd with Zn ($r = 59$), Table 2, these result to the same main sources of this metals

Table 2: Correlation Matrix for the Heavy Metals of the Studied Samples

	Cd	Fe	Zn	Cu	Pb	Mn
Cd	1					
Fe	-0.015	1.000				
Zn	0.590	0.098	1.000			
Cu	0.194	0.741	0.414	1.000		
Pb	-0.095	-0.191	-0.237	-0.288	1.000	
Mn	-0.241	0.302	-0.137	0.268	-0.231	1

5.1.2 Enrichment Factor (EF)

The results of EF in Table 3, indicate that high concentrations of Zn and Cd are present in the analyzed samples Fig. 4. This may result with risky pollution in Zn and Cd considering that the value for extreme pollution according to EF is >40 . These heavy metals can be derived from anthropogenic source, such as; fertilizers and pesticides used in agricultural activities. The fluctuation in EF values can be accredited to the changes in the amount of contribution for each metal in the sediments or to the variance in the removal rate of each metal from the sediments. Th high percent of the EF for Cd and Zn in the samples 3, 4 and 5 reflections to the main sources in the along the stream for the agricultural activity and traffic emissions which include: exhaust emissions, brake wear, car body wear, and road surface wear cross in study area[32, 33].

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Table 3: Enrichment Factor (EF) of the heavy metal samples study

Enrichment Factor (EF)					
Sample	(Cd)	(Zn)	(Cu)	(Pb)	(Mn)
1	26.521	277.434	0.192	0.065	9.891
c2	28.884	83.468	0.022	0.093	12.218
3	130.101	514.788	0.129	0.352	41.345
4	35.458	562.115	56.000	0.037	4.831
5	21.358	617.568	0.159	0.051	29.381
6	16.338	282.626	0.034	0.338	5.053
7	1.925	20.470	0.051	0.012	6.169
8	13.902	87.879	0.060	0.086	49.502
9	9.008	33.250	0.013	0.756	35.872
10	18.023	39.794	0.024	0.150	53.435
11	23.250	92.356	0.029	0.125	22.741
12	16.746	150.506	0.027	0.098	30.232
13	18.122	283.158	0.060	0.211	46.912
14	27.312	350.341	0.035	0.079	19.460
15	14.045	41.396	0.051	0.188	52.459
16	26.743	131.326	0.083	0.293	33.370
Maximum	12.604	617.568	56.000	0.756	53.435
Minimum	18.484	20.470	0.013	0.012	4.831
Average	19.607	223.030	3.560	0.183	28.304

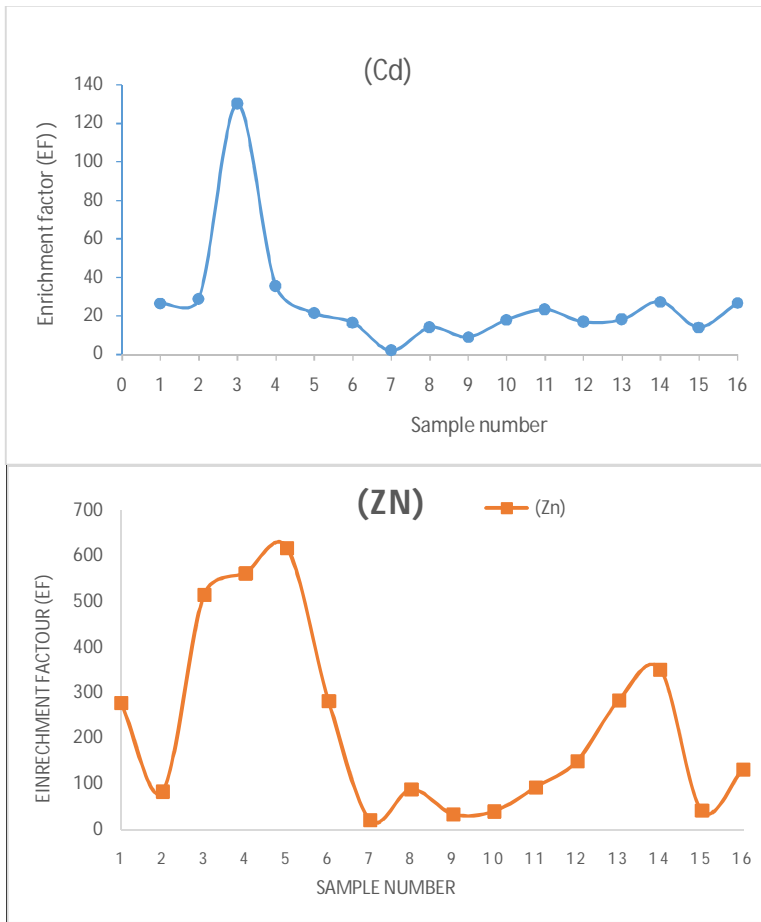


Fig. 4: The Enrichment Factor (EF) distribution for Cd and Zn of the study samples

5.1.3 Geoaccumulation Index (Igeo)

The Igeo result and distribution in the study samples are shown in Table 4 and Fig. 5. The percent of Igeo differ according to the type of metal and its location. Fe, Pb and Cu remain in grade < 0 (unpolluted) in all stations suggesting that the study area sediments are in background value with respect to this metal. While, Mn, Zn and Cd are in the range of moderately to strongly polluted; depending on the location of the sample and the contributors in elements concentrations. The highest Igeo grade was attributed to Zn as it exceeds 5 in some places showing that the sediment samples are extremely polluted due to industrial waste and gasoline additives used in industries and automobiles [34]. This suggests that the sediments of Wadi Al Wala are having background concentrations for Mn, Cd, and Zn; these elements are practically unchanged by anthropogenic influences. These dangerous metals can be derived from industrial waste and gasoline additives used in industries and automobiles [33 and 34]. In addition, they might be derived from corrosion agricultural activities in the Wadi and traffic and industrial

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activities, in addition to anthropogenic effects such as excavated construction materials and randomly dumping of the wastes [35, 36, and 37].

Table 4: The Igeo values of the heavy metal for the study samples.

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Geoaccumulation Index (Igo)						
sample	Cd	Zn	Cu	Pb	Fe	Mn
1	1.457	4.844	-5.65544	-7.205	-3.272	0.034
2	1.600	3.131	-8.75166	-6.687	-3.253	0.358
3	2.502	4.486	-7.4735	-6.029	-4.522	0.848
4	2.044	6.031	-7.26683	-7.878	-3.104	-0.832
5	1.075	5.929	-5.99739	-7.623	-3.342	1.535
6	0.180	4.292	-8.71887	-5.416	-3.850	-1.513
7	-0.209	3.202	-5.45651	-7.480	-1.154	1.471
8	-0.373	2.287	-8.24041	-7.703	-4.170	1.459
9	-1.200	0.684	-10.671	-4.774	-4.371	0.794
10	-0.254	0.889	-9.80229	-7.165	-4.425	1.314
11	0.304	2.294	-9.36171	-7.236	-4.235	0.272
12	0.174	3.342	-9.12851	-7.243	-3.892	1.026
13	-0.727	3.239	-8.96578	-7.152	-4.907	0.645
14	1.243	4.924	-8.37442	-7.193	-3.529	0.754
15	-0.807	0.752	-8.9092	-7.033	-4.619	1.094
16	-0.667	1.629	-9.00478	-7.179	-5.408	-0.347
maximum	2.502	6.031	-5.457	-4.774	-1.154	1.535
Minimum	-1.200	0.684	-10.671	-7.878	-5.408	-1.513
Average	0.820	3.247	-8.236	-6.937	-3.878	0.557

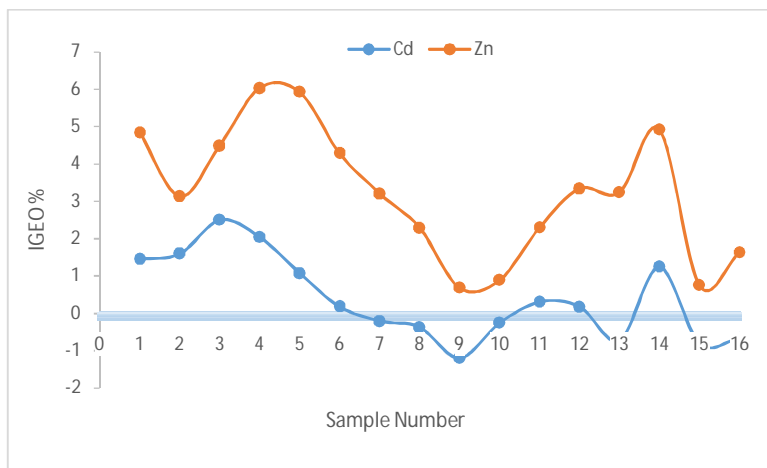


Figure 5: The Igeo Values Distribution for the Heavy Metals for the Studied Samples

5.1.4 Pollution Load Index (PLI)

Pollution severity and disparity in the study area were determined by applying pollution load index method. This index is a tool to compare the pollution grade in different places [35]. The contamination factor (CF) can be calculated from the following relation:

(CF) = Metal concentration in the sediments /Background value of the metal; (6) number of toxic metal for the samples study. Where; background value is in average shale [21]. The PLI value of > 1 is polluted, whereas, < 1 indicates no pollution [26].

The study results in Table 5, indicate that CF values of all metals such as Fe, Cu, and Pb are low (<1). Indices fluctuation is a result of various indices' sensitivity towards sediment pollutants [38]. PLI results indicate that there are no pollution threats in the study area as low indices reported[37].

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Table 5: PLI values (CF) of the heavy metal for the study samples.

Sample No.	Cd	Fe	Zn	Cu	Pb	Mn	Pl
1	4.117	0.155	43.071	0.030	0.010	1.536	0.012789
2	4.546	0.157	13.137	0.003	0.015	1.923	0.000916
3	8.497	0.065	33.621	0.008	0.023	2.700	0.009765
4	6.186	0.174	98.063	0.010	0.006	0.843	0.005538
5	3.160	0.148	91.379	0.023	0.008	4.347	0.033192
6	1.699	0.104	29.389	0.004	0.035	0.525	0.000341
7	1.298	0.674	13.800	0.034	0.008	4.159	0.014411
8	1.158	0.083	7.321	0.005	0.007	4.124	0.000104
9	0.653	0.072	2.411	0.001	0.055	2.601	0.000015
10	1.258	0.070	2.778	0.002	0.010	3.730	0.000016
11	1.852	0.080	7.357	0.002	0.010	1.811	0.000045
12	1.692	0.101	15.205	0.003	0.010	3.054	0.000211
13	0.906	0.050	14.158	0.003	0.011	2.346	0.000048
14	3.550	0.130	45.537	0.005	0.010	2.529	0.002462
15	0.857	0.061	2.526	0.003	0.011	3.201	0.000015
16	0.945	0.035	4.640	0.003	0.010	1.179	0.000006
maximum	8.497	0.674	98.063	0.034	0.055	4.347	0.033192
Minimum	0.653	0.035	2.411	0.001	0.006	0.525	0.000006
average	2.648	0.135	26.525	0.009	0.015	2.538	0.004992

6. Conclusions

Wadi Al-Wala sediments contamination assessment was carried out using the pollution indicators; enrichment factor (EF), pollution load index (PLI), and geo-accumulation index (Igeo). Correlation coefficients analysis of concentrations among TOM, CO, Cu, Zn, Cd, Mn, Fe, and Pb was also applied showing that there are varying correlations among them indicating complex geochemical behaviors. The following conclusion for the study result:

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- The Igeo analyses of Wadi Al-Wala sediments proved that concentrations of Mn, Cu, Pb, and Fe are safe and these elements are practically unchanged by anthropogenic influences, while the concentration of Zn and Cd exceeded the average value. The elevated concentrations of Cd and Zn can be due to anthropogenic sources, such as phosphate fertilizers and pesticides used in agricultural lands in the Wadi and agricultural use of sewage sludge and seepage of domestic wastewater from cesspits in nearby villages to the Wadi and natural weathering of surrounding geological formations [39 and 40].
- The PLI analysis proved that Wadi Al-Wala is moving towards a probable environmental pollution with regard to heavy metals (Zn and Cd) if experts did not control these external sources.

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- EF showed high concentrations of Zn, Cu and Cd in the study area; the concentration of Cd increased in some samples due the use of cadmium-containing raw phosphate to prepare fertilizers which used on the frames within studied area and watering of livestock at the Wadi and seepage of domestic wastewater from cesspits in nearby villages to the Wadi and alzibar put material up through the valleys and the increasing number of farmers in the Wadi Al Wala and the use of organic materials.

- The current study confirmed that long-term use of phosphate fertilizer that contains a high level of Cd may lead to accumulation of Cd in the soil, and this may eventually increase plant Cd uptake [29].

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- The soil characteristics, such as Clay content of the soil organic matter and calcium carbonate and degrees of salinity and acidity with a key role on the content of the soil from cadmium [41]. Natural weathering of surrounding rock formations can act as another source of heavy metals in the sediments, increase the proportion of lime in the soil with a high temperature help to increase the adsorption cadmium in calcareous soils [42 and 43].

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- The chief pollution sources of Zn and Cu in some samples are agricultural use of sewage sludge and the use of agro-chemicals such as phosphate fertilizers and pesticides, Furthermore. The proliferation of septic tanks in residential communities bordering put him in addition to its cargo tanks seepage in the neighboring valleys.

- The variation of Mn concentration in the study area was due to irrigation of land by industrial wastewater and other agronomic practices and high value of organic matter. The major anthropogenic sources (human activity) include the release of heavy metals into the atmosphere through the burning of fossil fuels or other industrial activities and thereafter into the streams through rainfall and of the release of industrial effluents and sewage water into streams and surface-water bodies [44, 45 and 46]. The sources of Mn include municipal wastewater discharges, sewage sludge, industries in the jiza area oil shale mines and processing plants.

Comment [DSS51]: ?

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