

Heavy Metals Distribution in the Dead Sea Black Mud, Jordan

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Abstract

The concentrations of trace metals (Fe, Mn, Ni, Zn, Co, Cr, Cu and Pb) were investigated in the Dead Sea black mud and river sediments in the northern basin of the Dead Sea region, Jordan. The pH of the mud was slightly above 8 while it was around 6 for the seawater. All analyzed heavy metal content in the black mud, except Pb, was less than their contents in other types of mud. This might be due to the effect of the mildly acidic pH of seawater, which would enhance the metal solubility or incorporation within salt mineral structure, rather than precipitation. The sequential extraction results showed that Ni and Co transferred into the carbonate fraction, Mn is found mostly as manganese-iron oxide, and the residual phase contained Cr, Cu, Fe and Pb. This study illustrated that the black mud had low heavy metal contents, thus indicating low toxicity. Additionally, it shows insignificance effect of the mixing of freshwater with seawater on the heavy metal contents in the black mud.

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1. Introduction

The Dead Sea is one of the most famous sites for climatotherapy. It is the lowest point on earth at 422 m below Sea level; its level is declining with rate equal to 1m/year, and evaporation rate is equal to 0.5 cm/day (APC, 2007). The Dead Sea is among the saltiest water bodies on the earth, its salinity reaches 340 g/kg compared with oceans 35 gkg⁻¹ (Al-Nawayseh, 2003).

The Dead Sea is only 35 km west of Amman and 30 km east of Jerusalem; it is located in the middle of Jordan rift valley region, extending from north to south along Wadi Araba and Jordan River (Oumeish, 1996). The Dead Sea is as old as the history of Jordan and Palestine. It was mentioned in the world Old Testament and the Holy Koran, the Dead Sea was given many names for example, Sedom, dragon Araba, Asphalt Sea and Lutt Sea (Oumeish, 1996). It is 28 million years old; and is divided into two lakes: the northern lake comprises 76% of the whole Sea with a maximum depth of 360 m, and the southern one comprises 24% of whole Sea and it is 10 m deep, the two lakes are separated by the Lisan Island, the total length of the Sea is 67 km, and the width ranges from 12 to 17 km, the total surface area is 1000 km² (Abdel-Fattah, 1997).

The Dead Sea is the lowest lake in the world, and it is considered the saltiest one among all the hyper saline lakes of the world. The chemical composition of the Dead Sea brines are Potassium Chloride which consists of 1.2 % (weight/weight) or (w/w) of the brine salt, Magnesium

Chloride 14.5%, Sodium Chloride 7.5%, Calcium Chloride 3.8% and Magnesium Bromide 0.5% (Es-Shahat et al., 2003). These chemicals provide the raw materials for fertilizers, salts and cosmetic products. Abdel-Fattah and Nicholas (2009) studied the toxic element contents in the natural black mud of the Dead Sea that is used in cosmetics production. They found no toxic enrichment of elements either in the raw mud or its derivative products.

The climate in the Dead Sea area is characterized by it is hot dry summer season, with mean temperature about 33 °C. In winter the temperature is pleasant, with average temperature 16.8 °C. The maximum temperature is 40.6 °C in July, the hottest month, while the minimum temperature is 10.8 °C in January, the coldest month. The average relative humidity ranges from 40.6% to 44.3% in summer and from 59% to 63.3% in winter season. Rainfall is very low with an annual rainfall of 70 mm (Al-Nawayseh, 2003).

The atmosphere over the Dead Sea is rich in oxygen 10% more than any other seas, which might be due to its lower altitude. Water evaporation is relatively low because the dissolved salts lower the vapor pressure over the sea surface (Oumeish, 1996). The geology of the investigated area is controlled by the Rift valley, which is a continuation of the East African Rift valley and the Red Sea and began during the Eocene-Oligocene age (Powell, 1988).

The Dead Sea represents a rich source of black mud, which is used in climatotherapy for many skin diseases (Oumeish, 1996). The Dead Sea black mud was used as facial masks and skin curative since ancient times (Abdel-Fattah and Schultz-Makuch, 2004). Therefore, it is essential to evaluate its chemical feature, especially heavy metal content.

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A previous study, dealing with the Dead Sea mud geochemistry and mineralogical features in four places along the eastern shore, has found that the level of trace elements in the Dead Sea mud was less than those in any other sea mud and its composition was 40% of the total mud is carbonate, 20% is clay, 5% feldspar, 25% quartz, 6% pyrite and 0.7 % organic matter (Abdel-Fattah, 1997).

Abdel-Samie et al., (2004) studied the groundwater and the surface water of the Dead Sea area especially in Wadi Issal, Mazra'a area, Es-Safi area and Wadi Ibn Hammad. They found that the surface water has low salinity 700 mg/L, but the groundwater has a higher salinity 569 mg/L - 2266 mg/l. Also high level of nitrate was noticed in Es-Safi and Mazra'a. Furthermore, and they found that the surface and groundwater resources of the Dead Sea were not highly contaminated with heavy metals except for Fe and Mn. Al-Nadaf, (1992) found that the levels of trace elements (Zn, Cd, Cu, Co, Cr, Ba, Sr, Pb, and Ni) in soil of Kitim-Nueimeh, north Jordan valley; were higher than the average soil values, and in some cases exceed the maximum tolerable limits, which is attributable to using large quantities of nutrients and heavy traffics.

A study on the physiography, structure, stratigraphy, paleo-limnology, water, and sediments of the Dead Sea has illustrated many interrelationships between geology, chemistry, and limnology (Neev and Emery, 1967). Moreover, another study indicated that the sulfate-reducing bacteria is present in the reducing bottom sediments of the Dead Sea and that they were the most probable source of the dissolved sulfide in the bottom water (Nissebaum, 1969).

This work aims to determine the concentration of heavy metals in the Black mud and their spatial distribution along the eastern shore of the Dead Sea. The physiochemical parameters of the black mud such as pH, EC, and organic matter (OC) were used to study the heavy metal distribution profiles. Furthermore, the sequential extraction technique was used to investigate the distribution of heavy metals and the chemical forms in which those elements might be associated in the black mud. Finally, the mixing of fresh and salty waters and its effect on the black mud composition was studied too.

1.1. Study area settings

The Dead Sea is located in the center part of the Jordan rift valley and consists of two basins, the northern basin (a longer and deepen one) and the southern basin (a smaller and shallow) (Abed, 1985). The southern basin had completely dried out and exposed through pumping of the brine to the Potash factories. The northern basin contains the hotels and tourism sites. Therefore, the investigated area concentrates on the eastern shore of the Dead Sea northern basin, where the black mud and the main streams supply the Dead Sea by freshwater, Fig. (1). Particularly, this study covered the area between Swimah in the north to the Lisan Island in the south, passing through three sources of fresh water: Swimah, Zarqa - Ma'en and Wadi Al-Mujeb, Fig. (1).

2. Materials and Methodology

2.1. Sampling collection and preparation

A total of 30 samples of black mud were collected in the summer of 2005 from different sites on the eastern shore of the Dead Sea starting from Swimah to the Lisan Island passing through three sites of mixing with fresh water. These sites are Swimah, Zarqa - Ma'en and Wadi Al-Mujeb.

The mud samples had been collected from the area covered with the Dead Sea water, ranging from 1-3 meters off-shore. Another 4 samples were collected from outside the sea; they are covered only by freshwater Fig. (1). The samples were collected from 5 cm deep at the mud/water interface. The sample sites were separated by about one kilometer from each other. The samples were characterized in detailed descriptive procedure including: location of mud sample, depth, color, smell, etc. The electrical conductivity (EC) was measured by conductivity meter (WTW, LF-320, Weilheim, Germany) and was calibrated by using 0.01 M KCl at 25°C. The seawater pH was measured on sites by using glass electrode pH meter (WTW, pH 523, Weilheim, Germany) that was calibrated based on pH 5 and pH 9 at 25°C, all these data are presented in Table (1).

The collected samples of black mud were stored in polyethylene bags and carried to the laboratory, where they air-dried for two days and stored in Polyethylene bags in cold and dark place. The mud pH values were determined by treating the mud with de-ionized water (soil-to-water ratio = 1:2.5) that was equilibrated over night (Abul-Kashem and Singh 1999).

2.2. Analytical methods

One gram of each black mud sample was accurately weighted, then dried in an oven at 105 °C for 12 hours to reach constant weight in order to determine the moisture content. The weight loss was calculated based on the difference between the final and the initial weights. The same samples were burned in furnace at a 550 °C for 4 hours to determine the organic matter content in the form of Loss On Ignition (LOI), which then was calculated gravimetrically based in the weight difference (Preer et al., 1980).

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2.2.1. Heavy metals extraction

One gram of the mud sample was digested with 15 ml of high purity concentrated HNO₃ by using a 50 ml Polyethylene test tube. The mixture was heated to 95°C for 2 hours by using a water bath, ultrasonicated for 30 minutes at 80°C, then was filtered by Whatman pre-washed filter paper (45 µm) with 1% HNO₃. Then sample was diluted into a 25 ml Polyethylene volumetric flask with 1% HNO₃. Heavy metals (Mn, Pb, Cu, Co, Zn, Cr, Ni and Fe) were analyzed by using a Flame Atomic Absorption Spectrophotometer (FAAS) model Spectra

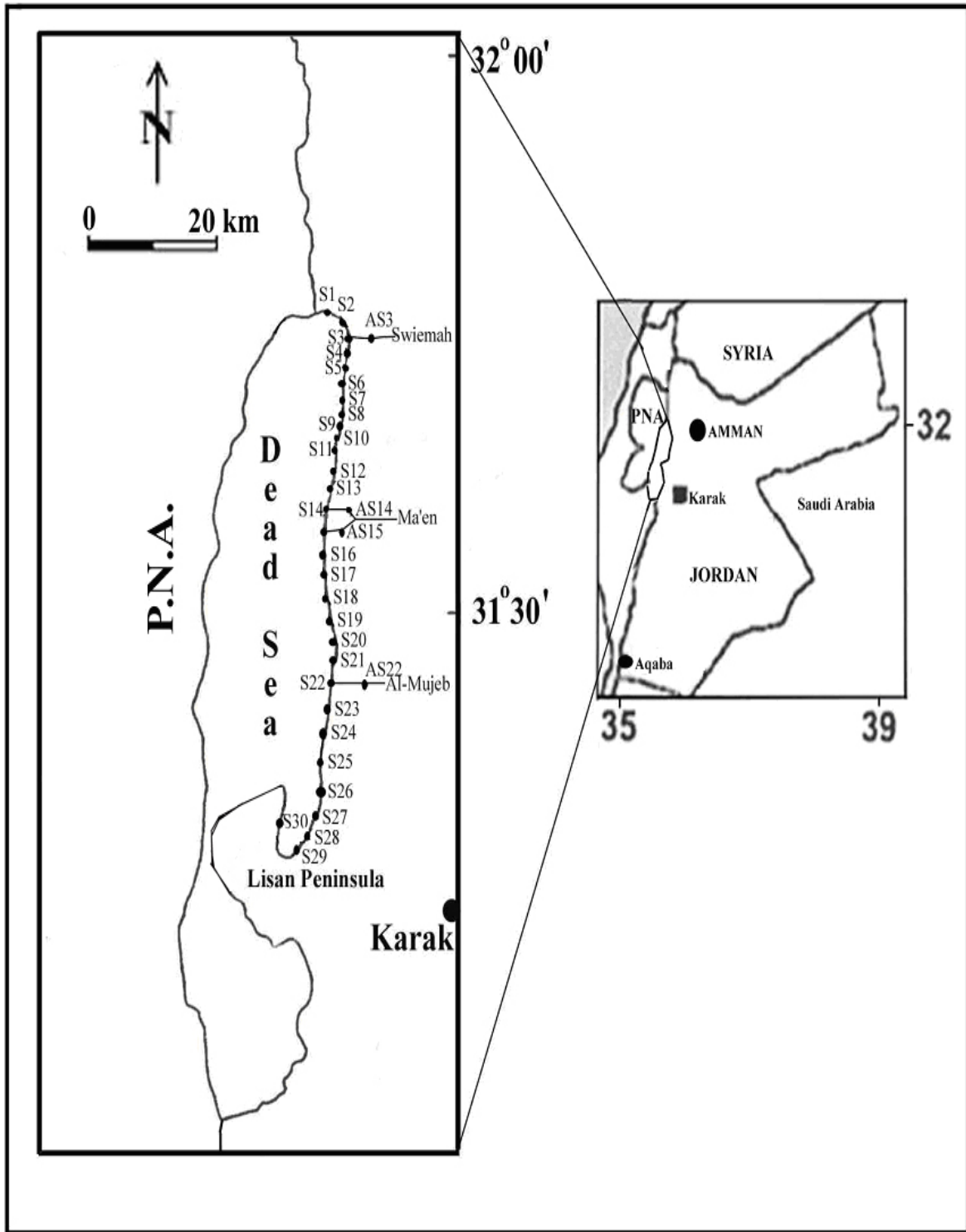


Figure (1): Location map of the study area showing the two basins of the Dead Sea and the samplings sites.

Table 1. Black mud description, location, depth, pH and EC parameters.

Sample	Location	Mud Description color, odor	pH water	EC water (mS/cm)	pH Mud
S1	Salt	Black – bad odor	6.01	180.3	8.05
S2	Salt	Black – bad odor	5.97	181.4	7.80
S3	Mixing	Black – bad odor	6.04	185.7	7.95
AS3	Fresh	White – bad odor	6.97	26.5	7.80
S4	Salt	Black – bad odor	5.92	180.8	8.08
S5	Salt	Black – bad odor	6.03	186.9	8.25
S6	Salt	Black – bad odor	6.05	163.4	8.24
S7	Salt	Black – bad odor	6.05	180.0	8.13
S8	Salt	Black – bad odor	6.04	180.1	7.85
S9	Salt	Black – bad odor	6.05	181.9	8.04
S10	Salt	Red – bad odor	5.91	180.7	7.98
S11	Salt	Black – bad odor	6.02	180.5	7.83
S12	Salt	Black – bad odor	6.28	188.5	7.73
S13	Salt	Black – bad odor	5.95	188.0	7.93
S14	Mixing	White – bad odor	5.94	180.6	8.51
AS14	Fresh	White – bad odor	6.94	10.19	8.31
S15	Mixing	Black – bad odor	5.96	180.7	8.24
AS15	Fresh	White – bad odor	6.84	38.9	8.24
S16	Mixing	Black – bad odor	5.97	180.7	8.02
S17	Salt	Black – bad odor	5.95	181.6	8.03
S18	Salt	Black – bad odor	5.94	181.3	7.99
S19	Salt	Black – bad odor	5.94	180.6	7.83
S20	Salt	Black – bad odor	5.91	181.9	7.95
S21	Mixing	Black – bad odor	5.92	182.1	8.29
S22	Mixing	Black – bad odor	5.92	181.6	8.03
AS22	Fresh	Black – bad odor	7.25	30.9	8.09
S23	Salt	Black – bad odor	6.03	180.6	8.08
S24	Salt	Black – bad odor	6.02	180.3	8.04
S25	Salt	Black – bad odor	6.01	180.6	8.04
S26	Salt	Black – bad odor	6.01	182.9	8.21
S27	Salt	Black – bad odor	5.98	181.0	8.22
S28	Salt	Black – bad odor	6.01	180.8	8.10
S29	Salt	Black – bad odor	6.03	181.9	8.1
S30	Salt	Black – bad odor	6.03	180.7	8.23

Atomic Absorption Varian 800 (Varian, Australia). Quality control was done for Cd, Fe, Zn, Mn, Cu, Ni, Pb and Cr by using (Merck ICP4) standard solutions. The errors were within 95% confidence level.

2.2.2. Sequential extraction procedure

The sequential extraction procedure of (Tessier et al., 1979) was used because it was widely employed in studying the chemical fractionation of soils, dusts and marine sediments (Tessier et al., 1979; Navas and Lindhofer, 2003; Sulkowski and Hirner, 2006 and Momani, 2006).

The quality control procedure including reagent blanks, duplicate samples, and analysis of standard reference material was used to assess precision and accuracy of the obtained data. Blanks were prepared in a similar manner and were analyzed before each measurement. All extractions and analyses were made with duplicate samples for quality control assessment, and the average results were reported. The analytical accuracy for the total heavy metal content was confirmed by analyzing the standard reference material (SRM, soil 7) from the National Institute of Standards and Technology (NIST), USA. The level was better than $\pm 6\%$. The detection limits for heavy metals by using the flame AAS technique (FAAS) of (Varian, 800) are as follows in ($\mu\text{g/l}$): Co

(0.05), Cr (0.06), Cu (0.04), Fe (0.1), Mn (0.02), Ni (0.01), Pb (0.1), and %RSD was less than 1.3.

3. Results and Discussion

3.1. Black mud physicochemical properties

The saltwater mud samples are generally black in color; with few exceptions of reddish black color Table (3). The freshwater mud samples (AS3, AS14, AS15 and AS22) are white in color. The depth ranges from 3-10 cm from mud surface. All freshwater and saltwater mud samples has bad odor, due to higher organic matter content.

The pH value of seawater ranged from 5.91 to 6.28 with an average of 5.99. While the freshwater has higher pH values ranged from 6.84 to 7.25 with an average of 7.05. The pH values of both saltwater ranges: 7.74 to 8.51 with an average of 8.05, and the freshwater mud sample ranges 8.11 to 8.31 with an average of 8.11. Therefore, they possess almost similar average pH; which was above 8; which indicates the alkaline nature of this type of water. The interesting feature was the conversion between seawater pH value (5.99) and saltwater mud pH value (8.05) from mild acidic to alkaline. Therefore, the mild acidic media of the seawater would cause the heavy metals to remain in solution rather than to precipitate into the black mud.

Table 2. Sequential extraction procedure.

Fraction	Procedure
Exchangeable	1 g of sample is extracted with 8 ml of pH = 7, unbuffered 1.0 M MgCl ₂ in Polyethylene centrifuge tubes for 1 hour at 25°C with continuous agitation
Carbonate	Residue from exchangeable fraction extracted with 8 ml of pH 5, 1.0 M NaOAc for 5 hours at 25°C with continuous agitation.
Fe-Mn oxides	Residue from Carbonate fraction, extracted with 20 ml of 0.04 M NH ₂ OH.HCl in 25% acetic acid (v/v) for 5 hours at 96 °C with occasional agitation.
Organic	The residue from Fe-Mn oxides fraction extracted with 3 ml of 0.02 M HNO ₃ and 5 ml of 30% H ₂ O ₂ adjusted to pH 2 with concentrated HNO ₃ . The mixture was heated to 85 °C for 2 hours with occasional agitation. A second 3 ml aliquot 30% of H ₂ O ₂ (pH 2 with concentrated HNO ₃) was then added and the sample was heated again to 85°C for 3 hours with occasional agitation. After cooling, 5 ml of 3.2 M NH ₄ OAc in 20% (v/v) HNO ₃ was added and the sample diluted to 20 ml and agitation continuously for 30 minutes.
Residual	The residue from the organic fraction was digested with 15 ml conc. HNO ₃ , heated to 95°C for 3 hours sonicated for 1 hour at 60 °C, filtered and diluted with 1 % (v/v) HNO ₃ in a 25 ml Polyethylene volumetric flask to the mark and then stored at 4°C until the time of analysis.

The electrical conductivity (EC) of seawater ranges (163.4-188.5 mS/cm) with an average value of 181.27 mS/cm. whereas freshwater samples characterized by low EC values vary from 10.19 to 38.90 mS/cm with an average of 26.62 mS/cm. High EC value of Dead Sea mud compared to freshwater mud can be due to its enrichment with salts and other alkaline minerals such as calcite, aragonite, and gypsum which are often precipitated from saltwater (Abdel-Fattah, 1997).

3.2. Heavy metal abundances

The concentrations of the heavy metals and the Loss On Ignition (LOI) were illustrated in Table (3). Generally, the Dead Sea black mud does not show anomalous or even high heavy metal levels. This might be attributed to the lack of metallic-rich occurrences in the catchment areas of the Dead Sea (Abed, 1985). Furthermore, in the Dead Sea area there are no main sources of pollution compared with other urban areas.

The heavy metals content in the black mud of the Dead Sea was compared with freshwater and saline water sediments such as hemipelagic sediments (Deep Sea sediment), near shore sediments, and freshwater sediments (Lake and River mud), Table (4) and Figures (2a, b, c and d). These figures indicate clearly that most of the heavy metals (Fe, Mn, Cr, Cu, Co and Ni) are depleted in the Dead Sea black mud when compared with hemipelagic mud, lake mud, river mud and the near shore sediments, representing both freshwater and saline water sediments. The only exceptions were Pb and Zn to lesser extent, which were enriched in the Dead Sea black. The findings of this study are in agreement with that reached by (Oumeish, 1996). Moreover, the heavy metals contents of the studied black mud agree with (NRA, 1991). The average of LOI which was obtained by NRA laboratories (37.16 wt%) was higher than what reported in this study (32.69 wt%). This might be attributed to the differences in analytical methods used in LOI measurements, where in this study the LOI was measured at 550°C, following the procedure of (Jaradat et al., 2005). Whereas, the NRA data are measured at 1000°C, which means more structural halogens were evaporated and thus increases the LOI values.

The Dead Sea water is highly enriched with various heavy elements. However, the relative depletion of heavy metals in the Dead Sea black mud, compared with other sediments worldwide, might be attributed as most of these heavy elements are incorporated into salt complexes rather than being precipitated or co-precipitated with neither sediments nor organic matter, Figures (2a, b, c and d). Furthermore, the average saltwater pH value was 5.99, indicating a mild acidic media, which would enhance the heavy metals solubility rather than precipitation. This can explain the enrichment of the heavy metals in the seawater

while it is depleted in the black mud. Similar findings were reported by several researchers (Oumeish, 1996; Nissenbaum, 1969 and 1974).

3.3. Speciation of heavy metals in the black mud

The sequential extraction results in grouping the heavy metals, based on their preferred phases as following: carbonate phase [Ni and Co], Fe-Mn Oxides [Mn], residual phase [Cr, Cu, Fe and Pb]. There were no preferences of any metal to the exchangeable and organic phases. The correlation coefficients of heavy metals and LOI are in agreement with the sequential extraction results, Table (6). The correlation coefficient results showed that none of the heavy metals have positive correlation with Loss On Ignition (LOI) and Mn. This might be interpreted that none of them preferred the organic phase. Particularly, Mn had no significant correlation with any other metals confirming the fact that Mn is associated with iron-manganese oxides phase only. The manganese was found on the Dead Sea shores as black incrustations in form of Mn-Oxides such as psilomelane, cryptomelane and pyrolusite (Garber et al., 1981). This would explain the reason why Mn was confined particularly to this phase.

Moreover, Cr, Cu and Fe had significant correlations with each other, Ni and Co that had moderate correlation values while a positive correlation among Cu, Cr and Zn was observed. Nevertheless, the combination between sequential analysis and correlation coefficient was highly in agreement with each other, where these groups of heavy metals are concentrated in the residual fraction. These results were found in agreement to high extent to those findings of heavy metals in the Dead Sea sediments (Nissenbaum, 1974).

Table 3. Table showing the average heavy metal concentrations (mg/kg) and LOI (wt%) in the saltwater mud samples.

Sample	Fe	Cu	Ni	Zn	Cr	Mn	Co	Pb	LOI
S1	1230.8	9.2	31.4	16.3	25.6	195.8	10.0	59.5	27.6
S2	1348.0	10.8	33.3	19.9	31.4	324.9	11.0	62.0	34.2
S3	1610.3	12.9	43.8	29.3	39.7	380.9	12.0	68.0	36.7
S4	1579.3	13.3	36.2	25.5	34.3	365.8	10.0	56.3	36.3
S5	1318.5	11.0	35.7	26.4	33.5	288.6	9.0	58.3	28.4
S6	1232.8	12.4	41.4	43.1	36.1	348.7	11.0	72.0	32.9
S7	1386.0	12.0	48.3	45.6	42.8	140.2	7.0	55.3	31.1
S8	855.8	12.5	66.4	52.7	35.0	206.4	10.0	61.0	33.4
S9	926.8	10.7	60.5	38.9	36.5	216.9	7.0	58.5	34.0
S10	1725.3	5.1	45.9	9.5	41.0	393.6	6.0	42.5	30.5
S11	1086.0	11.1	64.3	29.1	38.5	227.6	11.0	49.5	35.8
S12	1270.0	13.1	63.9	26.9	42.4	320.3	12.0	64.7	32.2
S13	1100.0	13.0	62.9	37.2	42.3	234.8	11.0	70.8	33.2
S14	1240.5	12.7	64.2	31.8	39.6	293.8	15.0	52.8	31.0
S15	1999.0	13.1	59.1	30.7	35.4	189.9	14.0	65.8	22.2
S16	1344.5	10.9	56.9	29.9	37.5	255.7	13.0	61.3	36.0
S17	1331.0	12.4	61.4	46.5	44.7	167.2	13.0	57.5	33.5
S18	746.5	8.6	51.7	17.5	32.7	109.5	11.0	58.5	31.3
S19	365.3	5.5	41.8	9.0	23.9	176.1	9.0	29.5	31.0
S20	1584.8	15.2	68.7	46.2	50.2	150.2	13.0	47.0	33.7
S21	1873.3	15.2	71.7	66.7	59.5	114.2	13.0	60.0	31.8
S22	1736.3	14.7	66.8	38.2	56.4	143	12.0	53.8	32.8
S23	1589.3	16.2	69.0	96.8	48.7	131.0	14.0	58.3	34.7
S24	1624.3	15.7	68.1	69.7	50.4	136.7	12.0	49.3	35.2
S25	1610.8	16.7	72.1	67.3	51.2	145.2	13.0	46.3	32.5
S26	924.0	12.4	61.9	32.2	43.2	99.2	9.0	51.0	34.8
S27	1530.8	12.2	62.7	42.1	53.8	162.4	9.0	53.8	32.3
S28	1503.3	16.0	68.7	46.0	47.6	118.3	10.0	73.8	33.2
S29	1167.8	13.1	62.4	38.7	45.2	121.2	9.0	62.5	33.1
S30	2137.5	18.9	73.2	70.3	65.6	285.3	13.0	60.8	32.9
Mean	1365.9	12.6	57.2	39.3	42.2	214.8	11.0	57.3	32.6
Max.	2137.5	18.9	73.4	96.8	65.6	393.6	15.0	73.8	36.7
Min.	365.3	5.1	31.4	9.0	23.9	99.2	6.0	29.5	22.2
σ	324.5	3.0	19.6	9.7	12.8	78.8	3.79	9.3	2.9

Table 4. Comparison of heavy metal contents in several types of mud and sediments from freshwater and saline water, all are in ppm except Fe in wt%

Elements	Dead Sea This Study*	Hemipelagic Mud ¹	Lake Mud ²	River Mud ¹	Near Shore Sediments ³
**Fe	0.195	4.75	3.64	3.4	-
Mn	254	760	378	620	850
Cu	13	30	29	32	48
Co	12	20	57	14	13
Cr	43	97	68	85	100
Ni	58	53	40	32	55
Zn	39	24	73	23	95
Pb	58	130	27	78	20

*The data is for saltwater mud samples only.

**Fe as Fe₂O₃ (% by mass); ¹ Govindaraju, (1989); ² Dasa, et al., (2006); ³ Wedepohl, (1960)

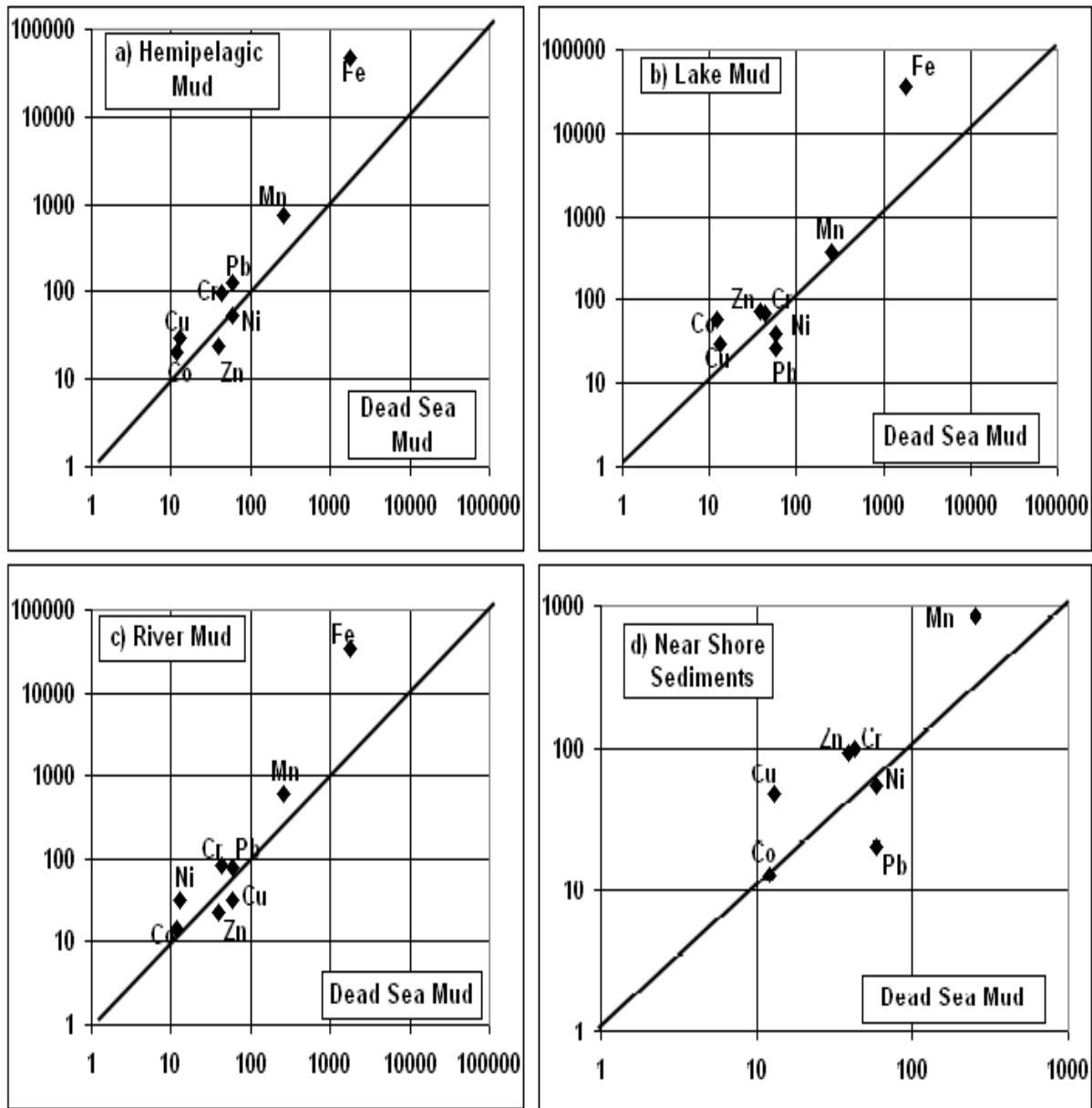


Fig. (2): 1:1 ratio scatter plot shows the comparison of heavy metals between the Dead Sea Mud and (a) Hemipelagic mud and (b) Lake mud (c) River mud and (d) Near Shore sediments.

Table 5. Distribution of heavy metals based on sequential extraction in various chemical fractions of black mud.

Sites	Fraction	Cr	Mn	Cu	Ni	Co	Fe	Pb
S1	Exchangeable	4.0	5.8	0.8	5.3	2.0	0.3	1.3
	Carbonate	6.0	33.5	3.5	12.0	4.0	5.7	7.8
	Fe-Mn Oxides	5.5	109.8	1.3	5.3	1.9	156.2	7.0
	Organic	2.0	33.5	3.5	5.5	1.5	478.9	8.8
	Residual	7.0	13.8	4.0	5.0	1.8	607.1	18.3
S6	Exchangeable	4.0	7.3	0.8	4.3	1.5	1.2	0.8
	Carbonate	7.5	42.5	3.8	12.8	4.1	1.4	5.5
	Fe-Mn Oxides	9.0	216.3	1.8	7.8	2.8	65.0	7.5
	Organic	3.0	36.5	2.8	6.8	1.3	322.6	7.0
	Residual	11.0	33.5	4.5	6.3	1.8	631.2	20.0
S15	Exchangeable	4.5	6.3	0.8	5.3	1.5	0.3	2.5
	Carbonate	8.5	33.3	3.8	14.8	4.3	4.6	5.8
	Fe-Mn Oxides	9.0	108.3	1.0	5.3	2.2	133	7.3
	Organic	4.0	22.0	2.0	3.3	0.8	228.9	9.3
	Residual	10.5	12.8	4.0	6.0	1.7	581.1	25.8
S22	Exchangeable	5.0	15.8	0.8	6.3	1.6	1.3	4.3
	Carbonate	8.5	52.0	3.8	18.3	4.2	18.9	6.8
	Fe-Mn Oxides	10.0	45.3	2.0	6.8	1.9	568.6	9.0
	Organic	9.0	14.0	1.8	5.8	0.5	426	8.0
	Residual	19.0	26.5	7.3	10.8	2.1	758	22.3
S28	Exchangeable	5.0	14.8	0.8	7.3	1.6	0.4	4.0
	Carbonate	7.5	15.5	3.8	17.8	4.1	2.3	9.8
	Fe-Mn Oxides	10.5	49.5	1.3	8.0	2.2	127.1	7.8
	Organic	5.5	35.5	3.8	7.0	1.2	535.6	11.8
	Residual	12.0	13.0	3.8	6.5	1.4	744.5	25.3

Table .6. Correlation coefficient matrix; significance threshold at 99% confidence level is (0.4357) (n=34)

	Fe	Cu	Cr	Zn	Ni	Pb	Co	Mn	LOI
Fe	1.00								
Cu	0.52	1							
Cr	0.56	0.76	1						
Zn	0.42	0.74	0.69	1					
Ni	0.27	0.66	0.75	0.67	1				
Pb	0.17	0.37	0.07	0.1	0.002	1			
Co	0.23	0.64	0.42	0.37	0.42	0.23	1		
Mn	0.00	0.17	0.04	-0.16	-0.18	0.23	0.35	1	
LOI	0.17	-0.04	-0.10	0.09	0.07	-0.13	-0.37	-0.49	1

3.4. Effect of mixing with freshwater

The samples were divided into two groups, based on Table (1): (a) Normal samples which are totally covered by Dead Sea saltwater alone (thirty samples), (b) Mixed samples, those affected by the mixing of freshwater and Dead Sea saltwater, and they were seven samples namely (S1, S2, S3, S14, S15, S21 and S22), those samples are

located in front of the big tributaries at Swimah, Zarqa-Ma'en and Al-Mujeb. The comparison of the heavy metal concentrations with LOI values for the mud samples in the mixed water and Dead Sea saltwater showed no significant difference across them, thus no effect of the mixing processes was dominant, Fig. (3).

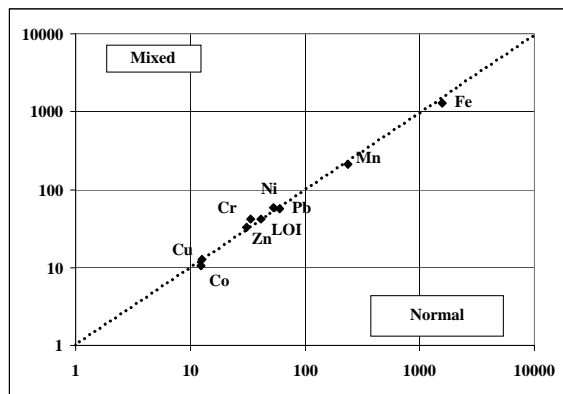


Fig. (3): 1:1 ratio scatter plot to compare the average heavy metals and LOI between the mixed water and normal seawater samples.

4. Conclusion

The heavy metal levels in the Dead Sea black mud samples were depleted comparatively to other saline and freshwater sediments worldwide. This might be attributed to the fact that there are no geological exposures of metallic rich deposits in the catchments area of the Dead Sea. The mud samples are not exposed to anthropogenic pollution sources such as aerial deposition. Although Dead Seawater is rich in heavy metals, the black mud is depleted in the most of trace elements. Thus, it was found that heavy metals prefer to be incorporated in the soluble salt complexes rather than precipitating due to the mild acidic environment of the Dead Sea water.

The findings of the sequential extraction and the analysis of correlation of various chemical parameters showed that none of heavy metals preferred the organic phase of the black mud. Finally, there was no effect of mixing the freshwater entering the Dead Sea from surrounding streams with saltwater on the components of the Black mud.

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