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Assessment of Natural Radioactivity and Some Heavy Metals Contamination along Aqaba Gulf, Egypt

Abou Bakr Ramadan[1], Hanan M. Diab[1], E. A. Saad[2], Amir E. A. El Hassan[2], M. Shahin[1]

[1]*Nuclear and Radiological Regulatory Authority,Egypt*
[2]*Ain Shams University, Egypt*
Corresponding Auther:Abou Bakr Ramadan

Abastract:*Aqaba Gulf is an economically important marine environment in Egypt. Its coastal area was subjected to anthropogenic impact of urbanization and economic development during the last decades. The study was oriented to investigate the natural radioactivity levels as well as assess the physicochemical properties of marine water and heavy metal pollution in selected some environmental samples like shore sediment, water and algae samples collected from 18 sites along the Egyptian coastline of the Gulf of Aqaba. The samples were prepared and the activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the samples were measured using Hyper Purity Germanium detector. The results for the measurements of natural radioactivity revealed that, the mean average of absorbed dose rate (D), annual effective dose rate (AEDE), radium equivalent (Ra_{eq}), external and internal hazard indices and the total hazard index (H_{ex}+H_{in}) fall within the worldwide averages. The Transfer Factor (TF) average values were 0.19, 0.13, and 2.65 for ^{238}U, ^{232}Th and ^{40}K, respectively. The TF for ^{40}K was greater than unity, which means that 40K was bio accumulated in algae and available in marine environment. The recorded and calculated values were lower than the acceptable limits published in the different localities around the world. The investigations of the physicochemical properties of the surface water indicated that there no significant change was observed in the water temperature, TDS, salinity, pH levels and well-oxygenated seawater. In general, the concentrations levels of heavy elements in seawater and shore sediments in northern part of the Gulf were higher than the concentrations in southern part for most of the elements where there are human activities. The results also suggest that the majority of the Egyptian coast is not polluted or seriously affected by human activities in spite of rapid recreational and residential developments in the area during the past period.*

Keywords:*Aqaba Gulf, Radioactivity, Radiological Hazard Indices. Heavy Metals, Environmental samples*

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I. Introduction

The Gulf of Aqaba in the northern Red Sea is a warm water body, approximately 180 km long and on average 8 km wide. It is a deep basin with narrow shelves, which comprises two isolated depressions separated by a submarine sill. The northern depression is about 1,100 m deep and the southern depression is about 1,420 m deep. The maximum depth within the Gulf of Aqaba is observed near the east coast with a depth of 1,829 m. The maximum depth within the Gulf of Aqaba is observed near the east coast with a depth of 1,829 m. It has a hot and dry climate with rare rainfall. The Gulf of Aqaba is a marine environment enclosed by arid lands that experience extremes of temperature and exceedingly low levels of precipitation. These conditions have led to the evolution of unique, and hence internationally important, coral reef and marine ecosystems, which are particularly susceptible to damage from pollution or other forms of environmental impact. The Gulf is of significant strategic and economic value to all gulf-bordering states, particularly to Jordan, where it provides Jordan with its only marine outlet. Lack of significant wave activity along with the low rate of water circulation and renewal, among others, render the Gulf particularly susceptible to pollution. Thus, the impact of intense and widespread human activities from the neighboring countries, poses a potential threat to the Egyptian coast. Evidence of human impact has been documented[1,2].

Studies on radiation levels and radionuclide distribution in the environment provide vitalradiological baseline information. Such information is essential in understanding human exposure from natural and man-made sources of radiation and necessary in establishing rules and regulations relating to radiation protection [3,4].

In marine environment, radio-nuclides transferred through seawater by terrestrial radiation that originates predominantly from the up-per 30 cm of the soil and cosmic rays, which fall out of the atmosphere

into marine environment by direct or indirect processes. Three primordial long-lived radionuclides are known as sources of natural radioactivity: ^{238}U, ^{232}Th and ^{40}K.

Natural radio-nuclides especially ^{238}U and its progenies are settled at the seafloor through many processes like fixation on suspended particulate matter and sedimentation, direct precipitation of colloidal forms, adsorption on clay minerals and complexion with organic material [5]. On the other hand, anthropogenic radionuclides are produced from man-made activities (nuclear and non-nuclear industries) such as phosphate industries, coal combustion, cement production, and other industries [6,7]. Many studies had been presented worldwide to determine both the natural and artificial radioactivity in marine environment. Unfortunately, few studies investigated the radioactivity levels at the Egyptian coastline in Aqaba.

Among the pollutants are heavy metals that are known by their toxic serious threats on marine environments. Heavy metals have a considerable environmental concern. Also, they possess wide sources, non-biodegradable properties, and accumulative behaviors. When metals enter into the marine environment, most of them will settle down. Additionally, heavy metals can incorporate marine sediments together with organic matters, Fe/Mn oxides, sulfides, and clay. Indeed, sediments act as scavengers for trace metals and often provide an excellent proof of man's impact [8].

The purpose of this study is to determine the levels of radiological measurements for a large number of different types of samples like soil, shore sediment, algae, plant and water collected from different sites along the coastline of the Gulf of Aqaba (Fig. 1) in order to construct baseline information for radioactivity in this area and to detect if there is any artificial contamination by TENORMs.The obtained data will be used to determine the radiological hazards due to the different anthropogenic stress by calculating radium equivalent, the absorbed dose rate, annual effective dose rate, the internal and external hazard index and the excess lifetime cancer risk. The study also, assesses the current status and spatial distribution of trace elements along the Egyptian coastline and to identify potential sources of contamination. This evaluation helps develop effective coastal management guidelines and strategies for better management of coastal activities

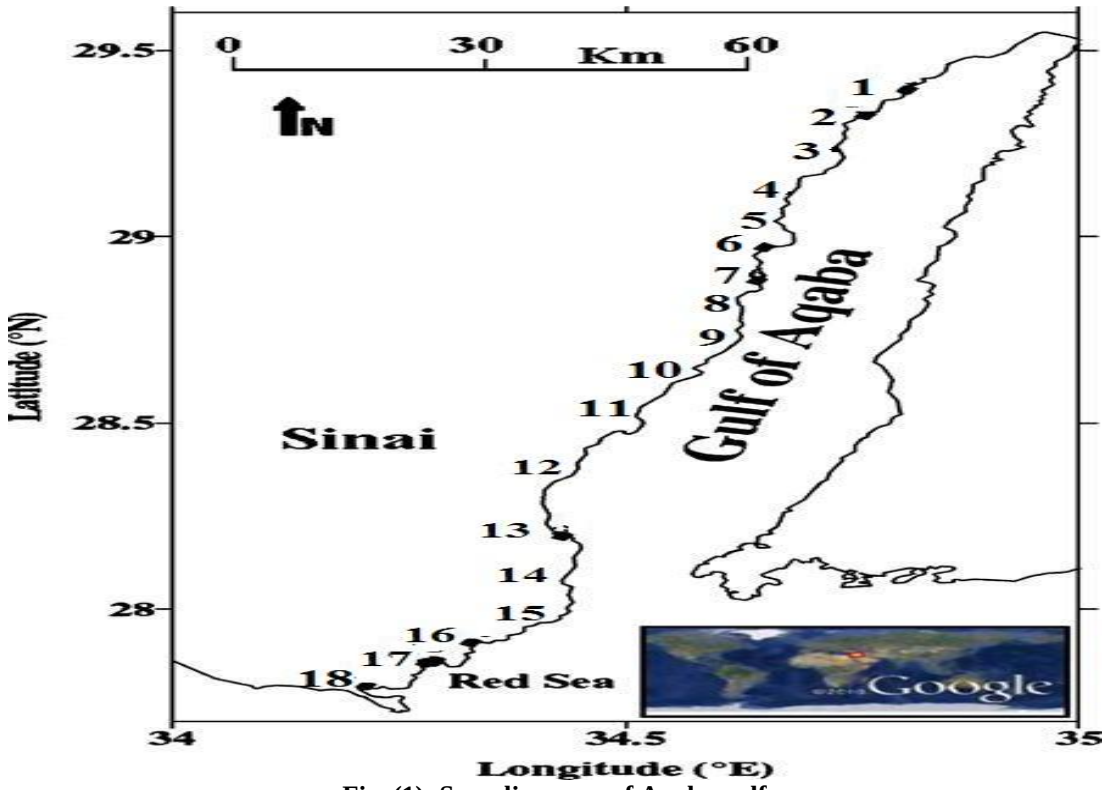

Fig. (1): Sampling map of Aqaba gulf

II. Experimental Work

II.1 Sampling and Sample Preparation for Gamma Spectrometry:

Sampling process was conducted during the period in April 2016.Sixteen shore sediment samples, four algae samples and seventeen water samples were collected from the area under study. Preparation of shore sediment samples for γ-ray measurements were carried out by drying the samples in an oven at a temperature of 105^{o}C. For algae, the samples were dried for 48 hour in an oven at temperature of 70^{o}C [9]. They were weighed before and after drying to determine its water content, and then minced homogenized. The prepared samples

were weighed, packed and sealed in polyethylene plastic container for gamma-ray analysis. The samples were prepared at the Central Laboratory for Environmental Radioactivity Measurements, Inter-comparison and Training (CLERMIT), Nuclear and Radiological Regulatory Authority (NRRA) in Cairo. The water samples were prepared volumetrically packed in polyethylene containers sealed and left nearly one month to reach secular equilibrium between radium and thorium and theirprogenies [10,11]. Measurements of the activity concentrations of ^{238}U, ^{232}Th and^{40}K in Bqkg^{-1} dry wt. of the collected samples were carried out using γ-ray spectrometry based on highly pure germanium coaxial detector (HPGe) of40% relative efficiency [10,11]. The resolving power of the spectrometer wasfound to be 1.92 keV for 1332 keV gamma-ray line of ^{60}Co. The detector wascoupled with an 8192-channels computer analyzer and GENIE 2000 software. The measurement time for gamma spectrometry was 80,000s [10]. The IAEAstandard reference materials RGU-1, IAEA-375,IAEA-326 and IAEA-444 were used for the spectrometer efficiency calibrationin the same geometry of the sample measurements. The gamma transitions used foractivity calculations of ^{40}K were 1460.7 keV [12].

II.2 Calculation of Radiological Effects:

II.2.1 Radium equivalent activity (Ra_{eq}):

The distribution of ^{238}U, ^{232}Th and ^{40}K in sediments is not uniform. Uniformity with respect to exposure to radiation has been defined in terms of radium equivalent activity (Ra_{eq}) in BqKg^{-1} to compare the specific activity of material containing different amounts of ^{238}U, ^{232}Th and ^{40}K. This radium equivalent activity represents a weighted sum of activities of ^{40}K, ^{238}U and ^{232}Th radionuclides and is based on the estimation that 1Bq/kg of ^{226}Ra, 0.7Bq/kg of ^{232}Th, and 13Bq/kg of ^{40}K produce the same radiation dose rates. It is calculated from the following relation [13]:

$$\mathbf{Ra_{eq} = C_{Ra} + 1.43C_{Th} + 0.077C_K} \quad \textbf{(1)}$$

Where C_{Ra}, C_{Th} and C_K are the radioactivity concentration in Bq/kg of ^{238}U, ^{232}Th, and ^{40}K, respectively.

2.2 Dose rate calculation:

The absorbed dose rate was calculated from the measured activities of ^{238}U, ^{232}Th and ^{40}K in the shore sediment samples using the formula of [14].

$$\mathbf{D(nGyh^{-1}) = 0.462C_u + 0.604C_{Th} + 0.042C_K} \quad \textbf{(2)}$$

where **D**, is the absorbed dose rate (nGyh^{-1}). C_U, C_{Th} and C_K are the activity concentrations (Bqkg^{-1}) of ^{238}U, ^{232}Th and ^{40}K respectively. To estimate the annual effective dose rates, the conversion coefficient from absorbed dose to effective dose, 0.7 SvGy^{-1} and outdoor occupancy factor of 0.2 proposed by [15] were used.

II.2.3 Annual effective dose equivalent (AEDE):

The annual effective dose (mSvy^{-1}) was calculated by the formula of [16]:

$$\mathbf{AEDE(mSvy^{-1}) = D(nGyh^{-1})x8760hx0.2x0.7SvGy^{-1}x10^6} \quad \textbf{(3)}$$

Where, 0.2 is the occupancy factor for outdoor, 8760 is the total time of the year in hours and 0.7 SvGy^{-1} is the conversion factor for external gamma irradiation.

II.2.4 External hazard index (H_{ex}) and internal hazard index (H_{in}):

The external hazard index (H_{ex}) represents the external radiation exposure associated with gamma irradiation from radionuclides of concern. The value of H_{ex} should not exceed the maximum acceptable value of one in order to keep the hazard insignificant. The external hazard index (H_{ex}) and internal hazard index (H_{in}) were defined by equations (4,5) [17]:

$$\mathbf{H_{ex} = (C_u/370 + C_{Th}/259 + C_K/4810) \leq 1} \quad \textbf{(4)}$$

$$\mathbf{H_{in} = C_{Ra}/185 + C_{Th}/259 + C_K/4810 \leq 1} \quad \textbf{(5)}$$

II.2.5 Representative level index ($I\gamma$):

It is used to estimate the gamma radiation hazard associated with the natural radionuclide in specific investigated samples. It is given by the equation:

$$\mathbf{I\gamma = C_{Ra}/150 + C_{Th}/100 + C_K/1500} \quad \textbf{(6)}$$

Where C_{Ra}, C_{Th} and C_K are the radioactivity concentration in Bq/kg of ^{238}U, ^{232}Th, and ^{40}K[18].

II.3 Field and in-situ measurements of physico-chemical Characteristics

For water samples analysis, the electrical conductivity, salinity, oxidation reduction potential (ORP), pH, total dissolved solids (TDS) and temperature were measured in-situ. These parameters were determined online by using a portable multi-meter model 197i from WTW (WissenschaftlicheWeilheim) in combination with special probes for conductivity, oxygen content, pH and redox potential including a built in temperature

sensor. Before their first use the sensors were calibrated and checked with corresponding standard solutions for specific conductance and pH, and the partial pressure of oxygen in water-saturated air for dissolved oxygen.

II.4 Samples preparation for Inductively Coupled Plasma:

For shore sediments, microwave digestion system was used.Fissured it according to the program; filtered the obtained extract in 50 ml measuring retort, washed off residue on the filter with deionized water; measured metals in the obtained filtrate. For algae samples the wet digestion was used with strong oxidizing acids to yield a cleaner decomposition mixture.For surface water, the samples were stored in a polyethylene bottle in the dark at a temperature of 4°C for metal analysis (Acidification). All samples were filtrated before analysis through a 0.45µm filter (GHP-Filer, Pall, Germany). Heavy Metals in the sediment, water and algae were determined using ICP-OEs (Varian Liberty 150) and AAS (SeptrAA-800, Varian, Germany). Calibration standards were prepared from 1000 ppm solutions (VWR Company, Darmstadt, Germany). If necessary the samples were diluted with 5.0% HNO_3. To check the validity of the calibration to each sample sequence several standard samples were considered.

III. Results And Discussion

III.1 Analysis of Radionuclides in the samples collected from the Egyptian coast of the Aqaba Gulf.

III.1.1 Shore sediment samples

The activity concentrations of ^{226}Ra (^{238}U series), ^{232}Th series and ^{40}K in the collected shore sediment samples areshown in Table1 and Fig. 2.The ^{226}Ra concentrations vary between (4.6 ± 0.3- 21.2 ± 0.9) Bq/kg with an average (12.9 ± 0.6) Bq/kg while ^{232}Th concentrations vary between (3.9 ± 0.4 - 27.9 ± 0.9) Bq/kg with an average (11.57 ± 0.6) Bq/kg and ^{40}K (47.5 ± 2.3 - 1182.5 ± 11.8) Bq/kg with an average (623.4 ± 7.1) Bq/kg.From the data obtained, it can be shown that there is a wide range of the measured activities along Aqaba Gulf (sample 6, 8 and 12 with comparable with samples 4, 7, 9 and 15). This may be attributed to their physical, chemical and geo-chemical properties and the pertinent environment. Mean while in Egyptian soil, the average activities of ^{226}Ra (^{238}U) series, ^{232}Th series and ^{40}K are 17 (5–64), 18 (2–96) and 320 (29–650) Bq/kg dry weight, respectively [15].

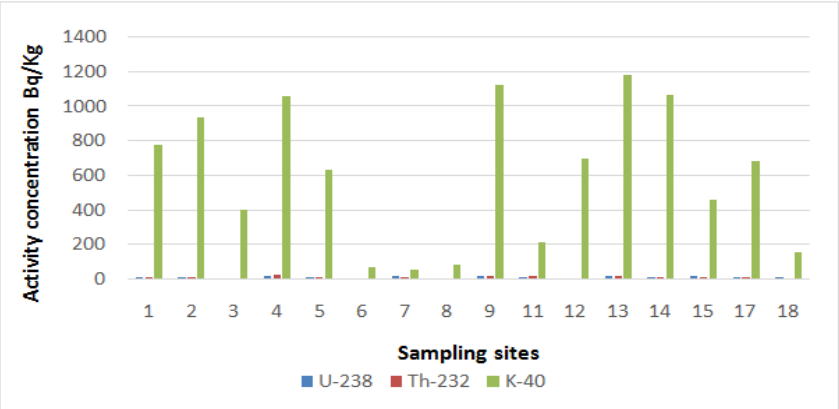

Fig. (2): The activity concentration of ^{238}U (^{226}Ra), ^{232}Th and ^{40}K (Bqkg^{-1}) in shore sediment samples

Table (1): Activity concentrations of ^{238}U, ^{232}Th and ^{40}K (Bqkg^{-1}) in shore sediments

Point	^{238}U	^{232}Th	^{40}K
1	11.3 ± 0.5	8.2 ± 0.5	774.2 ± 9.5
2	12.3 ± 0.7	10.9 ± 0.7	937.5 ± 12.9
3	8.1 ± 0.5	6.6 ± 0.5	401.2 ± 6.9
4	20.6 ± 0.8	27.9 ± 0.9	1056.0 ± 9.4
5	10.6 ± 0.5	11.9 ± 0.6	631.3 ± 8.6
6	4.6 ± 0.3	4.0 ± 0.3	63.2 ± 2.2
7	20.5 ± 0.8	11.1 ± 0.6	47.5 ± 2.3
8	6.6 ± 0.6	3.9 ± 0.3	77.8 ± 2.4
9	21.2 ± 0.9	16.0 ± 0.7	1125.9 ± 10.2
11	10.1 ± 0.6	16.1 ± 0.7	207.4 ± 5.1
12	7.1 ± 0.5	6.7 ± 0.5	696.7 ± 9
13	18.0 ± 0.7	16.7 ± 0.7	1182.5 ± 11.8
14	10.7 ± 0.5	7.8 ± 0.5	1069.4 ± 11.1
15	20.9 ± 0.6	14.1 ± 0.6	459.4 ± 5.8
17	10.6 ± 0.4	7.8 ± 0.4	684.6 ± 7.2
18	9.6 ± 0.6	3.9 ± 0.4	151.8 ± 3.8

The contour map for shore sediment samples along the area under study for ^{238}U (^{226}Ra), ^{232}Th and ^{40}K ($Bqkg^{-1}$) are shown in (Fig. 3).

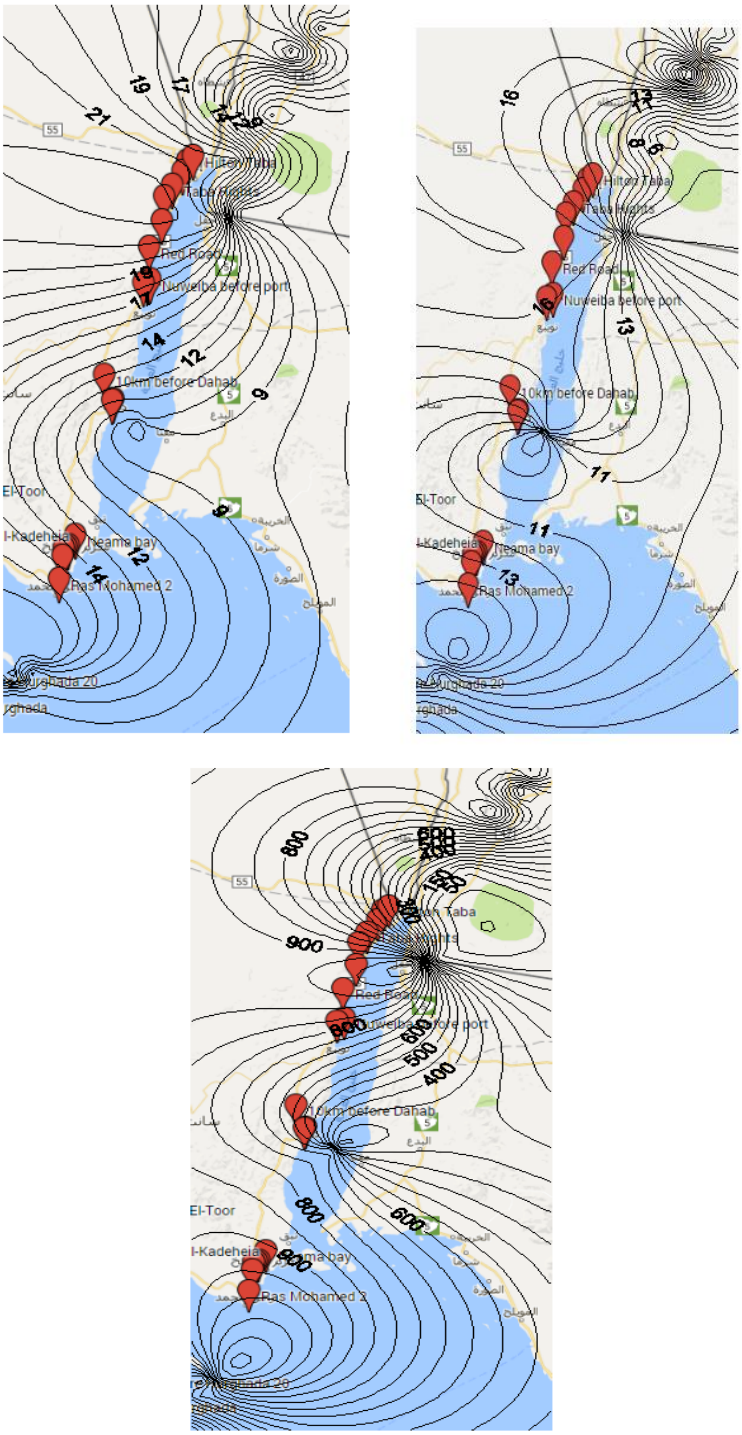

Fig. (3):Contour map: Distribution of ^{238}U (^{226}Ra), ^{232}Th and ^{40}K ($Bqkg^{-1}$) for the shore sediments samples along Aqaba gulf

III.1.2 Algae samples

The specific activity concentrations of the radionuclides ^{226}Ra (^{238}U series), ^{232}Th series and ^{40}K in the collected algae samples considered in our study are presented in Table (2).The data obtained, Shown that it can be seen that the ^{226}Ra concentrations vary between (2.8 ± 0.2- 8.2 ± 0.7) Bq/kg with an average (5.2± 0.5) Bq/kg while ^{232}Th (3.8 ± 0.3- 10.3 ± 0.8) Bq/kg with an average (6.5 ± 0.5) Bq/kg and ^{40}K (134.9 ± 4.5 - 676 ± 8.9) Bq/kg with an average (380.9 ± 10.7) Bq/kg. The contour map for algae samples along the area under study for ^{238}U, $^{232}Th$and ^{40}K are shown in Fig. (4).

Table (2): Activity concentrations of ^{238}U, ^{232}Th and ^{40}K in algae samples (Bqkg^{-1})

Point	^{238}U	^{232}Th	^{40}K
5	4.614 ± 0.48	10.32 ± 0.78	332.04 ± 8.34
6	8.22 ± 0.66	3.402 ± 0.3	134.928 ± 4.5
13	2.796 ± 0.24	5.868 ± 0.42	676.08 ± 8.34
18	3.072 ± 0.24	2.754 ± 0.3	181.8 ± 5.82

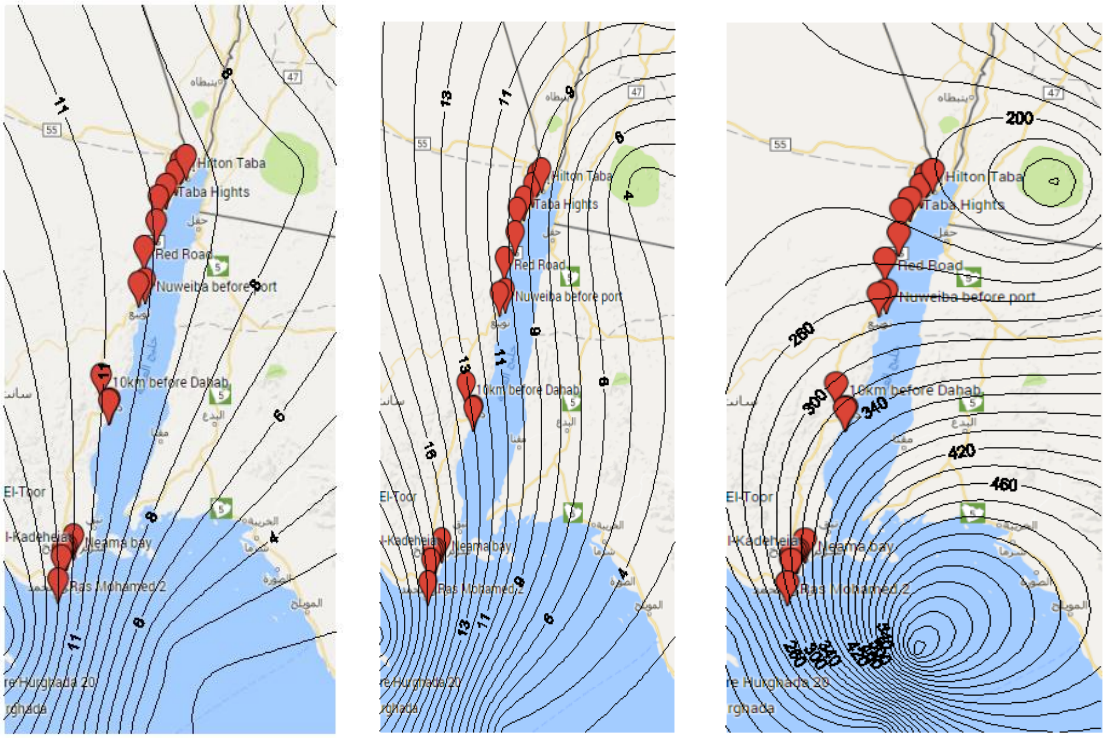

Fig. (4): Contour map: Distribution of ^{238}U, ^{232}Th and ^{40}K (Bqkg^{-1}) for the Algae samples along Aqaba gulf.

III.1.2.1 Transfer factor (TF)

The transfer of radionuclides factor (TF) is the ratio of activity concentration of certain radionuclide in algae to its activity concentrations in sediments [19]. The activity concentrations of sediments were calculated. Radionuclide bioaccumulation exists in aquatic organisms when TF > 1. The higher the TF value, the more mobile and available of this element is in the surrounding ecosystem. TF of ^{238}U, ^{232}Th and ^{40}K were calculated for algae samples collected from some sites. The TF average values were 0.19, 0.13, and 2.65 for ^{238}U, ^{232}Th and ^{40}K, respectively. The TF for ^{40}K was greater than unity, which means that 40K was bio accumulated in algae and available in marine environment.

III.1.3 Water samples

The activity concentrations of the natural radionuclides ^{226}Ra, ^{232}Th series were below the detection limit of the gamma spectrometry in all water samples. The activity concentration of ^{40}K in the collected water samples were ranged from the detection limit to 78.61 Bqkg^{-1}as shown inTable(3).Potassium is the seventh most abundant element in the crust of the earth and the sixth most abundant element in solution in the oceans [20].

Table (3): Activity concentration of ^{40}K(Bqkg^{-1})in water samples collected from the Gulf.

Sampling No.	^{40}K(Bqkg^{-1})	Sampling No.	^{40}K(Bqkg^{-1})
1	52.9 ± 2.8	11	78.61 ± 3.8
2	41.46 ± 2.2	12	50.05 ± 2.7
3	< DL	13	66.18 ± 3.2
4	38.89 ± 2.4	14	52.61 ± 2.8
5	55.77 ± 3.3	15	53.06 ± 2.8
6	40.7 ± 2.5	16	59.39 ± 3
7	76.13 ± 3.4	17	13.87 ± 1.4
8	25.61 ± 1.8	18	23.06 ± 1.9
9	42.68 ± 2.3		

The detection limit of the device used is 0.2, 0.2 and 0.6 (Bq/kg) for Ra-226, Th-232 and K-40 respectively.

III.2 Radiological hazard indices

The radiological hazards indices: radium equivalent activity (Ra_{eq}), absorbed dose rates (D), annual effective dose (AED), external and internal hazard indices (H_{ex} and H_{in}) and the representative level index (I_γ) were calculated and listed in Table (4). The results obtained show that the radium equivalent activity (Ra_{eq}) values for the shore sediment samples varied from 15.2 to 141^{-1}Bq kg^{-1}, with an average of 73.9Bq kg^{-1}. This average is below 370 Bq/kg, which is acceptable for safe use as building materials by the [21]. The mean absorbed gamma dose in the air was lower than the world average of 57 nGy $h^{-1}$with an average of 37.4nGy h^{-1}[15]. The lowest dose rates were found in the surface layer of public beach, whereas the highest dose rates were at the surface layer of rocky area.The calculated average values of external and internal hazard index obtained in this study were lower than unity in all samples, so we can conclude that the radiation hazard is acceptable in Aqaba shore sediment samples. The calculated values of annual effective dose ranged from 0.03 to 0.34 mSv y^{-1}, with a mean value of 0.17 mSv y^{-1}, which is below the world average of 0.48 mSv y^{-1}[15]. The Representative Level Index ($I_{\gamma r}$) is used to estimate the hazard from Gamma ray associated with natural radioactivity. An increase in the Representative Gamma Index greater than the world's standard value of unity may cause a severe damage to human beings and hence causes cancers. The values inshore sediment samples ranged from 0.11 to 1.11 with average value 0.58Bq/kg. The average value of $I_{\gamma r}$ indicates no health risks from the exposure to sediment of Aqaba gulf as its value lies below 1Bq/kg.

Table (4): Radiological Hazards Indices inthe Egyptian coast of Aqaba gulf

Point	Type	Ra eq.	D	AED	I_{yr}	H_{ex}	H_{in}
1	Shore 1	82.4	42.5	0.2	0.67	0.22	0.25
2	Shore 2	100	51.5	0.25	0.81	0.27	0.3
3	Shore 3	48.4	24.5	0.12	0.38	0.13	0.15
4	Shore 4	141	70.8	0.34	1.11	0.38	0.43
5	Shore 5	76.1	38.5	0.18	0.6	0.2	0.23
6	Shore 6	15.2	7.25	0.03	0.11	0.04	0.05
7	Shore 7	39.8	18.2	0.08	0.27	0.1	0.16
8	Shore 8	18.1	8.68	0.04	0.13	0.04	0.06
9	Shore 9	130	66.6	0.32	1.05	0.35	0.41
11	Shore 11	48.9	23.2	0.11	0.36	0.13	0.15
12	Shore 12	70.3	36.4	0.17	0.57	0.18	0.2
13	Shore 13	132	67.9	0.33	1.07	0.35	0.4
14	Shore 14	104	54.2	0.26	0.86	0.28	0.3
15	Shore 15	76.2	37.5	0.18	0.58	0.2	0.26
17	Shore 17	74.4	38.2	0.18	0.6	0.2	0.22
18	Shore 18	26.8	13.1	0.06	0.2	0.07	0.09

III.3 Chemical Analysis of the collected samples

III.3.1 Physicochemical Properties of the surface water

The average values of water temperature, TDS, salinity, pH, DO and Eh of the Aqaba Gulf surface coastal waters during 2016 are listed in Table (5).The maximum water temperature was 24.27˚C at AQ 01 north of the gulf; while the minimum temperature was 22.80˚C at AQ 18 south of the gulf. No significant regional variations in the distribution of water temperatures. The average concentrations of total suspended matter (TDS) showed spatial variability from the north to south of the gulf and ranged between 43.20 to 39.85 g/l in the southern part. The higher TDS levels observed in the northern part are related to dissolution and leaching of the adjacent limestone and evaporate deposits (anhydrite and gypsum). Mineral dissolution primarily occurred due to wave activity and irregular flash floods, where salts (and trace elements) are transported coastward.

The spatial distribution of salinity displayed a very slight increase moving from south to north during the period of study 2016. The highest mean value of salinity (40.13) was recorded in the north at the station AQ1, while the lowest one was recorded at the station AQ18. The highest value of the salinity recorded at the north part maybe due to the relative increase of human impact in area. Due to the high temperatures and no rivers flow into the gulf, there was no significant increase in the water salinity of the gulf area from the entrance of the gulf in the south (39.78) towards the north (40.13). The pH mean values were varied from 8.13 at station AQ18 to 8.28 at AQ1 indicating that there are no clear variations. The distribution pattern of DO indicates high values and well oxygenated waters in the investigated area. The average values of DO ranged from 7.42 mg/l (equivalent to 113.2 % DO saturation) calculated at station AQ1 and 6.83 mg/l (equivalent to 101.8 % saturation) calculated at station AQ18.Minor changes of studied variables (water temperature, salinity, pH and DO) reveal that the effect of human impact on the distribution pattern of different hydrographical conditions in the Gulf of Aqaba coastal water are still limited. This was expected due to the low population there, the absence of fresh water sources and limitation of land based source (i.e. sewage, agriculture, and / or industrial effluents). Accordingly, these conditions could be principally controlled by the circulation pattern of seawater in the area of study. The average Eh values of surface seawater ranged from 263 to 274 mV the highest value was in the

northern part while the lowest value was in the south part. Redox indicators suggest that the coastal water in predominantly oxidizing conditions. These oxidizing conditions are favorable for immobilization of most elements, and may contribute to the relative lower levels of some metals observed particularly in the south samples.

Table (5): Average values of the studied physicochemical characteristic of water

Sample No.	Temp. (°C)	TDS g/l	Salinity	Ph	DO mg/l	Eh (mV)
1	24.27	43.20	40.13	8.28	7.42	274
3	23.58	42.57	39.88	8.20	7.15	272
5	23.44	42.20	39.84	8.19	6.98	272
7	23.27	40.55	39.80	8.21	7.24	271
9	23.13	40.20	39.78	8.18	7.27	269
11	23.80	39.90	39.83	8.20	7.31	267
13	23.40	40.00	39.80	8.15	6.89	264
15	23.28	39.85	39.80	8.15	6.83	264
19	22.80	39.92	39.78	8.13	6.83	263

III.4 Analysis of Heavy Metalsin Water samples

The present study investigated the concentrations of Al, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn, in seawater samples collected from Aqaba Gulf, Egypt. Generally, the concentrations of the examined metals were more or less comparable to the previously published papers and indicated lack of riverine input, the absence of major local impacts of any land-based sources and/or any major negative impacts of coastal tourism in the investigated area. Al concentrations in Gulf seawater showed generally low values and higher levels were observed in the north part of the Gulf. The concentrationsof Al in surface seawater were 2.4µg/l and 1.7µg /l in the northern and southern, respectively. Boron is a common element in marine water and the highest concentrations were observed in the northern part and the levels ranged from 2.8 µg/l and 1.7 µg /l.Cd concentrations in seawater showed generally low values, though they exhibited similar spatial distribution to that of B. Higher Cd levels were observed in northern part in sample 1 which decreased to sampling site 18. The concentrations Cd in surface seawater were2.3 µg/l and 0.4 µg /l in the northern and southern, respectively.Co concentrations in Gulf seawater showed little spatial variations with average Co values of about 1.4 µg/l and 0.9 µg /l in the northern and southern, respectively.The average Co contents in offshore seawater were 0.15 lg/L and 0.17 lg/L in the north Red Sea and southern GoA, respectively [22]. Patterns of Cr showed high levels at site 1, which decreased afterwards (to site 18). Cr levels varied from 2.6 µg/l and 0.6 µg /l in the northern and southern, respectively.

Cu levels in Gulf seawater samples exhibited elevated values in the north part with apparent decreases toward the south. Cu concentrations values varied from 7.7 µg/l and 4.2 µg /l in the northern and southern, respectively. The Cu contents in seawater reported here are larger than that reported by [22] for the offshore surface seawater of 0.11 µg/l. The high level in northern part is attributed to the increased in human activities. Similarly, Fe showed substantial spatial variability in surface water concentrations, where the higher concentrations were observed in the northern water samples compared to that of the south. Fe levels in seawater varied from 44.3 µg/l and 28.3 µg /l in the northern and southern, respectively. Mn exhibited high values in the northern part of the Gulf and the concentrations ranged from 11.2 µg/l and 6.4 µg /l in the northern and southern, respectively. Mn is likely associated with water discharged from desalination plants (thermal multistage flash (MSF) and membrane-based reverse osmosis (RO)) in Eilat, Aqaba and Tabacities in the northern part[23]. Mo concentrations were variable but showed no trends It ranged in concentration between from 11.1 µg/l and 8.9 µg /l in the northern and southern, respectively. Higher concentrations of nickel were observed in the northern water samples compared to that of the south. Ni levels in seawater varied from 2.7 µg/l and 0.8 µg/l in the northern and southern, respectively. The lead distribution showed relatively low values with slight variations. The Pb concentrations values were higher in the northern part (5.5 µg/l) and lower in the southern part (2.8µg/l). The V concentration values in the Gulf waterranged from 1.1 µg/l and 0.2 µg/l in the northern and southern, respectively. The spatial distribution of Zn in surface seawater showed a decreasing pattern southern part. The highest level of Zn was observed in the northern part of the Gulf in sample 1 (17.2 µg/l**)** and the lowest value was recorded in sample 18 (11. µg/l).

Table (7): Heavy metals concentrations in surface water collected Aqaba Gulf (µg/l)

Sample No.	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
1	2.4	2.8	2.3	1.4	2.6	7.7	44.3	11.2	11.1	2.7	5.5	1.1	17.2
3	1.8	2.4	1.7	1.2	1.7	7.1	37.4	7.9	10.8	2.4	5.1	0.7	16.6
5	1.8	2.1	1.2	1.3	1.7	5.6	36.0	7.3	10.9	2.1	4.8	0.7	14.8
7	1.6	1.9	1.0	1.2	1.2	5.9	34.8	8.1	10.0	1.8	4.3	0.5	14.2
9	2.2	1.9	0.7	1.3	1.4	5.4	31.5	7.6	10.2	1.5	3.3	0.5	13.0.
11	1.8	2.2	0.6	1.3	0.7	4.9	30.1	7.7	9.7	1.4	3.2	0.7	13.3
13	1.7	2.2	0.5	1.2	0.5	5.1	28.3	6.9	9.9	1.2	3.5	0.3	12.4
15	1.7	1.9	0.4	0.9	0.8	4.7	29.7	6.5	9.2	0.9	3.1	0.3	12.1
18	1.7	1.7	0.6	0.9	0.6	4.2	30.2	6.4	8.9	0.8	2.8	0.2	11.4

III.4.1 Analysis of Heavy Metals in Shore Sediment Samples

Metals concentrations (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn,) in shore sediments are presented in Table (7). The results of the analysis shown that the elevated Al concentration in sediment samples, particularly in the northern part of the Gulf suggests that the relatively strong impact of mineral dust in this region compared to the southern part. Atmospheric dry flux of Al and Zn to the uppermost northwestern Gulf (Eilatcity) was estimated to be about1.68 mg/m2/year [24]. Boron content in the shore sediment samples also showed higher concentrations in northern coast 28.5 mg/kg compared to the south part half 18.5 mg/kg. Cadmium (Cd) concentration varies within a narrow range (2.1–3.8 mg/kg). Its minimum concentration is recorded at station 9 whereas stations 1 and 3 contain the highest concentration. These values of Cd reflect near shore values and are primarily attributed to local influences through dissolution and leaching from adjacent geologic materials. The high concentrations of Cd northern part are associated with discharge of wastewater from the desalination plants found adjacent to Aqaba, Eilat and Taba cities.

Cobalt in shore sediment of the northern showed a higher value of 15.3 mg/kg, whereas 10.5 mg/kg was found in the southern samples. Potential sources of Co in seawater are likely similar to those of Cr. Co content in aerosol dust particles collected from Eilat city was about 0.1 mg/m2/year [24].Chromium (Cr) concentration varies within a limited range (4.7–3.1 mg/kg). Moreover, sample 1 in the northern part contains the highest chromium (4.7 mg/kg). The pattern of Cr suggests that the relative higher Cr levels atthe northern part are probably attributed to dischargeof water from desalination plant [25]. Additional sources, include, cement producingplants from the Jordanian area and dust borne Cr fluxfrom aerosols to Eilat city was estimated to be 0.96mg/m2/year[24].Copper (Cu) shows a maximum concentration (5.1 mg/kg) in sample 1. Cu content in sediments of the northern part showedhigher levels relative to the southernsediments. Cu flux from dry deposition to Eilat city (at the northern western coastof the Gulf) was estimated to be 0.38 mg/m2/year [24] which was attributed to anthropogenic sources, and remainsa potentially important source of Cu to seawater in the northern part. As expected, iron (Fe) is the most abundant heavy metal in Aqaba Gulf sediments. Its concentration is fluctuated between 425.4 and 613.0 mg/kg at samples 15 and 1, respectively. However, the higher Fe content was found in sediments collected from the northern part. Mn For all studied samples, manganese (Mn) levels come after those of Fe. Mn varies from 192.7 mg/kg (sample 18) to 367.6 mg/kg (sample 1).

Mo in sediment samples showed relatively lower average value in the southern part of the study area compared to the northern part.Also, nickel shows lower concentrations (10.6– 16.7 mg/kg) than that recorded for marine in sediment contamination limit (>100 mg/kg) of the Swedish Environmental Protection Agency [26]. The higher Ni concentration was found in the samples collected from the northern part. Zinc (Zn) concentration fluctuates between 47.5.0 and 71.5 mg/kg at stations 15 and 1, respectively. Zinc concentrations in Aqaba Gulf sediments are considerably lower than that of Swedish EPA (360 mg/kg).The Pb concentration levels in shore sediments were 5.5 mg/kg and 10.3 mg/kg in the southern and northern parts, respectively. Vanadium concentrations in shore sediments were varies from 2.1 mg/kg in sample 13 in the southern part to 4.3 mg/kg in the sample 1 in the northern part. The uppermost part of the Gulf received high Pb flux of 0.8 mg/ m2/year from dry deposition [24] which was mainly attributed to emission of fuel burning.

Generally, the heavy metals concentrations comparison among the studied area reflects that southern part of the Gulf contains the lowest levels of the heavy metals. Unexpectedly, the sediments of the recreational beach of Taba (sample 1) contained the highest levels of heavy metals. This may be because Taba is close to Aqaba in Jordan and Eilat, where there are human activities including desalination plants [23]. It is documented that thermal desalination plants discharge copper, nickel, iron, chromium, zinc, and other heavy metals depending on the alloys present in the process line, which may have adverse effects on water and sediment quality [27].

Table (7): Heavy metals concentrations in Aqaba Gulf sediments (mg/kg dry weight)

Sample No.	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
1	39.4	28.5	3.8	15.3	4.7	5.1	613.0	367.6	12.6	16.7	10.3	4.3	71.5
3	34.3	27.4	3.4	11.5	4.1	4.5	591.5	351.2	11.4	15.9	9.5	4.1	64.6
5	31.8	24.1	3.1	10.3	3.6	4.2	505.3	303.5	9.8	13.8	8.1	3.7	67.4
7	29.5	22.6	2.7	11.4	3.3	3.9	576.2	339.2	9.2	12.3	7.2	3.1	63.7
9	27.8	23.2	2.1	9.8	2.3	3.1	565.4	233.5	10.3	9.9	6.1	2.6	53.6
11	31.7	19.1	2.6	12.2	2.7	3.0	545.5	217.6	8.7	13.7	7.8	2.9	51.0
13	24.2	22.8	3.1	12.8	3.4	3.7	521.0	180.8	5.4	11.8	5.5	2.1	47.8
15	23.5	18.8	3.0	11.3	3.3	3.6	425.4	131.6	7.5	11.5	7.4	2.7	47.5
18	29.1	18.5	3.1	10.5	3.1	3.8	451.0	192.7	7.2	10.6	7.5	3.2	48.4

III.4.2 Analysis of Heavy Metals in Algae Samples

Basic information on the concentration levels of heavy trace elements (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn) in marine algae collected from the Egyptian coast of the Aqaba Gulf at different locations has been obtained. The concentrations are measured in one common species of marine algae. The high bioaccumulation abilities of algae for selected metals have been confirmed. The investigation showed that algae species are well suited for monitoring heavy metals as trace content in coastal area and provide information about bioavailability which can be obtained in algae species. The results summarized in Table (8) indicated that the algae were characterized by having the highest properties of aluminum, lead, nickel and vanadium. The levels found in the algae reflect the high concentrations of these metals in the water of the Gulf of Aqaba. Most of the metals in the algae collected were of moderate levels. The high levels of Al, Ni, Pb and V were notable in all samples collected.

Table (8) Average concentrations of heavy metals (ppm) in algae samples

E S.N	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	V	Zn
1	46.2	4.5	0.07	0.34	6.6	7.82	137.0	103.6	0.31	0.82	1.83	0.76	9.52
3	43.3	5.4	0.09	0.32	6.4	7.55	141.4	104.2	0.34	0.76	1.64	0.88	10.30

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