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Evaluation of Heavy, Toxic and Trace Metals Contamination in Fish, Seawater, Sediments and Seashells of the Arabian Gulf Coastal, Kuwait

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ABSTRACT

A comprehensive environmental assessment of the Arabian Gulf Coast in the State of Kuwait was carried out by assessing levels of heavy, toxic and rare mineral pollutants in coastal sediments, beach sand, shells and sea water collected from the coastline. By Using (Inductively coupled plasma - Mass spectrometry) ICP-MS technique, we analyzed (Al, Mn, Mg, Na, K, Ca, Zn, Ba, Sr, Co, Cu, Cd, Pb, Ag, Ni, Fe). The results of potential environmental risks indicated that the study area was heavily enriched with (Al, Mn, Mg, Na, K, Ca), moderately enriched with (Zn, Ba, Sr, Co), and low levels of (Cu, Cd, Pb, Ag, Ni, Fe). However, in general, these pollutant levels were not exceed the EPA and the Canadian ISQG values and still lower than some standardized reference values all over the world. Furthermore, the bioaccumulation index indicated that gastropod shells and pelecypod shells had greater ability to concentrate Fe, Na, K and Al, which may be attributable to the shape of them. Regarding the seawater samples, Na and K levels were higher than their average oceanic metal concentrations. Moreover, the average concentrations of heavy metals in the studied area, especially those of Pb, K, Fe, and Zn, were lower than the coasts of many countries all over the world. The moderate enrichment of some metals in the studied area could be partially attributed to anthropogenic activities, notably oil spills from oil tankers and exploration, transportation and from saline water desalination plants in Kuwait Coast, the nearby nuclear reactors overlooking the Arabian Gulf and other industrial activities in the region. Results were in accordance with recommended daily intake allowance by WHO/FAO. From this study, it was noticed that the concentrations of Heavy, Toxic and Trace Metals for Kuwaiti Environmental Marine Samples are lower than the worldwide average value. Results obtained are discussed and compared with the international recommended data.

1. Introduction

Environment is an essential element of human existence. It is a result of interference of natural elements – earth, air, water, climate, biosphere – with elements created by human activity [1]. All these interact with/and influence the existential conditions and the possibilities for future development of society. To protect the environment, mainly affected areas must be identified, assessed the degree of damage and determined the causes that have produced these imbalances. It is necessary to preserve the quality of the environment mainly throughout reducing negative effects of human activities. Potentially toxic metals resulting from anthropogenic activities cause severe disturbance of ecosystems [2, 3].

Water pollution is a complex process that leads to changes in water composition, aquatic flora and fauna, and may result in a poor condition, water quality for economic and recreational use, being dangerous to human health [4, 5]. Importance of trace metal concentrations evidence in natural waters and/or environment is growing for the pollution monitoring studies. Some of these toxic trace metal levels are high, such as poisoning by Fe, Pb, Ni affects the central nervous system. Heavy metals presence in nature usually is not dangerous for the environment because they are present only in very small quantities [6]. Heavy metals are pollutants in the environment only if it's present in large quantities (this fact is usually attributed to industrial activities).

Some of elements such as mercury, arsenic, cadmium, lead and tin have no known role in biological systems. They are natural trace components of the aquatic environment, but their levels have increased due to industrial, agricultural and mining activities. Even low metal concentrations may threaten the health of aquatic and terrestrial organisms, man included [7]. Mercury is an element of special concern because its inorganic form is biologically transformed in aquatic environments into methyl mercury (MeHg), a lipophilic organic compound that bio accumulates and biomagnifies as it moves up the aquatic food chain [8, 9, and 10]. As a result, human populations with a traditionally elevated dietary intake have the highest potential exposure to MeHg and are at an increased risk for developing neurotoxic effects. This is a particularly important issue for children, pregnant women and breast-feeding mothers [11, 12].

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This study proposes to investigate the analyzing the major and trace elements and determination the concentration of metallic and some non-metallic elements in the samples by using Inductively-coupled Plasma/Mass Spectrometer (ICP-MS) Technique for some Environmental Marine Samples such as the Beach Muddy/Sands, Arabian Gulf Water, Shells and Different types of Marine Fish in the State of Kuwait in the Arabian Gulf region, and Comparing the research results for the mentioned samples in Kuwait with the local and worldwide ranges in different coastal areas around the world.

2. Experimental details

2.1 Sample Preparation and experimental procedure:

There are a number of steps that should be carried out during a survey of the sampling area.

They can be summarized as follows:

1- Samples collection.
2- Samples number.
3- Site geographical coordinates.
4- Sample mass and volume.
5- Removal of extraneous material.
6- Sample homogenization.
7- Sample splitting.

2.2 Marine Environment Samples

A total of 16 of marine environment Samples of the Arabian Gulf region (Beach Muddy/Sands, Arabian Gulf Water, Shells and Different types of Marine Fish) collected along the eastern coastline of the State of Kuwait. These samples were collected randomly from different locations in these sites (from north to south along the eastern coastline of Arabian Gulf) with geographical location of the samples by coordinates, as show in figure (1) and table (1).

Fig 1. Geographical location of Collecting Samples

3. Experimental Technique

The analyses of samples were performed in the Central Laboratory for Elemental and Isotopic Analysis, Nuclear Research Center, Atomic Energy Authority – Inshas. For elemental analysis of the collected samples, the High Resolution Inductively Coupled Plasma-Mass Spectrometery (ICP-MS) was used.

Inductively Coupled Plasma, or ICP analysis, is a powerful chemical analysis method which can be used to identify both trace amounts and major concentrations of nearly all elements within a sample.

Element provides a wide array of ICP analysis services including ICP Mass Spectrometry (ICP-MS).

ICP-MS is commonly used instrument in modern laboratories for the analysis of metals in various fields. ICP-MS provides a lower detection limit down to part per trillion (ppt). as shown in Figure (2).

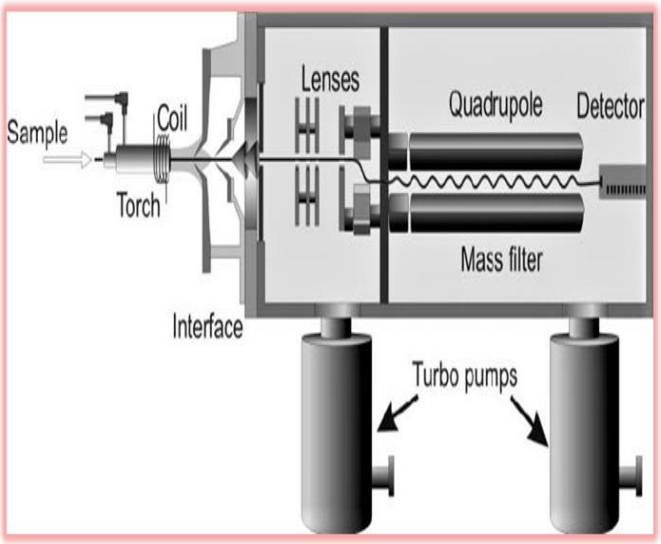

Fig 2. Cross section schematic of an ICP-MS [13]

4. Results and Discussion

Analysis of the Heavy Minerals from Samples

Sixteen samples were used for heavy minerals analysis by using technique to estimate their average contents of heavy minerals at very low concentrations. The concentrations of the economic minerals in each sample were summed to represent the economic fraction. The concentration values contents of the heavy minerals in the studied samples were determined as shown in *Tables (2), (3).*

Concentrations of elements in the collected samples were determined as shown in the tables below.

Table 1. Demonstration of the Kuwaiti Samples Collected.

Sample Type	Location	Latitude N (Deg. Min.)	Latitude E (Deg. Min.)	Sample Code	Mass (kg)
Sand of Muddy Shore	Al-Sulaibikhat bay Coast	29.33303	47.89676	KwS1	0.432
Sand of Muddy Shore	Ras Ushayrij Coast	29.37991	47.84395	KwS2	0.433
Beach Sand	Khiran Beach	28.66117	48.39197	KwS5	0.403
Beach Sand	Al-Egaila Beach	29.18127	48.12114	KwS7	0.501
Beach Sand	Wanasa Beach	29.43531	48.26949	KwS8	0.522
Beach Sand	Shuwaikh Beach	29.35694	47.94522	KwS9	0.537
Sea Water	Anjafa Beach	29.27856	48.08967	KwSW4	0.257
Sea Water	Khiran Beach	28.66117	48.39197	KwSW5	0.335
Sea Water	Al-Missila Beach	29.23483	48.10099	KwSW6	0.323
Sea Water	Wanasa Beach	29.43531	48.26949	KwSW8	0.271
Sea Water	Abdulla Port Beach	28.9925	48.16795	KwSW14	0.259
Sea Shell	Al-Egaila Beach	29.18127	48.12114	KwSS7	0.266
Starfish	Arabian Gulf	29.32521	48.25234	KwSF1	0.078
Marine Fish	Arabian Gulf	29.53405	48.00229	KwF2	0.289
Marine Fish	Arabian Gulf	29.18865	48.37733	KwF3	0.256
Marine Fish	Arabian Gulf	28.96752	48.42674	KwF5	0.235

Table 2. Concentrations of heavy minerals in Some Coastal Samples in Kuwait by using ICP-MS Technique.

Analysis Concentration of Heavy Elements (ppm) in Some Coastal Samples in Kuwait by using ICP-MS Technique								
Element	S1	S2	S3	S4	S5	S6	S7	S8
	KwF5	KwF2	KwSF1	KwF3	KwSS7	KwS9	KwS1	KwS2
Na	10930.21	27375.64	39068.6	660.6	10308.86	23076.89	10020.53	11862.77
Mg	6513.56	12848.73	65549.54	281.99	8997.38	7737.19	1417.82	9890.72
Al	667.83	6043.18	197.27	22.2	113.98	21407.55	18925.44	8856.48
K	11108.28	5380.86	7128.63	1415.26	1439.71	13466.09	15562.94	7322.99
Ca	5960.74	7525.78	44384.58	419.916	1951.92	17438.48	690.38	23066.1
Cr	10.37	38.63	5.3	0.49	3.27	49.24	5.58	6.24
Mn	22.11	171.61	142.61	1.45	88.57	136.85	31.37	85.48
Fe	137.5	5811.28	341.23	8	1123.47	5307	2305.82	2009.8
Co	ND	2.04	0.38	ND	ND	0.13	ND	ND
Ni	14.7	52.12	17.74	0.72	42.19	64.41	33.37	20.19
Cu	ND	21.46	30.81	0.0023	58.52	24.9	5	0.45
Zn	137.93	310.88	154.97	19.38	329.59	123.56	74.26	113.39
Sr	384.84	398.23	3726.59	9.04	3675.64	3254.2	226.02	4359.78
Ag	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.72	0.95	2.091	0.03	4.11	4.79	1.44	0.33
Ba	9.69	48.46	22.16	0.36	61.87	609.88	520.92	304.72
Pb	5.93	13.69	7.74	0.33	25.92	80.04	26.96	19.54

ND: Non Detected Value.

Table 3. Concentrations of heavy minerals in Some Coastal Samples in Kuwait by using ICP-MS Technique.

Analysis Concentration of Heavy Elements (ppm) in Some Coastal Samples in Kuwait by using ICP-MS Technique								
Element	S9	S10	S11	S12	S13	S14	S15	S16
	KwS5	KwS7	KwS8	KwSW4	KwSW8	KwSW5	KwSW6	KwSW14
Na	14123.49	24737.48	12956.19	22485.99	22928	18235.12	17541.97	23255.92
Mg	7793.21	48812.34	1067.84	1859.98	3504.53	793.45	1578.42	2674.67
Al	1282.96	69048.16	ND	ND	ND	ND	ND	ND
K	11423.65	20749.53	299.4	518.11	949.27	182.02	410.155	680.833
Ca	17558.72	12905.67	56.48	71.39	77.201	73.94	52.265	90.393
Cr	23.2439	284.34	ND	ND	ND	ND	ND	ND
Mn	124.94	881.19	0.1	1.0233	ND	0.42	ND	ND
Fe	6724.05	54491.41	ND	ND	ND	ND	ND	ND
Co	0.19	26	ND	ND	ND	ND	ND	ND
Ni	26.08	261.17	2.6	4.24	3.31	3.07	2.295	1.73
Cu	9.09	121.74	ND	ND	ND	ND	ND	ND
Zn	116.43	353.87	ND	1.63	ND	1.86	ND	ND
Sr	4107.87	1171.635	8.58	14.34	21.49	7.66	11.65	19.823
Ag	ND	ND	ND	ND	ND	ND	ND	ND
Cd	0.15	2.11	0.11	0.08	0.04	0.02	0.02	0.03
Ba	365.62	509.08	ND	ND	ND	10.98	ND	ND
Pb	26.56	47.18	1	1.38	1.01	1.5	1.27	0.65

ND: Non Detected Value.

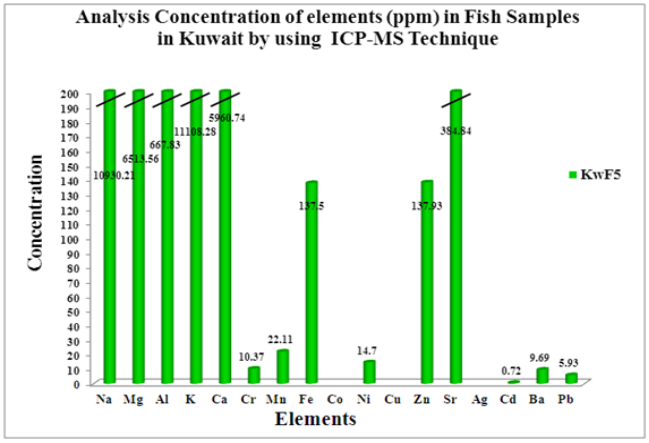

Fig 3. Concentrations of some heavy elements detected (in ppm) in the Fish sample code (KwF5).

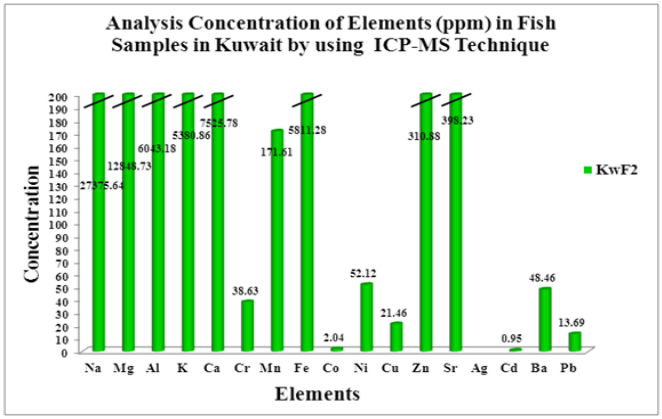

Fig 4. Concentrations of some heavy elements detected (in ppm) in the Fish sample code (KwF2).

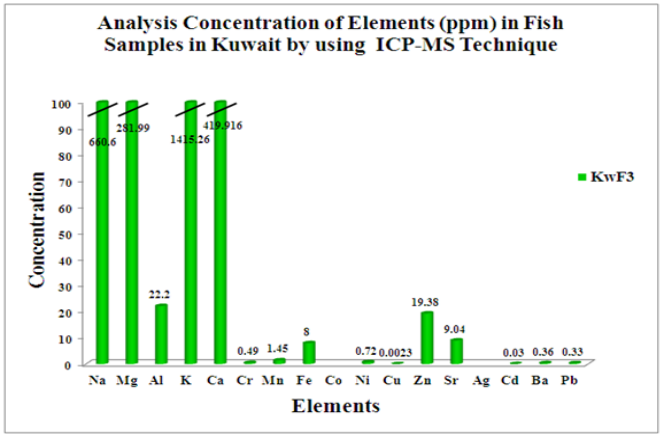

Fig 5. Concentrations of some heavy elements detected (in ppm) in the Fish sample code (KwF3).

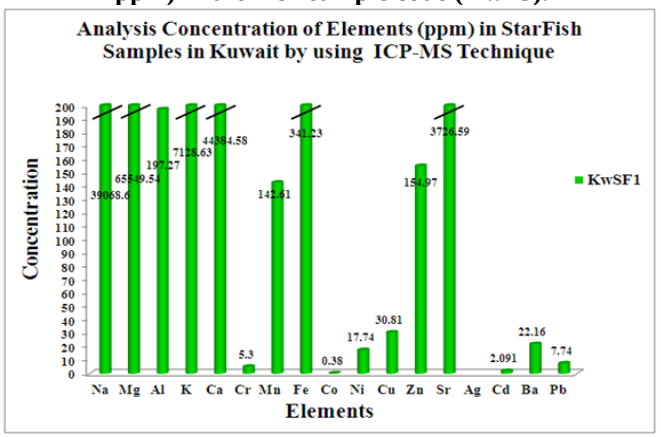

Fig 6. Concentrations of some heavy elements detected (in ppm) in the Star Fish sample code (KwSF1).

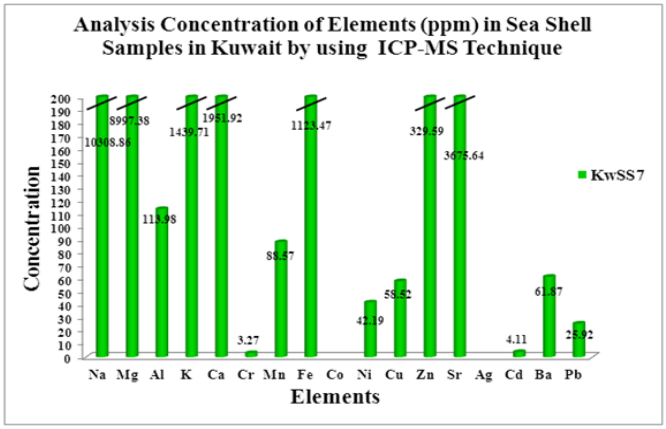

Fig 7. Concentrations of some heavy elements detected (in ppm) in the Sea Shell sample code (KwSS5).

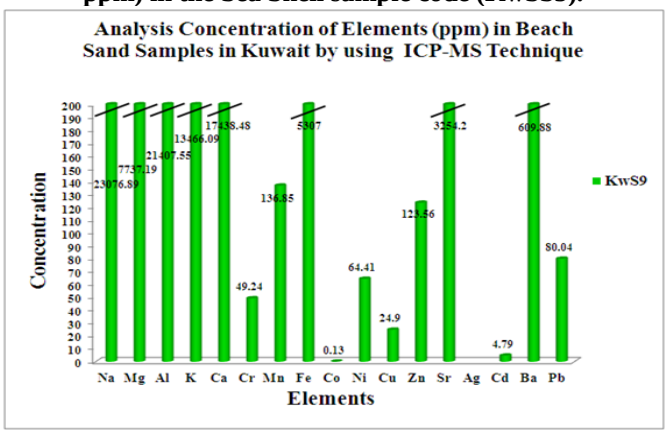

Fig 8. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS9).

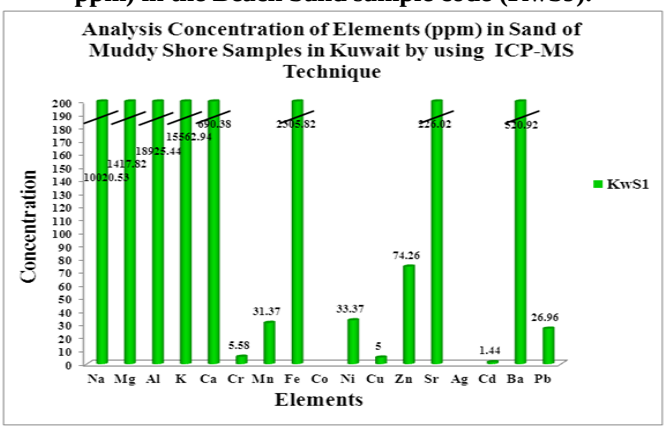

Fig 9. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS1).

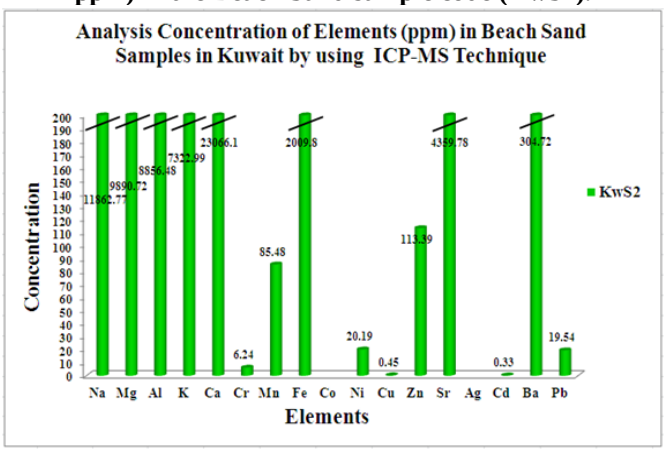

Fig 10. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS2).

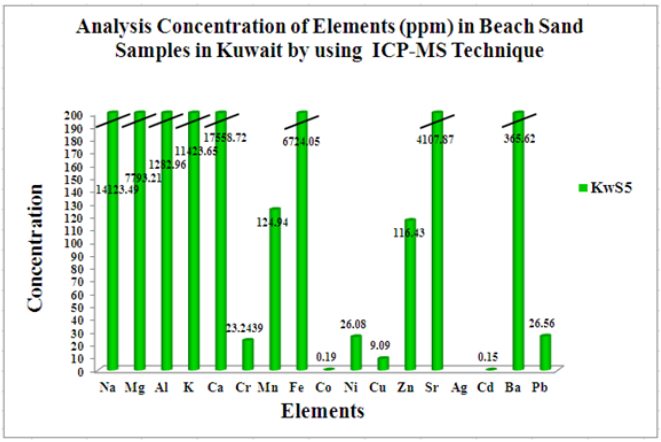

Fig 11. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS5).

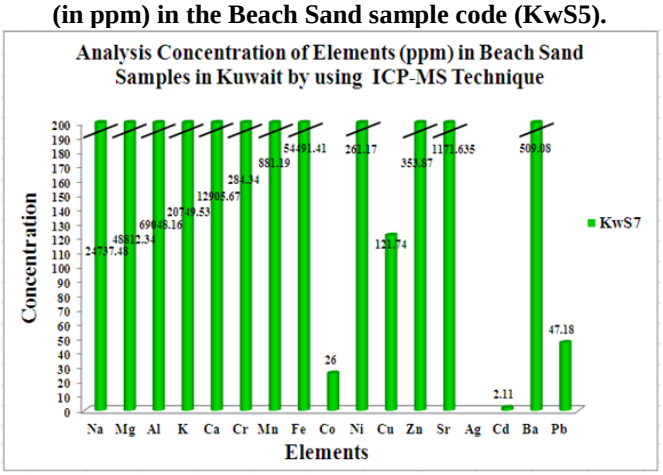

Fig 12. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS7).

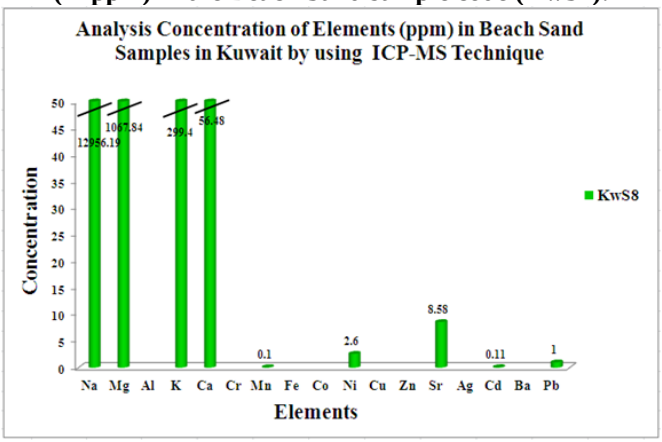

Fig 13. Concentrations of some heavy elements detected (in ppm) in the Beach Sand sample code (KwS8).

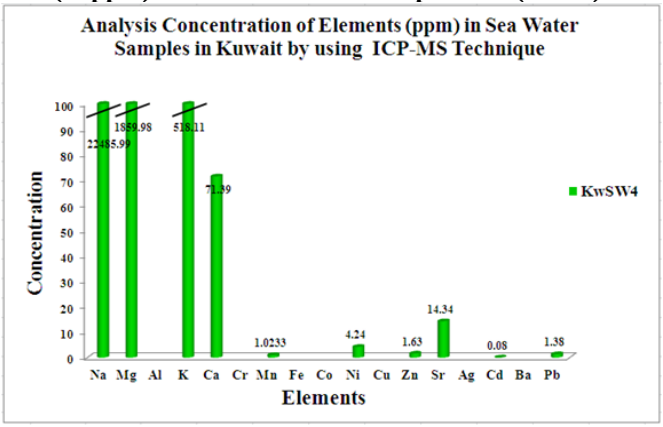

Fig 14. Concentrations of some heavy elements detected (in ppm) in the Sea Water sample code (KwSW4).

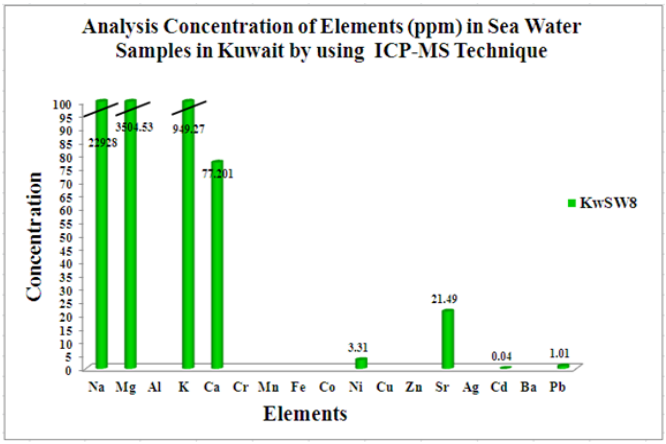

Fig 15. Concentrations of some heavy elements detected (in ppm) in the Sea Water sample code (KwS8).

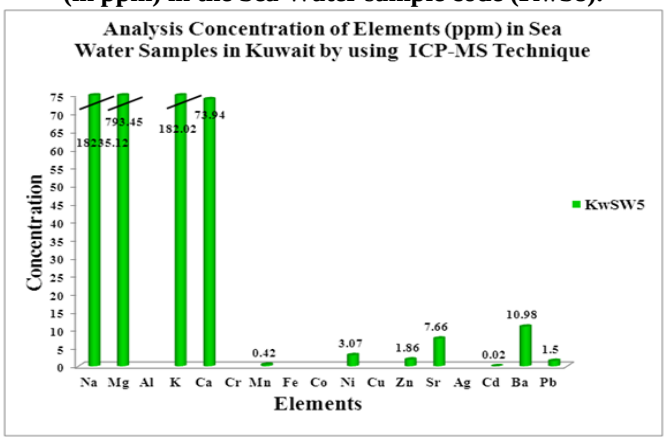

Fig 16. Concentrations of some heavy elements detected (in ppm) in the Sea Water sample code (KwSW5).

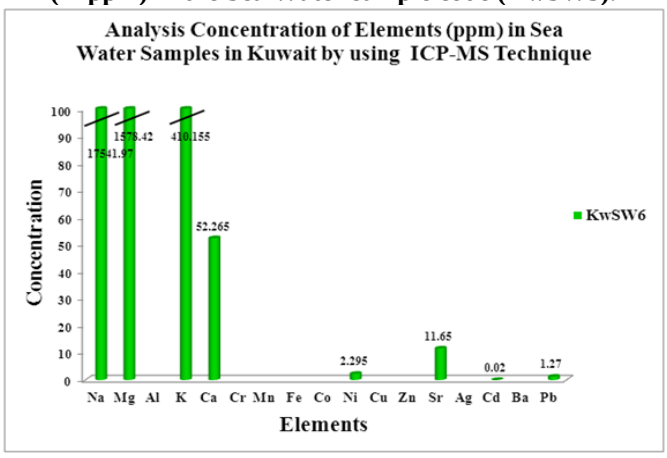

Fig 17. Concentrations of some heavy elements detected (in ppm) in the Sea Water sample code (KwSW6).

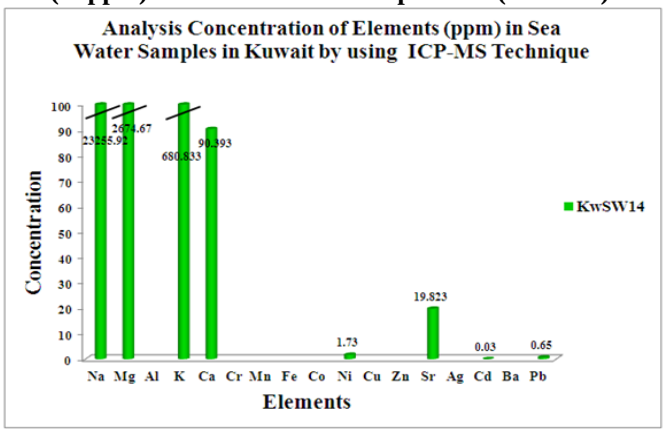

Fig 18. Concentrations of some heavy elements detected (in ppm) in the Sea Water sample code (KwSW14).

Distribution of most concentrated elements through the collected samples

4.1 In the Marine Fish samples

(Na, Mg, K, Ca) shows much increase in the concentrations with values of [39068.6ppm - 3.9%], [65549.54ppm - 6.7%], [11108.28ppm - 1.1%], [44384.58ppm - 4.4%], respectively. And in other hand, (Al, Ni, Zn, Sr, Cd, Ba, Pb), shows very low in the concentrations with value of [6043.18ppm - 0.6%], [52.12ppm - 0.01%], [310.88ppm - 0.03%], [3726.59ppm - 0.4%], [2.091ppm - 0.0002%], [48.46ppm - 0.005%], [13.69ppm - 0.001%], respectively, and other elements (Co, Cu, Ag) were not detected in most Fish samples as shown in the Fig (3), (4), (5) and (6).

4.2 In the Sea Shell samples

(Na, Mg, Al, K, Ca, Fe, Sr) shows much increase in the concentrations with values of [10308.86ppm - 1%], [8997.38ppm - 0.9%], [113.98ppm - 0.01%], [1439.71ppm - 0.14%], [1951.92ppm - 0.2%], [1123.47ppm - 0.1%], [3675.64ppm - 0.4%], respectively. And in other hand, (Cr, Mn, Ni, Zn, Ba, Pb), shows very low in the concentrations with value of [3.27ppm - 0.0003%], [88.57ppm - 0.009%], [42.19ppm - 0.004%], [329.59ppm - 0.03%], [61.87ppm - 0.006%], [25.92ppm - 0.003%], respectively, and other both elements (Co, Ag) were not detected in the sea shell sample as shown in the Fig (7).

4.3 In the Beach Sand samples

(Na, Al, K, Ca) shows much increase in the concentrations with values of [24737.48ppm - 2.5%], [69048.16ppm - 6.9%], [20749.53ppm - 2.1%], [23066.1ppm - 2.3%], respectively. And in other hand, (Cr, Ni, Zn, Sr, Cd, Ba, Pb), shows very low in the concentrations with value of [284.34ppm - 0.03%], [261.17ppm - 0.03%], [353.87ppm - 0.04%], [226.02ppm - 0.02%], [4.79ppm - 0.0005%], [609.88ppm - 0.06%], [80.04ppm - 0.008%], respectively, and other both elements (Co, Ag) were not detected in some samples as shown in the Fig (8), (9), (10), (11), (12) and (13).

4.4 In the Sea Water samples

(Na, Mg, K) shows much increase in the concentrations with values of [23255.92ppm - 2.3%], [3504.53ppm - 0.4%], [949.27ppm - 0.09%], respectively. And in other hand, (Ca, Mn, Ni, Zn, Ba, Pb, Sr), shows very low in the concentrations with value of [77.201ppm - 0.008%], [1.0233ppm - 0.0001%], [4.24ppm - 0.0004%], [1.86ppm - 0.0002%], [10.98ppm - 0.001%], [1.5ppm - 0.0002%], [21.49ppm - 0.002%], respectively, and other both elements (Al, Fe, Cr, Cu, Co, Ag) were not detected in most sea water samples as shown in the Fig (14), (15), (16), (17) and (18).

By comparison of the obtained results for the collected samples Marine Fish, Sand, Shell and Sea Water in Tables (2), (3), (4) and (5). It was found that it is within the World Health Organization (WHO), World Bank (WB), Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (ISQG), and United States Environmental Protection Agency (USEPA) allowable limits.

5. Conclusion

According to the present results, it appears clearly the following:

A total of 16 of marine environment Samples of the Arabian Gulf region (Beach Muddy/Sands, Arabian Gulf Water, Shells and Different types of Marine Fish) collected along the eastern coastline of the State of Kuwait. Elemental analyses of some marine samples were performed by using the technique of the Inductively-Coupled Plasma/Mass Spectrometry (ICP-MS), it is faster and very useful for in series determination of many Heavy, major and minor elements. By the comparison of the obtained results for the collected samples Marine Fish, Sand, Shell and Sea Water by using ICP-MS Technique, it was found that it is within the World Health Organization (WHO), World Bank (WB), Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (ISQG), and United States Environmental Protection Agency (USEPA) allowable limits. After measuring the concentrations of radioactive materials in the marine life in the Arabian Gulf Region and in the state of Kuwait in particular, clearly, the marine life in the Arabian Gulf region being free from any radioactive contamination which may harm the environment and human health under the existing nuclear activities in the region. The protection of coasts and regional waters from the impact of radioactive and environmental pollution requires knowledge of the Maritime Force and Coast Guard personnel regarding radiation protection and radiation safety, and keenness to train them in using the latest radiation level measuring devices and preparing for radiological emergencies if necessary. The general recommendation states that precautions must be taken to protect the coastal area in Kuwait and as a first step in the evaluation of coastal, marine, soil, and air environment in the Arabian Gulf area.

Table 4. The Maximum, Minimum and Mean values for the Concentration of Heavy and Toxic Elements in Marine Samples

The Maximum, Minimum and Mean values for the Concentration of Heavy and Toxic Elements in Marine Samples			
Element	**Mean**	**Min**	**Max**
Na	16663.01	660.60	39068.60
Mg	14154.62	281.99	65549.54
Al	7029.24	22.20	21407.55
K	7853.10	1415.26	15562.94
Ca	12679.74	419.92	44384.58
Cr	14.89	0.49	49.24
Mn	85.01	1.45	171.61
Fe	2130.51	8.00	5811.28
Co	0.85	0.13	2.04
Ni	30.68	0.72	64.41
Cu	20.16	0.00	58.52
Zn	158.00	19.38	329.59
Sr	2004.29	9.04	4359.78
Ag	ND	ND	ND
Cd	1.81	0.03	4.79
Ba	197.26	0.36	609.88
Pb	22.52	0.33	80.04

Table 5. Comparison of Ranges of Heavy elements concentrations of coastal samples (mg/kg) in the studied Marine Samples and their values for different countries all over the world.

Country/ Location	Heavy elements concentrations of coastal and Marine Samples all over the world. (mg/kg)								References
	Cd Range	Co Range	Cr Range	Cu Range	Mn Range	Ni Range	Pb Range	Zn Range	
Gulf of Aqaba, Jordanian coast	0.8-3	8-28	-	3-12.3	44-189	9-28	15-83	16-135	[14]
Gulf of Aqaba, Jordanian coast, Phosphate-Polluted	5-9	30-32	-	10-25	227-288	27-38	117-148	80-180	[14]
Gulf of Aqaba	-	8-28	10	58-325	-	-	-	-	[15]
Haql, Aqaba gulf (Saudi coast)	1.7	0.5	9	2.6	60	2.2	8.6	4.7	[16]
EI-Qasr, Red Sea (Saudi coast)	1.5	-	-	5	20	-	-	11	[17]
Jeddah-Yanbu, Red Sea (Saudi coast)	0.9	-	-	13	51	-	-	10	[17]
Obhur creek, Red Sea (Saudi coast)	2-5	-	-	6-16	11	-	-	2-30	[17]
AI-Ghardaqa, Red Sea (Egyptian coast)	-	-	-	9-28	93-279	-	-	11-90	[18]
East of Suez gulf	0.2	6.4	-	5.2	-	16.1	10.3	29	[19]
Jordanian coast, (Porites Corals), before 1965	2.4	-	-	4.7	2.4	-	41.5	5.4	[20]
Jordanian coast, (Porites Corals), after 1965	5.2	-	-	5.4	8.2	-	47.9	5.5	[20]
Eilat town coast	-	8-28	-	10	58-325	-	-	-	[15]
Jordanian coast (Near Eilat)	5-9	30-32	-	10-25	227-288	27-38	117-148	80-180	[14]
Jordan industrial site, (coral core)	1.1	-	-	3.5	-	-	3.7	0.8	[16]
Jordan industrial site, (coral core)	2.6	-	-	16.6	-	-	7.3	7.5	[20]
Saudi coast, Haql	1.7	0.5	9	2.6	60	2.2	8.6	4.7	[16]
Addurrah beach at Saudi- Jordan border	0.05	2.4	519	10.3	218	11.2	11.5	19	[21]
Haql beach, 20 km away from the border	0.02	1.4	506	5.9	99	9.1	8.6	8	[21]
Arabian Gulf (Kuwait Coast)	003-4.8	ND-2.04	0.49-49.24	ND-58.5	1.45-171.6	0.72-64.4	0.33-80	19.4-330	Present Study

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