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The Interactions of Bioactive Heavy Metals between *Avicennia marina* (Forsk.) Vierh. and the Underlying Sediments in the Mangrove Swamps, Red Sea, Egypt

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Abstract Mangrove swamps have unique biogeochemical interaction between the plant and the underlying sediments. The bioactive heavy metals; Zn, Cu, Fe, Mn, Pb, Ni, Cd and Co were measured using Atomic Absorption Spectrophotometer (AAS) in the bulk sediment samples and the fine fractions; 125µ, 63µ and <63µ and slack water as well as different parts of the *Avicennia marina* mangrove (fruits, leaves and roots) collected from 9 mangrove swamps at the nearshore zone of the Red Sea. The average percentage of the fine sediment group (125µ + 63µ + <63µ) was varied between 18.78% and 51.22% from the total sediments with recognized occurrences for the fractions 125µ and 63µ. The bulk sediments recorded the highest averages of the bioactive Zn (69.91µg/g), Mn (186.91µg/g) and Ni (19.49µg/g), the fraction 125µ recorded the highest average of Pb (16.92 µg/g), while <63µ fraction showed the highest averages of Cu and Fe (26.45 and 2744.84µg/g). In the mangrove stands, the highest averages of Zn and Cu were recorded in fruits (Avs. ≈116.41 and 15.20 µg/g), Mn in leaves (Av. ≈ 43.72 µg/g) and the highest Pb was recorded in roots (Av. ≈ 30.14 µg/g). The bio-accumulation sequence of heavy metals in the fruits and roots was Fe>Zn>Pb>Cu>Mn>Ni and in leaves was Fe>Zn>Mn>Pb>Cu>Ni. The low contents heavy metals recorded in the slack water of the mangrove swamps attributed to the reducing nature of the underlying sediments that accumulate the heavy metals in insoluble sulphide forms. The effects of the elevated metal contents in the fruits, leaves and the roots of *A. marina* were at the studied forests were reflected in the ramified and shorten roots, pale yellowish colour and reduction the leaves number in many of the mangrove stands.

Keywords bioactive, *Avicennia marina,* Red Sea, mangrove sediments, bio-geochemical cycle

Introduction

Mangroves environment is considered as important intertidal estuarine wetlands of tropical and subtropical coasts [1]. Mangrove trees have very high capability to survive and tolerate the hypersaline and anoxic conditions as well as the different stressful pollutants as heavy metal and hydrocarbons [2]. Because of their rooting systems (pneumatephores), mangroves help in shore protection against erosion and even encourage seaward buildup of sediments [3-4]. Also, they act as a barrier for the anthropogenic pollutants dispersion into the aquatic environment [5]. Mangrove ecosystems are highly productive and play a vital role as a major primary producer within estuarine systems. Harbison [6] indicated that mangrove systems are physical traps for fine material and their transported load of metals, they also constitute a chemical trap for precipitation of metals from solution. They added, due to their inherent physical and chemical properties, mangrove mud have an extraordinary capacity to accumulate materials discharged to the near shore marine environment. The uniqueness of *A. marina* root system serves as habitat and nursery area for many juvenile fish and crustaceans, which have both direct and indirect socio-economic importance and are of great importance to many scientific studies. This root system also provides erosion mitigation and stabilization for adjacent coastal landforms [7].

Surface sediment is the most important reservoir or sink of heavy metals and other pollutants in the aquatic environments. The heavy metals released into aquatic systems are generally bound to particulate matter, which eventually settle down and become incorporated into sediments. These sediments bound metals can be taken up by rooted aquatic macrophytes and other aquatic organisms [8]. In a plant-soil system, strong absorption and fixation of heavy metals by soil can easily cause residual accumulation in the soil, resulting in over-absorption of heavy metals by the growing plants [9-10]. The uptake of heavy metals by plants are passive, and its translocation from roots to other plant organs is generally low [11-12]. Mangrove sediments are considered long-term heavy metal pollutants due to the great ability of these metals to accumulate in the organic rich sediments with high concentration of sulfide compounds [13]. Consequently; mangrove ecosystems are probably efficient biogeochemical barriers for the heavy metals transportation in the tropical coastal areas, hence mangrove trees can be used in the management of metal pollution in these areas [14]. However mangrove plants especially (*A. marina*) are known to be tolerant to metal stress due to their growth in inhospitable environment. Litter fall is an important factor in the cycling of trace metals in the mangrove ecosystem. Through litter fall, heavy metals are transferred from plant to sediments, incorporated into organic matter and eventually released by litter decomposition [14].

Mangrove forests in Egypt are estimated to cover about 525 ha [15] comprise two main species: *Avicennia marina* and *Rhizophora mucronata*. *Avicennia marina* is growing up as shrubs and small forests dispersed along the Red Sea Coast extending from Nabq in the western coast of Aqaba Gulf to Mersa Halaib near in the Egyptian-Sudanese borders [16], while *Rhizophora mucronata* occupies small forests in the nearshore zone of the Red Sea south of Egypt. Despite their limited occurrences, mangrove forests have the greatest ecological and environmental importance for the existence and maintenance of fish nurseries, shoreline protection, refuge for wildlife including birds and other livestock, sediment stabilization as well as they provide forage for camels and used as a source for firewood [17].

This current work aims to study the differential ability of fruits, leaves and roots of the mangrove species *Avicennia marina* to accumulate heavy metals and the effects of the elevated metals on mangrove status at the studied forests as well as to investigate the bio-geochemical cycle and extents of heavy metals in the underlying sediments of mangrove swamps.

2. Materials and Methods

2.1. Geomorphic settings of the studied localities

The studied mangrove swamps were located in the nearshore zone of the Red Sea (Fig. 1). They varied between mangrove shrubs (Um Dehais), small forests (Km 17 S. Safaga, Sharm Elbahari, Wadi El Gemal and Qula'an) to complete forests (Abu Minqar Island, Wadi Abu Hamra, Hamata and Wadi Lehmi). All of them are considered uni-species communities consist of *A. marina* plant. Most of the studied mangrove communities were separated from the direct effects of tides and waves by sand bars that forming isolated swamps with slack water nature. The mangrove stands at the studied forests were varied between dispersed mangrove shrubs with a height of about 0.5m to dense and high stands with average height reaching about 8m. The underlying sediments of the studied mangrove swamps were varied in thickness between few centimeters at some places to more than two meters at the others. They formed from a mixture of terrestrial and biogenic origin with different size grades. Some of the studied forest were located close to the urban activities and may expose to many anthropogenic and natural stresses as; land-filling, hydrocarbons, domestic sewage, brine water of desalination (Um Dehais, Abu Minqar Island and Km 17 S. Safaga) and the natural terrestrial runoff (Wadi Abu Hamra, Sharm Elbahari, Wadi El Gemal, Qula'an, Hamata and Wadi Lehmi). Some locations suffer from intensive sediment erosion due to the exposing to high wave action and the mangrove trees were invaded the coral reef terraces as (Km 17 S. Safaga and Wadi El Gemal). The maps of studied locations were drowning using Golden Software Surfer Ver. 10 depending upon GPS (Magellan Model) then converted to TIFF format.

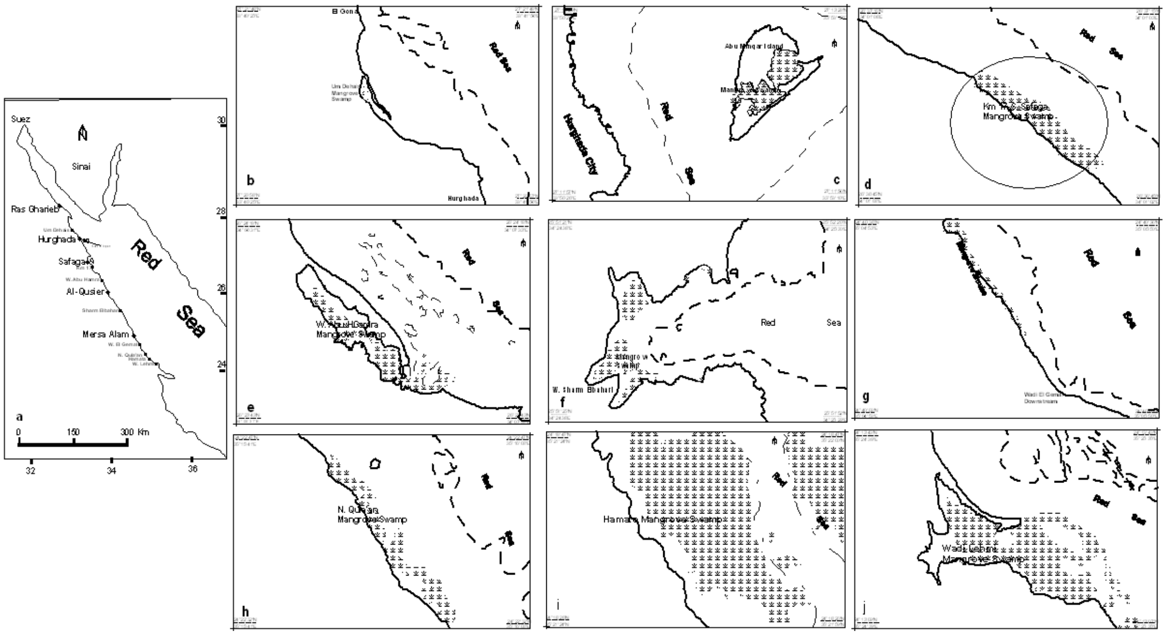


Figure 1: Location map for the studied mangrove swamps along the Red Sea

2.2. Sampling and Laboratory Analyses

A total of 135 of fruits, leaves and mangrove roots samples were collected from the different mangrove stands (45 samples of each part), 54 sediment samples represent the uppermost part (0-20cm) of the mangrove sediments and 44 of slack water samples were collected from the selected mangrove swamps (Fig 1). In the laboratory, fruits, leaves and roots samples of the mangrove were air dried then grinded in the homogenizer to reach the homogenized powder form.

The sediment samples were air-dried, disaggregated then sieved through a stainless steel mesh to differentiate the particle-size fractions. The grain-size analyses of these samples were performed using dry method depending upon Wentworth scale [18], subsequently, seven fractions were obtained; gravel (<2000µ), v. coarse sand (1000:2000µ), coarse sand (500:1000µ), medium sand (500µ to 250µ), fine sand (125µ), v. fine sand (63µ) and mud (<63µ). These fractions were categorized in three groups; coarse group (<2000µ to 1000µ), medium group (<1000 to 250µ) and the fine group that includes; 125µ, 63µ to <63µ. To study the interactions between the mangrove plants and the underlying sediments; the fine sediment group (125µ, 63µ and <63µ) as well as the bulk samples were intended for the geochemical analyses to determine the bioactive heavy metal contents. 1-3grams of each fraction if provided and 1-3grams bulk samples were powdered using agate mortar to less than 80mesh.

To measure Fe, Mn, Cu, Pb, Co, Zn, Ni and Cd contents in the fruits, leaves and roots of *A. marina* mangrove as well as the bioactive forms in the bulk sediment samples and the fine fractions (125µ, 63µ and <63µ); 0.5g of each pre-prepared samples was digested with a mixture of HNO_3 and $HClO_3$ to near dryness then diluted with DDW to 25ml [19]. The bioactive heavy metal forms were determined in these extracts using flame Atomic Absorption Spectrophotometer (AAS, GBC-932) at the laboratory of the National Institute of Oceanography and Fisheries (NIOF), Red Sea Branch. To insure that the maximum accuracies were obtained, three replicates of each measurement were applied and differences among these replicates were always less than 3%. The obtained data were expressed in (µg/g).

The heavy elements contents in the slack water of the mangrove swamps were determined in (mg/l) using AAS technique according to Martin (1972). One liter of each sample was filtered through 0.45µ membrane and adjusts the pH in the range 4-5 with HCl. The heavy metals of each sample were catch within ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) complex and then extracted using 6N HNO_3 acid. The extracted solution of each sample was evaporated on hot plate to near dryness then solved in about 10 ml of de-ionized water.

2.3. Statistical analyses

Correlation coefficient relationships and the uncertainties between the studied metals in the mangrove parts and within the different sediment fractions were estimated using Excel 2007 and illustrated in figures using WinGraph Prism Ver. 6.0.

3. Results and Discussion

3.1. Mangrove sediment characteristics

The mangrove swamps function as pump for the fine sediments from the coastal waters to the mangrove swamps. The mechanism of the pumping process depends on the high turbulence generated by the mangrove roots at the time that the water enters into the forest at the flood tide, keeping the fine sediments in suspension. Sedimentation process occurs during the period of near slack high tide when the turbulence vanishes [20]. At the studied mangrove swamps, the fine fractions group (125µ + 63µ + <63µ) was deposited under these slack conditions by the same pumping mechanism. This group formed the essential constituents of the surface layer with strong representation at the different swamps. Its average percentage was fluctuated between 18.78% and 51.22% (Fig 2a). The fractions 125µ and 63µ formed the main constituents of the fine sediment group; the average percentage of 125µ was varied from 9.65% to 25.69% however, the average percentage of 63µ fraction was fluctuated between 1.40% and 25.19%. The finest fraction (<63µ) recorded the lowest percentages at the studied mangrove swamps; it varied between 0.23% and 12.97%. Wadi El Gemal swamp recorded the highest occurrence of the fine group sediment with variation between 33.20% and 80.93%, while, Wadi Lehmi swamp recorded the lowest occurrence between 15.04% and 25.02% (Fig 2b). The significant occurrences of this group at the studied swamps are very effective in the geochemical cycle of the heavy metals and the accumulations forms in the sediment layer. Because of the fine sediments can easily pumped for long distances and re-deposited in the calm zones [21], the selected fractions have reached to the mangrove swamps from the highly turbulence areas by the wave action, drag currents and may be due to the flash floods. Consequently, the fine grained suspended matters are the most important medium for transporting metals and may be deposited to form contaminant sinks [22]. The deposit of fine sediments with high organic matter content produces anoxic environment with abundant sulfate with tend to become sulphides [23]. Sediment-bound pollutants can be taken up by rooted aquatic macrophytes and other aquatic organisms [8]. The continuous accumulation of suspended materials with high heavy metal contents in the substrates of the mangrove stands may retard the plant ability to produce new generations and aerobic roots of the mangrove (pneumatophores) or to replace the lost parts.

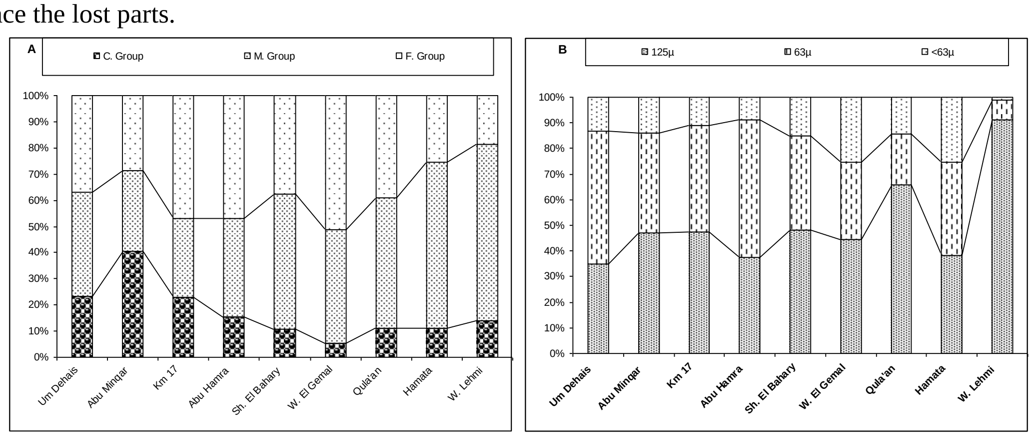


Figure 2: The distribution percentages of the fine sediment group (A), and the percentage variations between the fine fractions relative to each other (B) at the studied mangrove swamps

3.2. Heavy metals accumulation in the mangrove sediments

As shown in table (1), the bioactive average of Zn in the bulk samples was varied between 14.49 and 182.43µg/g, Cu between 5.66 and 39.28µg/g, Fe from 1925.05 to 3594.78µg/g, Mn from 39.33 to 568.20µg/g, Pb, Cd and Co were varied from below the detection limits to 8.68, 11.34 and 8.33µg/g respectively, while Ni was fluctuated between 6.30 and 48.93µg/g. Hamata mangrove swamp recorded the highest bioactive averages of Zn and Fe, Sharm Elbahari swamp recorded the highest averages of; Mn, Co and Ni, Um Dehais swamp recorded the highest average of Pb, Wadi El Gemal swamp showed the highest Cu average, while Abu Minqar Island showed the highest average of Cd. In the fraction 125µ, the average of Zn was changed from 21.15 to 81.53µg/g, Cu from 10.57 to 30.37µg/g, Fe between 1644.38 and 2672.68µg/g, Mn between 37.40 and 197.77µg/g, Cd from <1.00 µg/g, Co from below the detection limit to 3.35 µg/g and bioactive average of Ni was varied between 6.77 and 14.66µg/g. Um Dehais swamp recorded the highest averages of Fe, Mn and Co, Hamata swamp recorded the highest average of; Zn and Pb, Abu Hamra swamp showed the highest average of Cu, Sharm Elbahari swamp recorded the highest average of Ni and Abu Minqar Island recorded the highest Cd average.

In the fraction 63µ, bioactive Zn was varied between 17.78 and 55.98µg/g, Cu from 11.37 to 16.23µg/g, Fe between 1874.58 and 2878.35µg/g, Mn was varied between 28.50 and 196.63µg/g, Pb from 2.78 to 15.88µg/g, Cd and Co were changed between <1.00 µg/g to 1.3 and 3.35 µg/g respectively. Ni was changed from 7.23 to 15.03µg/g. The highest averages of; Fe, Mn, Co, Pb and Ni were measured at Sharm Elbahari swamp**,** Zn at Hamata swamp**,** Cu at Wadi El Gemal swamp and Cd at Abu Minqar Island. In the finest fraction <63µ**,** Zn was fluctuated between 25.88 and 89.93µg/g, Cu between 6.90 and 68.25µg/g, Fe from 1813.58 to 5419.07µg/g and Mn was varied between 46.17 and 237.40µg/g. Pb shows the changing from 2.80 to 19.75µg/g, while Cd and Co were changed from <1.00µg/g to 3.73 and 3.18 µg/g respectively. The bioactive Ni was varied between 8.33 and 18.25µg/g (Table 2).Um Dehais swamp recorded the highest averages of**;** Fe, Mn and Co, the highest averages of Zn and Pb recorded at Hamata**,** Cu at Abu Hamra swamp**,** Cd at Abu Minqar Island and the highest average of Ni was recorded at Sharm Elbahari swamp. The highest average of Zn, Mn and Ni (69.91, 186.91 and 19.49 µg/g respectively) were recorded in the bulk sediment, Pb in the fraction 125µ (16.92 µg/g), while the highest averages of Cu and Fe (26.45 and 2744.82 µg/g) were observed in fraction <63µ.

Mangrove sediments provide a sink for trace metals because the mangroves create a baffle that promotes the accumulation of fine-grained organic matter-rich sediment, which is usually sulphidic due to the presence of sulphate-reducing bacteria. Direct adsorption, complexing with organic matter, and the formation of insoluble sulphides all contribute to the trapping of metals [5, 24-25] and the subsequent oxidation of sulphides between tides allows metal mobilization and bioavailability [24]. The measured high concentrations of Fe in the mangrove sediments might be due to the precipitation of iron as iron sulphides which are common in mangrove ecosystems [26]. These sulphides form a major sink for heavy metals in the mangrove area. Within anoxic conditions, Fe and Mn were precipitated as carbonates [27]. Kehrig *et al.*, [28] pointed out that 87% of the concentrations of Pb, Fe, Cd and Cu were determined not to be bioactive due to the elevated organic carbon and sulphide contents in sediments. In oxidized conditions prevalence; Mn is remained in solid forms, which is retained in the sedimentary column. An oxidized rhizosphere within the anoxic soil environment may confer a reduction in complexing sulphides, a lowered stability of iron plaques, resulting in higher concentrations in the exchangeable form for some trace metals [11, 29]. MacFarlane *et al.*, [30] pointed out that the increasing concentrations of Pb and Zn in sediments resulted in a greater accumulation of Pb to both root and leaf tissues. They were attributed the increasing concentrations of Pb and Zn in sediments to both root and leaf tissues litters. The heavy metals enrichment in mangrove sediments may be caused by their strong soluble complexes with reduced sulphur [31] that increases the migration of these metals from sediments to the mangrove stands.

The accumulations of heavy metals follow the order of; Fe>Mn>Zn>Ni>Cu>Pb in the bulk sediments, Fe>Mn>Zn>Pb≥Ni≥Cu in 125µ fraction, Fe>Mn>Zn>Pb≥Cu≥Ni in 63µ and follows the sequence; Fe>Mn>Zn>Pb>Cu>Ni in the fraction <63µ. Che [32] and Defew *et al.*, [33] found that the heavy metals in the mangrove sediments follow the trend of; Fe>Zn>Pb>Ni>Cu>Cd. Cuong *et al.*, [34] reported that heavy metals were decreased in the order Zn>Pb>Ni>Cu>Cd in the underlying sediments at S. Buloh, while S. Khatib Bongsu had the same order for Zn, Cr, Cd and a different order for the remaining metals (Cu>Pb>Ni). Che [32] reported that the mean metal concentrations in mangrove sediments decreased in the order Fe>Zn>Pb>Ni>Cu>Cd.

Table 1: The average contents of heavy metals in the bulk sediments and the fine fractions; 125µ, 63µ and <63µ (values in µg/g) at the different mangrove swamps:

Swamp Name		Zn	Cu	Fe	Mn	Pb	Cd	Co	Ni
Um Dehais		18.73	6.57	2238.41	122.34	8.68	0.54	1.88	9.05
Abu Minqar		22.54	15.08	1969.16	39.33	5.88	11.34	1.83	12.91
Km 17		14.49	5.66	1925.05	53.63	4.00	0.59	ND	8.34
W. Abu Hamra		26.38	7.43	2360.06	91.04	5.77	0.48	2.24	14.16
Sh. Elbahari	**Bulk**	79.50	12.17	3531.63	568.20	3.35	0.15	8.33	48.93
W. El Gemal		36.85	39.28	2955.62	236.03	7.67	ND	ND	6.88
N. Qula'an		143.02	15.40	3052.48	234.80	0.00	ND	ND	22.55
Hamata		182.43	26.47	3594.78	265.73	0.35	ND	ND	46.32
W. Lehmi		105.27	12.32	2679.05	71.05	0.00	ND	ND	6.30
Av.		69.91	15.60	2700.69	186.91	3.97	2.62	3.57	19.49
Um Dehais		30.04	19.30	2468.57	163.31	6.05	0.28	2.84	9.95
Abu Minqar		23.47	13.63	2313.00	46.22	3.58	0.90	0.48	11.28
Km 17		21.15	19.31	2171.13	72.94	2.53	0.38	1.05	10.08
W. Abu Hamra		34.20	25.57	2432.97	104.20	30.44	2.41	3.35	14.66
Sh. Elbahari	**125µ**	51.93	30.37	2536.30	150.37	17.68	0.78	0.00	11.25
W. El Gemal		29.48	10.57	1934.78	33.80	14.75	0.97	ND	6.77
N. Qula'an		55.07	20.33	2672.68	197.77	20.02	0.77	ND	9.60
Hamata		81.53	18.88	2048.78	51.65	54.20	0.35	2.40	10.28
W. Lehmi		33.77	15.25	1644.38	37.40	3.05	0.35	0.65	9.32
Av.		40.07	19.24	2246.95	95.29	16.92	0.80	1.54	10.35
Um Dehais		21.66	11.72	2240.84	113.44	8.90	0.53	2.25	7.88
Abu Minqar		17.78	14.50	1943.52	28.50	6.25	1.30	1.38	9.31
Km 17		20.15	11.60	1889.89	51.29	2.78	0.22	2.70	7.23
W. Abu Hamra		28.83	15.03	2386.35	88.66	12.36	1.18	2.68	12.33
Sh. Elbahari	**63µ**	48.72	14.93	2878.35	196.63	15.88	0.98	3.35	15.03
W. El Gemal		45.82	16.23	2759.60	125.98	13.05	0.67	ND	7.83
N. Qula'an		51.37	12.90	2532.27	192.30	5.92	0.48	ND	15.00
Hamata		55.98	13.58	2188.07	63.28	28.10	0.90	1.50	12.52
W. Lehmi		30.75	11.37	1874.58	45.80	6.88	0.50	2.25	12.13
Av.		35.67	13.54	2299.27	100.65	11.12	0.75	2.30	11.03
Um Dehais		46.54	36.44	5419.07	237.40	7.40	0.33	3.18	12.66
Abu Minqar		41.86	40.41	2259.66	59.82	5.12	3.73	2.04	11.48
Km 17	**<63µ**	34.35	35.51	2356.76	92.94	2.80	0.28	ND	10.81
W. Abu Hamra		66.27	68.25	2586.88	145.81	10.98	1.18	1.68	16.71
Sh. Elbahari		47.88	11.47	2906.18	219.13	10.92	0.83	0.73	18.25
W. El Gemal		47.25	20.00	2749.33	158.32	11.15	0.42	ND	8.38

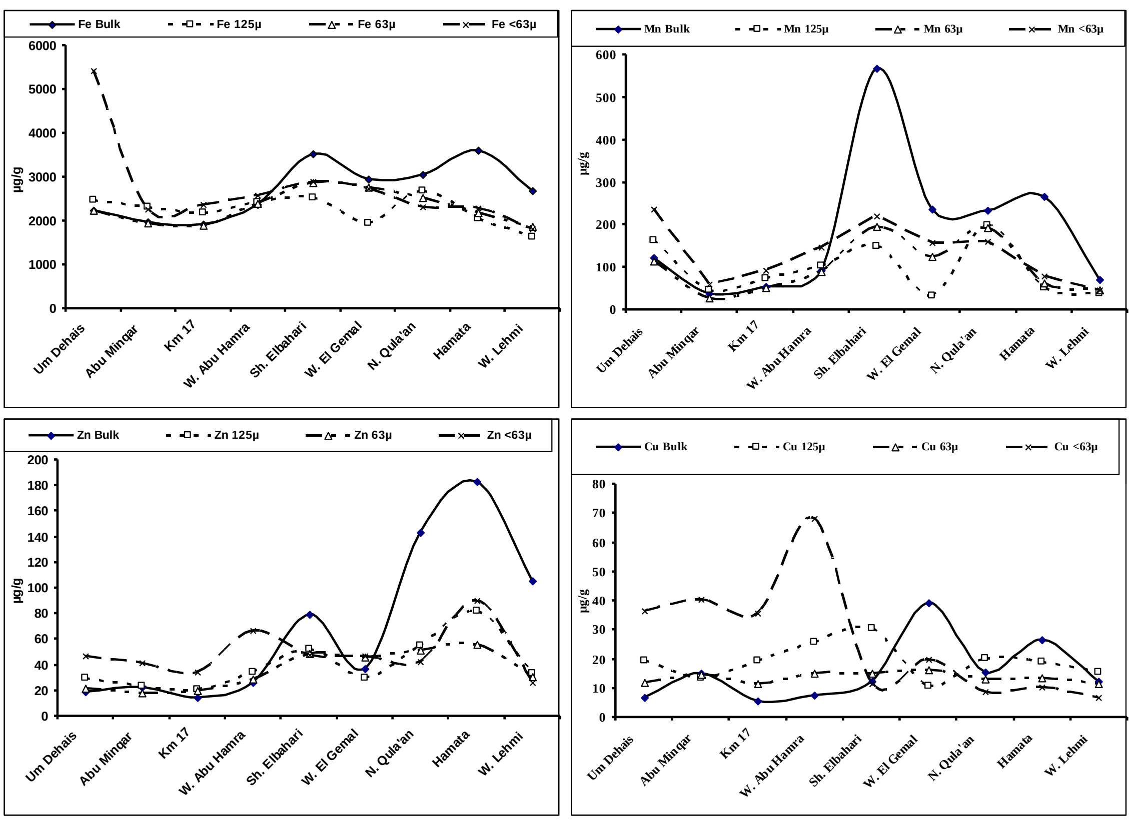
N. Qula'an	42.38	8.75	2316.67	161.50	11.42	0.45	ND	12.73
Hamata	89.93	10.28	2295.28	78.45	19.75	0.60	ND	13.98
W. Lehmi	25.88	6.90	1813.58	46.17	10.80	0.68	ND	8.33
Av.	49.15	26.45	2744.82	133.28	10.04	0.94	1.90	12.59

Table 2: The averages of heavy metals (µg/gm) in fruits, leaves and roots of *Avicennia marina* at the different swamps:

		Zn*	Cu*	Fe*	Mn*	Pb*	Cd*	Co*	Ni*
Um Dehais		76.99	28.28	71.37	6.26	18.61	0.94	ND	7.61
Abu Minqar		121.31	21.26	122.92	7.90	44.78	0.72	ND	3.45
Km 17		93.11	9.92	82.83	5.48	11.71	0.56	0.93	4.76
W. Abu Hamra		337.81	16.08	134.66	5.80	16.76	0.54	2.11	12.17
Sh. Elbahari	Fruits	76.98	15.18	181.18	6.22	8.26	0.05	ND	14.27
W. El Gemal		63.23	9.36	229.24	5.86	16.91	ND	ND	6.36
N. Qula'an		43.35	3.59	96.90	5.11	8.21	0.03	ND	1.92
Hamata		144.13	17.21	146.82	7.94	28.44	0.35	ND	8.41
W. Lehmi		90.78	15.95	195.81	9.25	29.51	0.42	ND	1.57
Fruits Av.		116.41	15.20	140.19	6.65	20.35	0.45	1.52	6.72
Um Dehais		106.91	30.89	363.62	68.71	21.89	0.41	ND	15.38
Abu Minqar		67.67	16.51	501.34	22.25	33.88	0.28	ND	5.49
Km 17		45.03	9.12	463.78	41.37	11.43	0.12	0.92	3.86
W. Abu Hamra		61.81	13.53	453.80	25.00	24.28	0.20	1.98	5.42
Sh. Elbahari	Leaves	119.67	13.45	524.14	53.07	8.62	0.14	ND	16.51
W. El Gemal		39.24	4.60	377.49	35.94	ND	0.21	ND	0.77
N. Qula'an		83.37	4.50	240.81	59.26	3.99	ND	ND	3.26
Hamata		86.75	12.11	277.33	25.32	56.57	0.14	ND	2.95
W. Lehmi		107.24	8.68	365.56	62.58	12.42	1.54	ND	2.26
Leaves Av.		79.74	12.60	396.43	43.72	21.63	0.38	1.45	6.21
Um Dehais		157.88	10.37	475.83	12.15	47.20	0.67	ND	2.91
Abu Minqar		71.48	15.98	361.57	8.53	37.99	0.88	ND	5.66
Km 17		140.85	13.01	363.80	8.82	13.66	ND	ND	5.53
W. Abu Hamra		143.51	12.62	401.92	9.40	69.74	0.44	2.35	12.08
Sh. Elbahari	Roots	100.68	11.13	368.32	14.00	21.40	ND	ND	14.68
W. El Gemal		60.69	4.31	239.08	8.12	20.07	ND	ND	2.77
N. Qula'an		59.11	5.39	371.06	12.30	16.91	ND	ND	3.02
Hamata		46.98	6.28	376.48	8.75	32.44	0.35	ND	2.12
W. Lehmi		74.22	6.77	255.00	15.84	11.81	0.53	ND	3.08
Roots Av.		95.05	9.54	357.01	10.88	30.14	0.58	2.35	5.76

3.2. Bioaccumulation of heavy metals in the mangrove stands

As shown in table (2), zinc recorded the highest average content in fruits (116.41µg/gm) followed by roots (95.05µg/gm) and leaves (79.74µg/gm). Abu Hamra mangrove swamp recorded the highest average (337.81µg/gm) in fruits and El-Gemal swamp recorded the lowest average (39.24µg/gm) in roots. Copper also recorded the highest average content (15.20µg/gm) in fruits followed by leaves (12.60µg/gm). Um Dehais showed the highest average of Cu in leaves (30.89µg/gm) and Qula'an has the lowest one (3.59 µg/gm) in fruits. Qari and Ahmed [7] found that Zn and Cu were enriched in fruits. MacFarlane [35] abstracted that Zn was the most mobile of all metals and was accumulated to the greatest quantities in leaf tissue in a dose dependant relationship. Zinc translocation to leaf tissue exhibited a dose dependant relationship with both root and sediment Zn levels. Shete *et al.*, [36] observed high concentration of Zn is in two mangrove species. Usman *et al.*, [37] measured high Cu in leaves and fruits of *A. marina*, they classified *A. marina* as potential metal bioaccumulator for Cu. The recorded values of Cu were higher than those measured in *Avicennia sp.*, Australia [35] and in *Laguncularia racemosa* at Pacific Panama [33]. Lead (Pb) showed the highest average in roots (30.14 µg/gm) followed by nearly equal values in leaves and fruits (21.63 and 20.35µg/gm respectively). The highest Pb value was recorded in roots at Abu Hamra swamp (69.74µg/gm) and the lowest value was below detection limit at Wadi El Gemal swamp. Shete *et al.*, [36] reported that Pb has less mobility towards the leaf tissue. According to MacFarlane [35], Pb and Zn are in combination resulted in an increased accumulation of both metals in leaf tissue and increased toxicity than individual metals alone. Kumar *et al.*, [8] recorded Pb values in roots and leaves higher than those recorded in the present study, while the Zn values were much lower. The highest average of Fe and Mn were recorded in leaves (396.43 and 43.72µg/gm) followed by roots (357.01 and 10.88µg/gm). The highest value of Fe (524.14µg/gm) was recorded in leaves at Sharm Elbahari swamp and the lowest values (71.37µg/gm) was recorded in fruits at Um Dehais swamp, while the highest value of Mn (68.71µg/gm) was recorded at Um Dehais swamp and the lowest one (5.11µg/gm) recorded at Qula'an swamp. The recorded values of Fe and Pb in roots and leaves were higher than those recorded by Qari and Ahmed [7] in the *A. marina* from Sonmiani, Pakistan Coast. The measured concentrations of; Fe, Zn, Cu, Co, Pb and Mn at the different mangrove swamps were lower than the recorded values at Kerala, India [26] and the recorded values of Cu, Zn and Pb were higher than those recorded in mangrove leaves at Punta Mala Bay [33]. Nickel recorded nearly equal averages in fruits, leaves and mangrove roots (6.72, 6.21 and 5.76µg/gm). Sharm Elbahari swamp recorded the highest Ni value (16.51µg/gm) and the lowest value (0.77µg/gm) was measured at Wadi El Gemal swamp (Fig 3). The recorded contents of Co and Cd in the different parts of *A. marina*, slack water and the underlying sediment fractions were mostly insignificant.



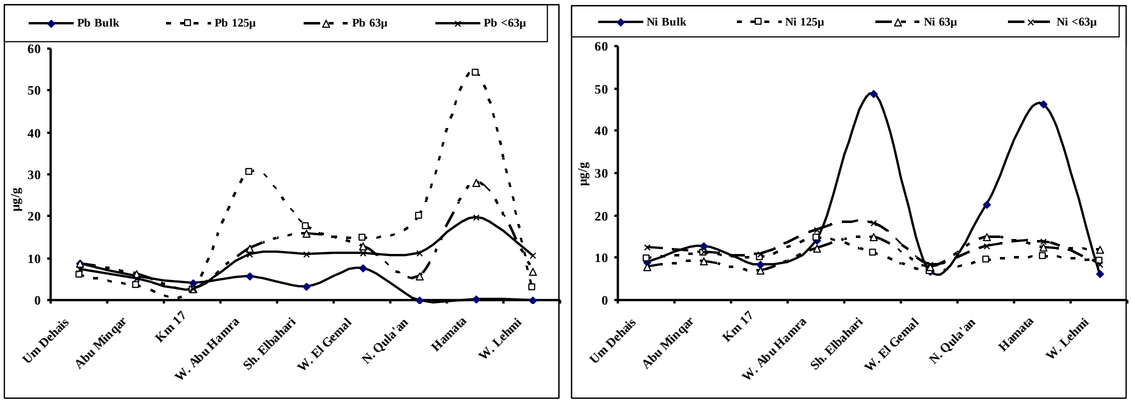


Figure 3: The differences in the bioactive heavy metals between bulk sediments, 125µ, 63µ and <63µ at the studied sites

The bioaccumulation of the measured heavy metals in mangrove fruits and roots follows the order; Fe>Zn>Pb>Cu>Mn>Ni and in the leaves follows the sequence of; Fe>Zn>Mn>Pb>Cu>Ni similar to the recorded pattern in Hong Kong mangroves [32]. The observed sequences were differing than heavy metal orders recorded in *Avicennia* mangrove at the eastern side of northern Red Sea Cu>Zn> Ni>Cd [37]. Qari and Ahmed [7] sequenced the heavy metals in the order of; Fe>Cd>Pb in leaves, stem and roots of mangrove, they observed high concentrations of Fe and Pb in roots compared with leaves and stems. Kumar *et al.*,[8] recorded that the heavy metal contents in the plant parts follow the order of Pb>Zn>Cd; they concluded that the concentrations of heavy metals in different parts of *Avicennia marina* were in the order Roots>stem>leaf except for Cd, which is higher in leaves.

Zn and Pb show significantly high accumulations tendencies in *A. marina* roots leaves and fruits much more in the underlying sediments. Fe and Mn recorded very high concentrations in sediments relative to *A. marina* parts. The concentrations of Cu and Ni were lower than in the underlying sediments. MacFarlane *et al.*, [30] observed that Cu, Pb and Zn were accumulated in the root tissue of *Avicennia marina* much more than the surrounding sediments, but MacFarlane *et al.*, [30] concluded that metals tended to be accumulated in roots to concentrations similar to those of adjacent sediments while metal concentrations in leaves were half that of roots or lower. *A. marina* fruits showed the highest tendency to bio-accumulate Zn and Cu, leaves tend to bio-accumulate Mn much more fruits and roots while the mangrove roots accumulated Pb more than fruits and leaves. Fe was highly bio-accumulated in leaves and roots and fruits followed by Zn and Pb, but nickel shows nearly approximate tendencies in the different parts of the mangrove. In the studied localities, the high heavy metal contents were effect on the leaf number and the old leaves were seen to turn yellow and fall down. Also, many of the mangrove stands show deformed and ramified pneamatophores. Yim and Tam [38] provided that the high heavy metal concentrations significantly reduced leaf number and stem basal diameter in *Bruguiera gymnorrhiza* and the old leaves were seen to turn yellow and shed off whilst young leaves continued to survive.

3.3. Heavy metals accumulation in slack water of the mangrove swamps:

Slack water in the mangrove swamps plays the vital role in the heavy metals bio-geochemical cycle between *A. marina* stands and the underlying sediment layer. Mangrove trees seem to be the best adapted to high situation in the intertidal zone, and to high pore-water salinities [39]. These trees may oxidize their rhizospheres and control concentrations of soluble sulfides in the soil pore-water thus demonstrating a strong biotic influence on the soil environment [40]. Zn was varied between 0.83 and 7.05µg/l, Fe was changed from 17.15 to 35.08µg/l, Cd from less than 1.00µg/l to 7.78µg/l, Cu, Pb and Ni recorded values lower than 3 µg/l, While Mn and Co were insignificant. Abu Minqar swamp recorded the highest Fe and Ni averages in the slack water (Table 3).

Table 3: The average contents of heavy metals in the slack water of the mangrove swamps (µg/l) at the different mangrove swamps:

	Zn	Cu	Fe	Mn	Pb	Cd	Co	Ni
Um Dehais	7.05	3.68	26.54	0.49	3.24	7.78	1.68	2.22

Abu Minqar	2.83	2.66	35.08	0.69	3.05	2.86	1.46	4.47
Km 17	2.56	1.97	17.15	0.15	2.01	0.27	0.27	0.83
W. Abu Hamra	2.64	1.62	19.08	0.26	2.96	3.93	1.70	2.14
Sh. Elbahari	2.053	1.58	32.36	0.39	0.42	0.57	0.44	0.76
W. El Gemal	0.83	1.04	28.48	0.25	ND	0.15	0.31	0.43
N. Qula'an	2.77	2.13	26.41	0.30	ND	0.14	0.29	ND
Hamata	2.23	1.46	26.80	0.24	0.43	0.14	0.08	0.46
W. Lehmi	2.73	1.73	19.55	0.06	0.43	0.09	0.28	0.02

The highest average contents of Zn, Cu, Mn, Pb and Cd were recorded at Um Dehais swamp. Water movement through burrows and mangrove root and pneumatophore inside sediment layer turnover the metals characteristics between reducible and oxidizing conditions. The transfer of dissolved metals to and from the sediment through burrows and mangrove root and pneumatophore casts is further enhanced by the variation in hydrostatic pressure during tidal cycles [41]. The rate of the slack water invasion inside the underlying sediment layer was highly affected the turnover between oxic and anoxic conditions. This process was controlled by the fine and particulate sediment percentages within the sediment layer. The measured heavy metals in the slack water of the mangrove swamps were lower than the expected may be due to the continuous bioaccumulation the ionic forms of metals by the mangrove roots and the reducing nature of these swamps that transform these metals from the dissolved forms to insoluble sulphide from. For example, Mn in solution is able to be incorporated by mangrove plants [27]. Lacerda *et al.,* [42] observed relatively high Mn concentrations in mangrove leaves correlated with Mn concentrations in pore waters. Soto-Jiménez and Páez-Osuna [43] documented that; when reduced conditions predominate, as commonly occurs in mangrove sediments, soluble Mn is the dominant form migrating through the pore water to the adjacent water column. The recorded values were in the same range recorded by Cuong *et al.,* [34] in the subsurface water of Singapore mangroves. Consequently, the bioaccumulation processes in the plant were dependant on the metal availability in the underlying sediments and the surrounding water column. It is clear that there is a very close interaction between the plant and the underlying sediments in bio-geochemical cycle.

3.5. Bio-geochemical cycle and the factors influencing heavy metals enrichments and bio-availability:

Mangrove trees can be considered as a biochemical reactors, not only because of their physiological and biochemical processes but also due to their active role in organic matter decomposition within the sediments that greatly influence the mobility of heavy metals [39]. The luxuriant growth of *A. marina* in comparison to other mangrove species is evident of its adaptability even under polluted conditions [44]. Shete *et al.,* [36] indicated that roots of *A. marina* were able to bio-accumulate and survive despite of the heavy metal levels. Hydrogen sulphide and organic matter seem to be the most important factors regulating the amount of free or biologically available metals in sediments and in the metal exchange between the biota and the water [45]. Sulphides are known to control metal solubility and bioavailability in partially reducing environments, therefore decreasing the metal toxicity [46]. Marchand *et al.,* [27] recorded that metals are deposited in the mangrove mainly as oxides and/or oxy-hydroxides, that are subsequently dissolved by bacteria for the decomposition of organic matter, and which leads to a strong increase of metals in the dissolved phase.

The bio-geochemical cycle and metals availability were controlled by:

Litter production and the rate of organic matter decomposition:

Organic matter in the mangrove swamps are mainly from litter productions of the mangrove stands. About 70% of litters produced from mangrove leaves [47] and about 14% from fruits [1]. The amount of litter productions was dependent upon the area of mangrove swamp and trees height and density in each stand. Mangrove leaf fall is of the greatest importance in metal cycling in tropical mangrove forests because its organic matter is capable of controlling the mobility of heavy metals [48]. Litters decomposition produces organic matters enriched with nutrients and heavy metals. These decomposed litters with the accumulated particulate and fine sediments produce highly anoxic conditions. The increasing of organic matter contents in sediments enriching the metal contents in solid phase. The heavy metals distribution within sediments and pore-water appear to result from diagenetic processes linked to organic matter decomposition [39]. Organic digenesis in mangrove sediments leads to the transfer of transitional metals from oxide form to organic and sulfide forms Marchand *et al.*, [27]. Silva *et al.*, [48] found that the annual average transfer rates of heavy metals from the tree canopy to the sediment through leaf fall were: 0.56, 1.11, 0.01, 0.02 and 0.07 mol ha^{-1} for Fe, Al, Pb, Zn and Ni respectively. Doig and Liber [49] concluded that OM strongly influenced Ni partitioning, and demonstrated that organic-rich sediments may complex significant quantities of Ni under aerobic conditions.

Fine grained sediment contents

The highest concentrations for most metals occurred in fine-grained sediments [50]. The difference in grain-size distribution between the mangrove sites would affect the sediment metal concentrations [51]. Defew *et al.*, [33] documented that the metal variations in the surface sediments between localities may be attributed to effects of biological and physical phenomena, such as tidal inundation, salinity changes, wind and waves. These phenomena allow the processes of bioturbation, re-suspension and erosion that are known to affect the metal concentrations in surface sediments [52]. In the studied localities, the fine grained sediments considered the essential category in the different swamps and play the vital role in the heavy metals enrichments. The possible physiological mechanisms responsible for variation in uptake and translocation at the root level include processes at the root's rhizosphere [53]. The enrichment of the heavy metals in mangrove sediments may be caused by their strong soluble complexes with reduced sulphur [54], which increasing the migration of these metals from sediments to the overlying water column then reaching to mangrove stands. The slack conditions in the mangrove swamps help to the complete the translocation cycles of metals between the sediments, water column and mangrove stands.

The redox potential of the sediment layer

The high redox potential and texture characteristics have high capacity for metal capture [50]. In mangrove sediments, redox conditions are dependent on the quantity and reactivity of organic matter, sediment grain size, bioturbation activity, like in marine sediments, but also on forest age, physiological activities of the root system, extent of water logging and crabs burrowing [39]. The redox potential of the sediment can affect metal trapping directly through a change in the oxidation state of the metal itself, or indirectly through a change in the oxidation state of ions that can form complexes with the metal [24]. The redox conditions were mainly controlled by the length of water logging and the activity of root system. Because of the specificity of the *Avicennia* root system and their positions in the intertidal zone, heavy metals are more available and potentially more mobile to extract by the mangrove stands [39]. Dunbabin and Bowmer [55] documented that the major processes of metal retention include cation exchange, complexing with organic molecules, precipitation as oxides, oxyhydroxides and carbonates, and precipitation as sulphides.

The burrowing activities of the benthic organisms

Sediment turnover by burrowing fauna can have a major influence on the geochemical and physical characters of sediments. In addition to sediment turnover, burrows, and water pumping by their inhabitants, provide a means for oxygen to be transferred into the otherwise anaerobic sediment, and increase subsurface water flow [56]. Burrowing activity allowing slack water moves sulphidic sediments to the surface where they can oxidise and release any sulphide bound metals [24]. The increased accumulation of metals to plant tissues of *Avicennia* species is supposed to be through the translocation of air absorbed through lenticels in pneumatophores from underground roots. Within the organic-rich layers, organic bound and exchangeable phase formed the dominant fraction representing at least 75% of total Mn concentrations [27]. Most of the Mn oxides that are deposited in the mangrove, and which are subsequently dissolved during Mn reduction processes, are then associated with this organic matter.

Aerial roots (pneumatophores) density

Because of the specificity of the *Avicennia* root system, heavy metals in the dissolved phase present in higher concentrations and thus that heavy metals are more bioactive and potentially more mobile beneath *Avicennia* stands [39]. The root system in the studied localities showed different degrees of deformations and many of them were ramified that may be attributed to the effect of high heavy metal contents. Metals bio-availability to the plant occur in mangrove sediments that are characterized by negative redox potentials in the sediment–water interface, surficial sediment near the landward margin of the forest and subsurface sediment in some parts of the forest may be characterized by oxidizing conditions [24]. Otero *et al.*, [57] found that the upper 20cm of the mangrove sediments contained the largest quantity of roots, and the conditions were oxic or suboxic, acidic, and with high concentrations of Fe and Mn in the pore water. Marchand *et al.*, [27] reported, dissolved Fe increased in the surface sediment layer, where iron respiration is the dominant organic matter (OM) decay process and a part of the dissolved iron may also have been precipitated with OM. They attributed the high concentrations of Fe measured beneath *Avicennia* stands to both sulfide oxidation and oxide dissolution.

Correlation coefficient relationships

Most of the he interaction relationships between the heavy metals in *Avicennia marina* parts were insignificant except those have real interrelations with the underlying sediments. In the plant fruits showed the fairly positive correlations of Cu with Ni (Fig 5) and with Cd (r = 0.51), Zn with Co (r = 0.58) and Mn with Pb (r = 0.51) (Table 4). In the plant leaves, the significant correlations were restricted between Zn, Cu and Ni (Fig 6). In the roots system, Zn was positively correlated with Cu, Fe, Pb and Ni (Fig 7), while Cu was correlated with Fe and Ni (Fig., 8). It is clear the metals of Cu, Zn and Ni were the essential metals in the different parts of *A. marina* may be they have important role in the plant surviving and growing up. Metal concentrations in plant tissues such as Cu and Zn are triggered by metabolic requirements [58]. MacFarlane *et al.,* [30] recorded that Cu and Zn showed some mobility in the plant, being accumulated in leaf tissue in levels of approximately 10% root levels.

Table 4: Results correlation coefficients between metals in fruits, leaves and roots of *Avicennia marina* stands:

		Zn	***Cu***	***Fe***	***Mn***	***Pb***	***Cd***	***Co***	***Ni***
Fruits	Zn	1.00							
	Cu	0.24	1.00						
	Fe	0.12	-0.13	1.00					
	Mn	0.01	-0.05	0.39	1.00				
	Pb	0.16	0.44	0.18	0.51	1.00			
	Cd	0.33	0.51	-0.28	0.19	0.35	1.00		
	Co	0.58	0.03	-0.03	-0.18	-0.02	0.06	1.00	
	Ni	0.35	0.56	0.09	-0.28	-0.07	0.16	0.28	1.00
Leaves	Zn	1.00							
	Cu	0.50	1.00						
	Fe	-0.10	0.12	1.00					
	Mn	0.43	0.16	-0.24	1.00				
	Pb	0.15	0.33	-0.10	-0.43	1.00			
	Cd	0.08	0.28	0.02	0.14	0.06	1.00		
	Co	-0.14	0.08	0.23	-0.37	0.18	0.00	1.00	
	Ni	0.67	0.77	0.24	0.38	0.04	0.08	0.02	1.00
Roots	Zn	1.00							
	Cu	0.61	1.00						
	Fe	0.57	0.60	1.00					
	Mn	0.12	0.12	0.21	1.00				
	Pb	0.51	0.34	0.49	-0.18	1.00			
	Cd	0.22	0.25	0.41	0.19	0.37	1.00		
	Co	0.04	-0.06	-0.14	-0.33	0.30	0.00	1.00	
	Ni	0.51	0.75	0.45	0.21	0.19	-0.12	-0.03	1.00

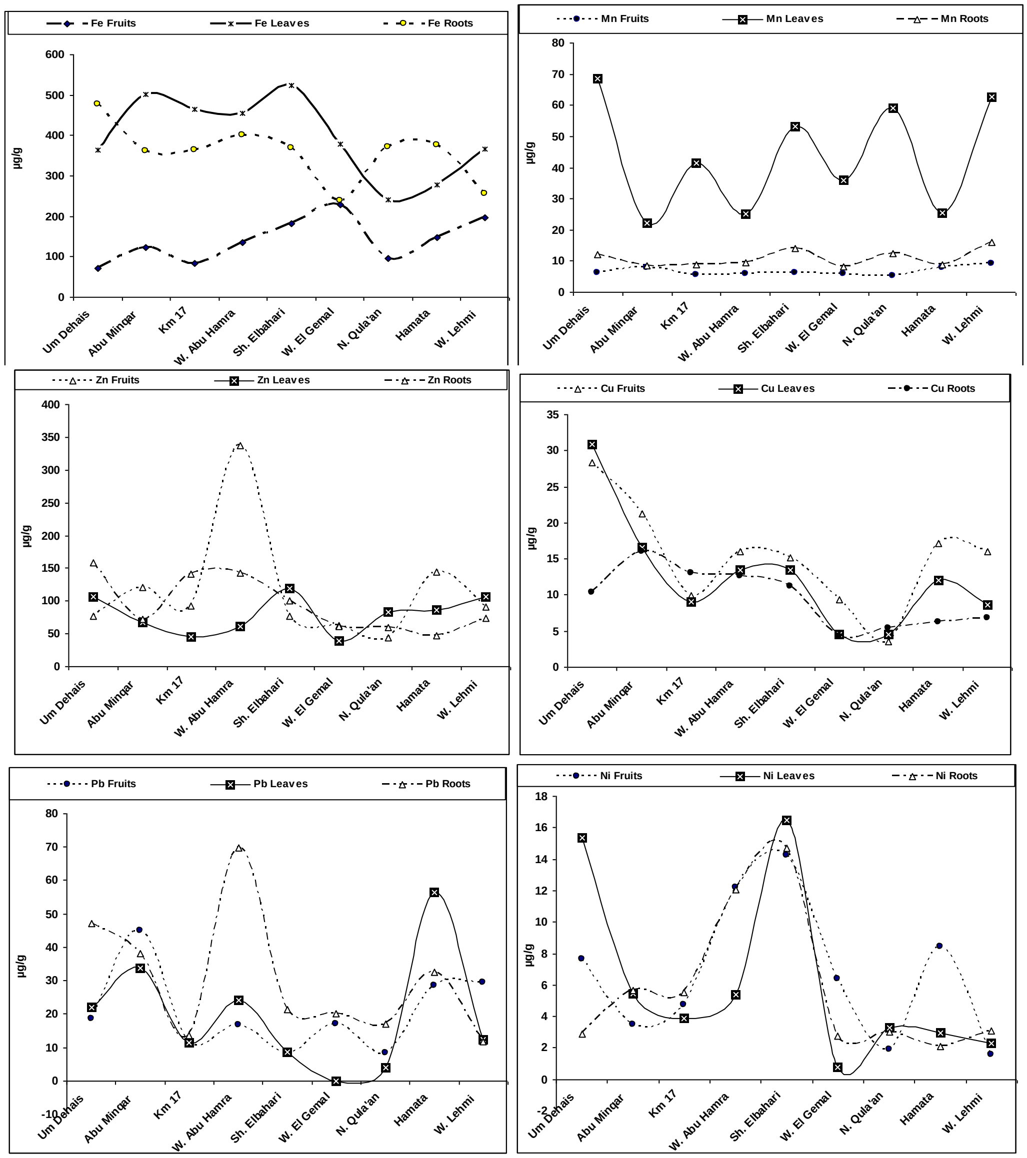


Figure 4: Heavy metal variations between the fruits, leaves and mangrove roots at the different mangrove swamps

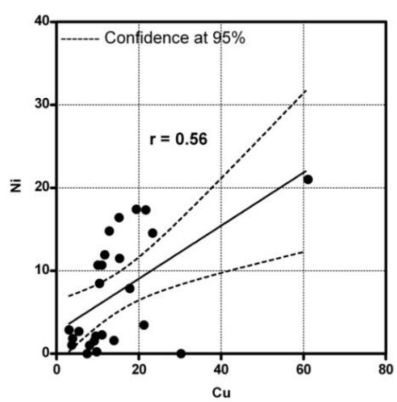


Figure 5: The significance correlation between Cu and Ni in the mangrove fruits

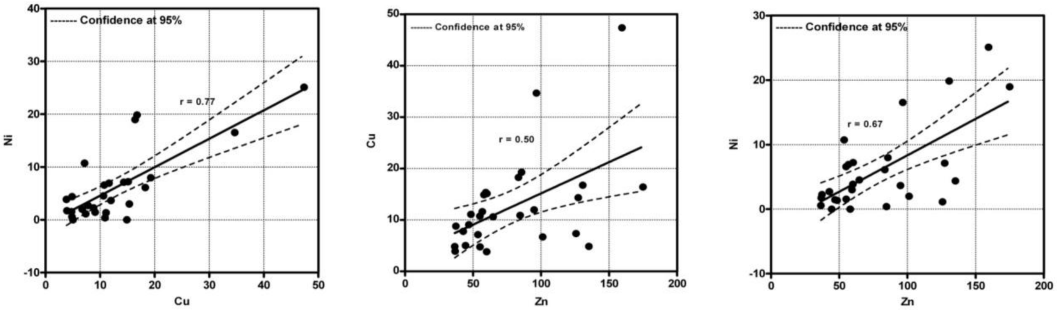


Figure 6: The significance interrelations between Zn, Cu and Ni in mangrove leaves

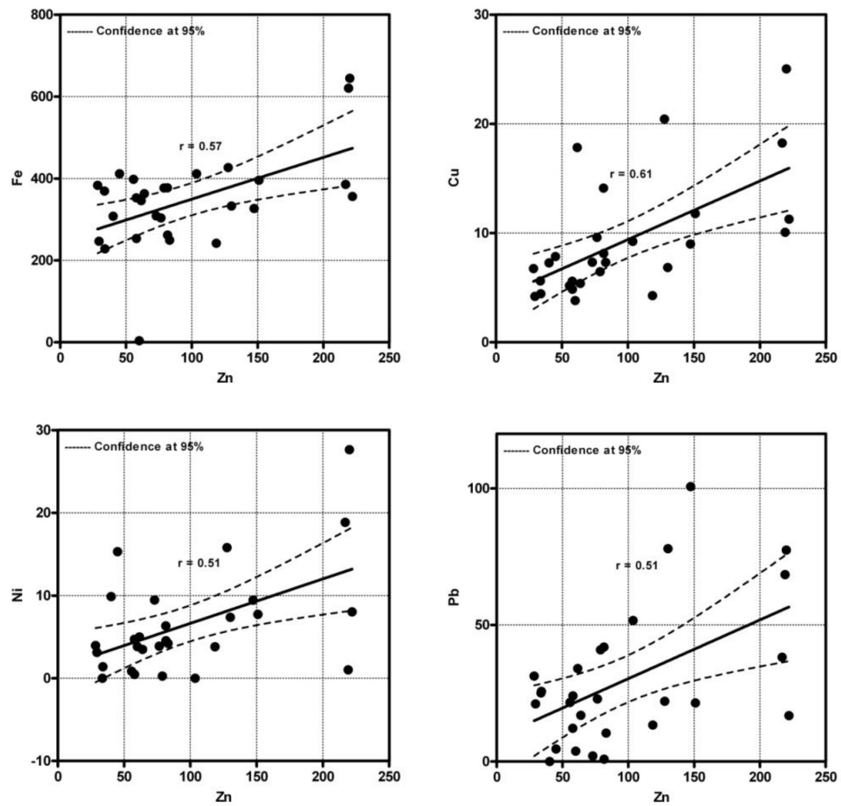


Figure 7: The correlations of Zn with; Fe, Cu, Ni and Pb in mangrove roots at 95% confidences

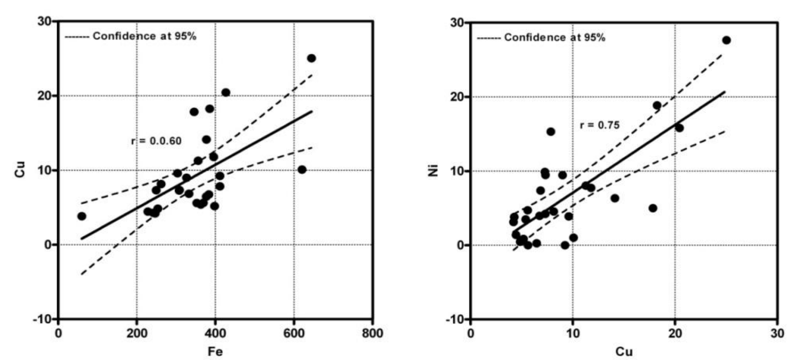


Figure 8: The significance correlations of Cu with Fe and Ni in mangrove roots

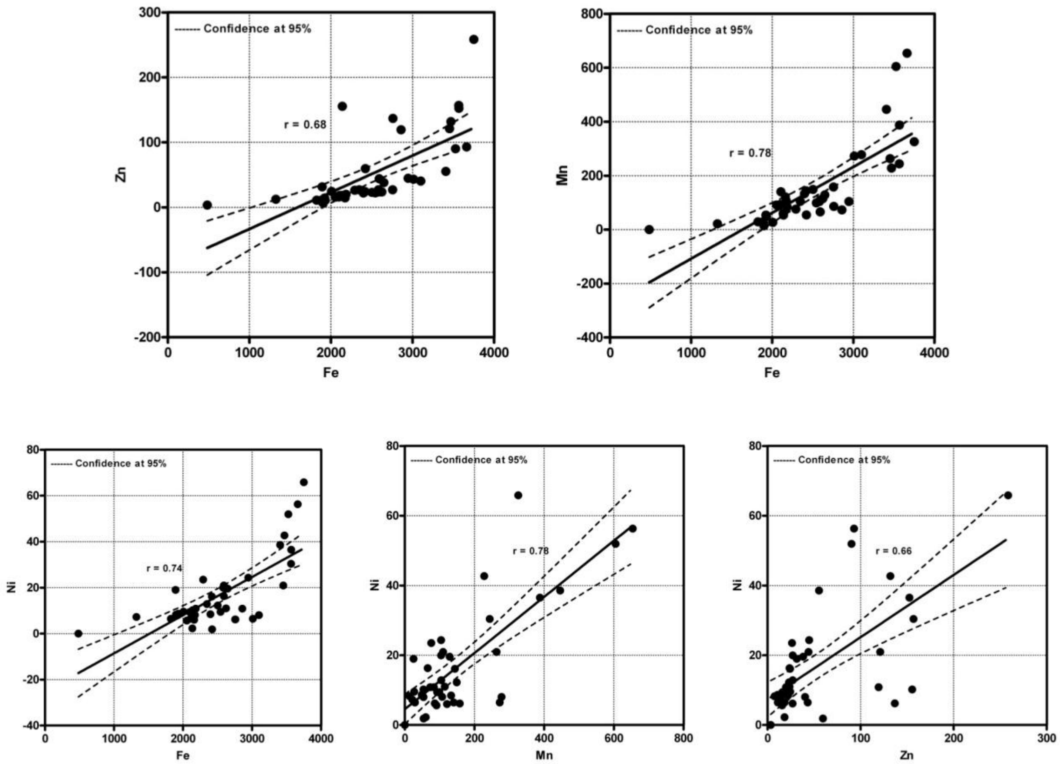


Figure 9: The significance interrelations of Fe with Zn, Mn and Ni as well as Ni with Mn and Zn in bulk sediments

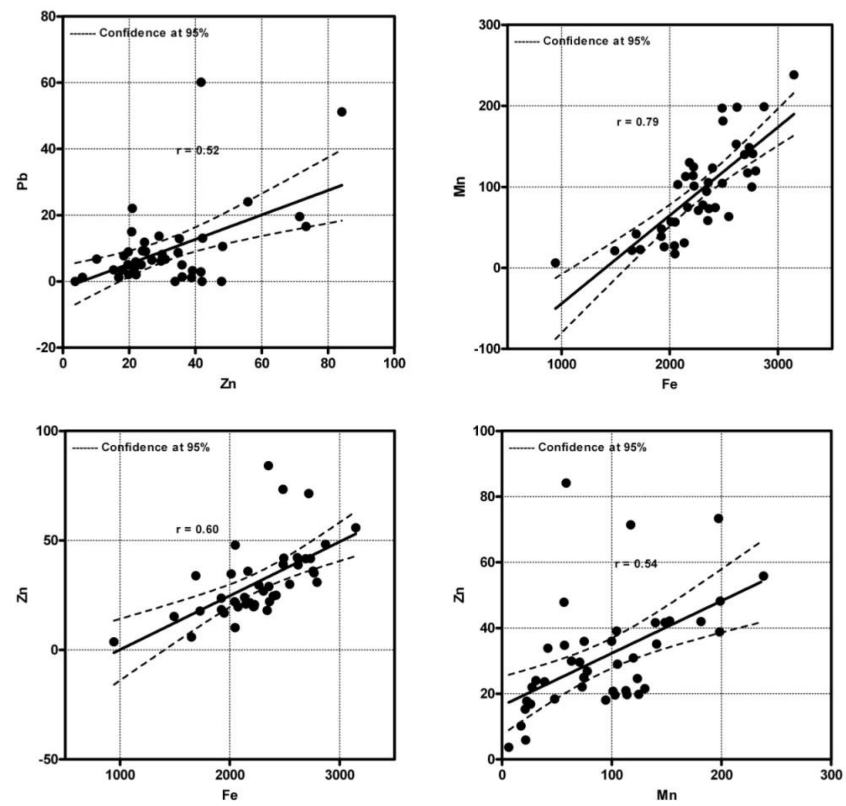


Figure 10: The interrelations of Fe, Zn, Mn and Pb in 63µ fraction at 95% confidences

MacFarlane and Burchett [59] pointed out that Cu was accumulated in root tissue in a linear relationship at lower sediment concentrations. MacFarlane *et al.*, [53] suggested that the patterns of metallic cation (Cu^{2+}, Pb^{2+} and Zn^{2+}) uptake by roots and translocation to the shoot were broadly similar for both salt secreting and non-secreting species. It is probable that metal influx and regulation of transport in mangroves are likely to be achieved through a variety of pathways in addition to those responsible for sodium influx/transport. Metal interactions in the bulk sediments were more significant than the sediment fractions. In the bulk sediments, Fe with positively correlated with Zn, Mn and Ni as well as Ni with Zn and Mn (Fig 9) while Mn with Co (r = 0.55). The interaction relationships of 125µ and <63µ fractions were insignificant (Table 5) but in 63µ, Fe showed positive correlations with Zn and Mn while Zn recorded positive correlations with Mn and Pb (Fig., 10). The positive correlation of Fe with the other metals in the sediment layer indicated that Fe is metal carrier for the bioactive metals in the translocation process. The transitional metals as Fe and Ni are deposited in the mangrove mainly as oxides and/or oxy-hydroxides, that are subsequently dissolved by bacteria for the decomposition of organic matter, and which leads to a strong increase of metals in the dissolved phase [27]. Zhou *et al.,* [60] found that the correlation analysis indicates that the concentrations of Zn, Cu, and Ni in the oxidizable fraction are strongly correlated with organic matter content in the mangrove sediments much more than with Fe/Mn oxides. Reitermajer *et al.,* [61] recorded, among all the metals studied, Fe and Zn showed significant positive correlation with clay. This indicates that these metals better bind with the finer particles than the larger sand particles. Tam and Yao [51] pointed out that Fe was found to be a good formalizer for Mn, Zn and Ni in the mangrove sediments. Marchand *et al.,* [27] reported that Ni was mainly associated with oxides and/or oxy-hydroxides minerals when being deposited in the mangrove, and that the dissolution of these minerals in suboxic conditions, lead to the release of Ni in pore water.

Conclusion

- The bio-geochemical cycle and the interactions of bioactive heavy metals between mangrove stands and the underlying sediments were studied at 9 mangrove swamps in the near shore zone of the Red Sea.
- The fine sediments group (125µ + 63µ + <63µ) represents the essential constituent of the mangrove sediments at the different localities. These fractions have the ability to transport for long distances throughout the water medium to the depositional area.
- The accumulation of heavy metals in the bulk sediments follows the order of; Fe>Mn>Zn>Ni>Cu>Pb, in fraction 125µ follows Fe>Mn>Zn>Pb≥Ni≥Cu, in 63µ was following; Fe>Mn>Zn>Pb≥Cu≥Ni and in <63µ follows the sequence; Fe>Mn>Zn>Pb>Cu>Ni.
- Mangrove fruits showed the highest tendency to bio-accumulate Zn and Cu, leaves tend to bio-accumulate Mn much more fruits and roots while the mangrove roots accumulated Pb. Fe was highly bio-accumulated in leaves, roots and fruits followed by Zn and Pb. The bioaccumulation orders of the heavy metals in mangrove fruits and roots follow the order of; Fe>Zn>Pb>Cu>Mn>Ni and in the leaves follows the sequence of; Fe>Zn>Mn>Pb>Cu>Ni.
- The bio-geochemical cycle and metals availability were controlled by; amount of litter productions, rate of organic matter decomposition, fine grained sediment contents, the redox potential of the sediment layer, burrowing activities and the root density.
- The correlation coefficients indicated to close correlations between Zn, Ni and Cu in the mangrove stands may be they have important role in the plant surviving and growing up.
- The recorded high heavy metal contents in *Avicennia marina* stands may be responsible about the widely distributed roots deformation and ramifying and the yellow colored leaves at the different locations.

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