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Trace metals and total organic carbon concentrations at intertidal area in Sulaibikhat Bay

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ABSTRACT

The area under investigation is located in the eastern part of Sulaibikhat Bay adjacent to Kuwait University in Shuwaikh. The area includes a wide mesotidal flat and low energy zone which is covered with mud and muddy sediments highly affected by pollutants from sewage discharges. Part of the area has been rehabilitated by removing wrecked ships and contaminated sediments.

The objectives is to study the levels of trace metals in that area and assess the relationship and behavior of different trace metals during the winter and summer season. Sixty sediment samples were collected from 30 stations during the winter 2006 and summer 2006 seasons. The levels of eleven trace metal elements (Fe, Pb, Hg, Si, Mn, Zn, Cd, Cu, Cr, Ni, and V) and total organic carbon were measured. Analyses of these parameters in sediments showed that most of these substances exist in high concentrations. Person correlations test between the parameters showed high correlations between the some elements in the two seasons. High correlations were found between iron, silicon, zinc, cadmium, copper, chromium, nickel, vanadium and total organic carbon. The main reason for such correlations between silicon, iron and different elements is the nature and characteristics of sediment in the area which is muddy rich of silt, the continuous discharges of sewage, the lack of proper water circulation, and continuous releases from Shuwaikh port.

To avoid future environmental problems, this study recommended that it has to isolate the sewage from Shuwaikh industrial area, treat domestic sewage efficiently before discharge into Kuwait bay, and adopt modern environmental techniques to minimize oil spills in Shuwaikh port.

Keywords: Sulaibikhat Bay, total organic carbon, traces metals, discharge waste, sediments.

INTRODUCTION

There is a global concern about pollution in the marine environment. Metals are chemicals that are present normally in the earth's crust. These metals are classified into noncritical, toxic, and very toxic (Förstner and Wittmann, 1981).

Trace metals found their way into the hydrological cycle ever since the first occurrence of water on the planet Earth. Trace metals are deposited in sediments from two main sources, either naturally or man-made inflow point pollution source. Harbors, estuaries, and sewage outlets are considered the main sources of trace metals in sea water and sediments (Salomons and Förstner, 1984; Montgomery, 2006).

Sediments are considered good reservoirs for capturing trace metals. Analysis of the top 1-2 cm sediment layer provides good data for the pollution levels in the aquatic environment (Abayachi and Douabul, 1985 and Adriano, 2001). In addition to the normal source for trace metals from land base sources, trace metals enters Kuwait's marine environment from Shatt al-Arab. Trace metals can cause toxicity to the aquatic organisms if they are present in higher lethal or toxic concentration (Andrlini *et al.,* 1982; Khan, 1998; Al-Ghadban and El-Sammak, 2005).

Sulaibikhat Bay is one of the most important features of Kuwait Bay which is located at the southwestern part of Kuwait Bay between latitudes 29^{0}19' and 29^{0}24' N and longitudes 47^{0}50' and 47^{0}55' E. Sulaibikhat Bay is a shallow muddy tidal flat that extends up to 20 km at the high tidal level, and its maximum width is 4 km the lower tidal level. The bay boards between Ras-Ushairij Peninsula in the northwest and Shuwaikh Port in the southeast (Figure 1). It is bounded by vegetated "sabkha" (muddy shallow water area near the sea) along its southern side. The area exhibits some remains of construction debris that extends several tens of meters over the upper flats (Al-Sarawi *et al.,* 1985). Most of the sediments that contain trace metals enter Sulaibikhat Bay from Shatt Al-Arab estuary, Aeolian dust fallout and direct chemical and biogenic precipitations (Al-Yamani, *et al.,* 2004). The sediments in Sulaibikhat Bay are divided into five types: sand, silty sand, silt, silt clay, and clayey silt (Al-Sarawi *et al.,* 1985 and Al-Sarawi *et al.,* 2002). Studies on the sediment quality of Kuwait Bay indicate that Sulaibikhat Bay contains high concentrations of total petroleum hydrocarbons resulting from activities at Shuwaikh and Doha Ports (Khan, 1998).

There are several coastal developments and socio-economic activities at the Sulaibikhat Bay area. The most important activities, from north to south, are: 1) Power and desalination plants that discharge industrial sewage, 2) The Entertainment City that discharges mainly sanitary wastewater, 3) The

Sulaibikhat Sport Club that discharges sanitary wastewater, 4) Hospital complex which is located at the eastern part and is considered the largest socio-economic activity at the Bay; the complex includes two main hospitals (Maternity hospital and Chest hospital), 5) Kuwait Institute for Scientific Research and Kuwait University complex which are located at the eastern corner of the Bay, and 6) Shuwaikh Port, which is located at the eastern end of the Bay, it is the main cargo port in the State of Kuwait. The port has many docking yards, marinas and coast guard facilities. In addition, there are two main outlets that affect the study area: Al Ghazali outlet which discharges sewage water from Shuwaikh industrial area and the Free Zone area outlet which discharge sewage from the Free Zone area located in Shuwaikh Port. The facilities at Shuwaikh Port discharge waste, mainly oily sludge directly into the marine environment (Khader, 1997). There is one island in Sulaibikhat Bay Um Al-Namil, which is located at the Northern corner of the Bay (Figure1).

source: Google Earth

Figure 1: Sulaibikhat Bay location (Satellite image)

MATERIAL AND METHODOLOGY

Description of the study area

The study area is located at the eastern part of Sulaibikhat Bay between latitudes $29^0$19’ and $29^0$21’ N and longitudes $47^0$52’ and $47^0$54’ E. It has the same characteristics of Sulaibikhat Bay in terms of waves, current and type of sediment.

Daily tide ranges from 2 to 4 m. The seasonal tide ranges from 1.46 to 4.30 m. The lagoon construction which links Shuwaikh Island to the mainland has reduced the tidal movement, and therefore affected the dilution of sewage water that has been pumped to the area (Clark *et al.*, 2001)

Al-Baroudi, (1985) and Khan, (1998) have identified 17 potential discharge points in Sulaibikhat Bay for water outfalls, sewers, or manholes that overflow during storms into the sea (Figure 2). There are many discharge points near Shuwaikh Port such as Al-Ghazali and Free Zone outlets, Shuwaikh harbor, and several sanitary wastewater outlets. Al-Ghazali outlet is a sanitary wastewater overflow from overloaded sewage pumping station system which discharges large quantities of industrial effluents from Shuwaikh industrial area (Figure 2).

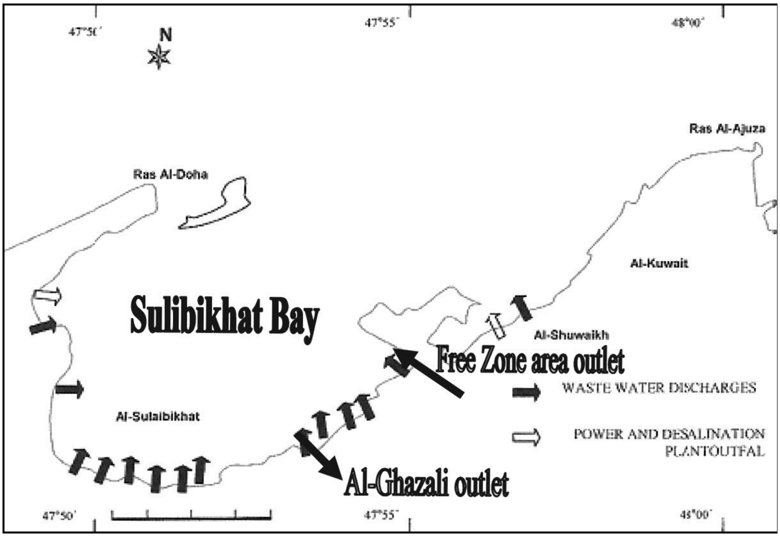

Figure 2: industrial discharge points in Sulaibikhat Bay (after Khan, 1998)

The Ministry of Communications starts a project to dredge and remove the contaminated sediments located north of Kuwait University Shuwaikh campus within Sulaibikhat Bay. The project is located about 1 km to the south of the Free Trade Zone, and about 900 m E of the University campus. The total size of the working project area is 400,000 m^2.

A total number of 31 shipwrecks have been removed from the project area and 3 from outside the project area. The area has been divided into different zones and at each zone the contaminated sediments have been removed and replaced with clean sand from Al-Jahra according to The Environmental Public Authority (E.P.A) regulations. The two main outlets (Al-Ghazali and Free Zone outlets) have been isolated totally by building a barrier in the project area, and two channels one near Free Zone area outlet and the other near Al-Ghazali outlet for the sewage water. The contaminated sediments have been transported and disposed under EPA and Kuwait Municipality regulations and standards for sanitary landfill (Figure 3) (The Ministry of Communications report 2006).

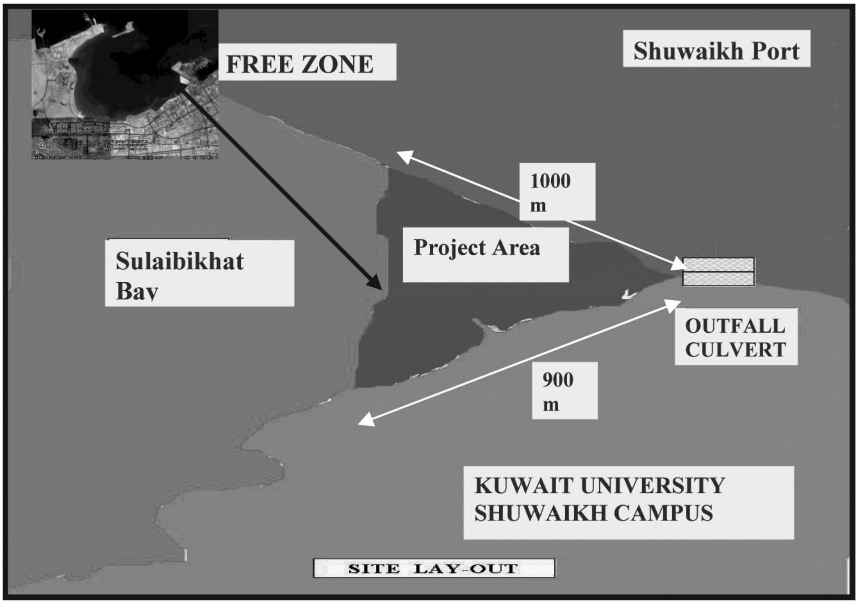

Figure 3: the contaminated sediments - Kuwait University campus (2003)

The study area includes major coastal activities that may affect the environment. These activities include a hospital area complex that consists of two main hospitals (Maternity Hospital and Chest Hospital), Kuwait Institute for Scientific Research, Kuwait University Complex, and Shuwaikh Port.

Sample Collection

A total of 60 sediment samples were collected from 30 stations located in the eastern corner of Sulaibikhat Bay during winter (February 2006) and summer (June 2006) seasons. Location of the sampling stations are shown in Figure 4.

The samples were collected using a hovercraft belonging to the Marines search and Rescue Department (Fire Department). Sediments were collected from each station using Van Veen grab sampler. The sediments for trace metals analysis were numbered and stored in ice boxes.

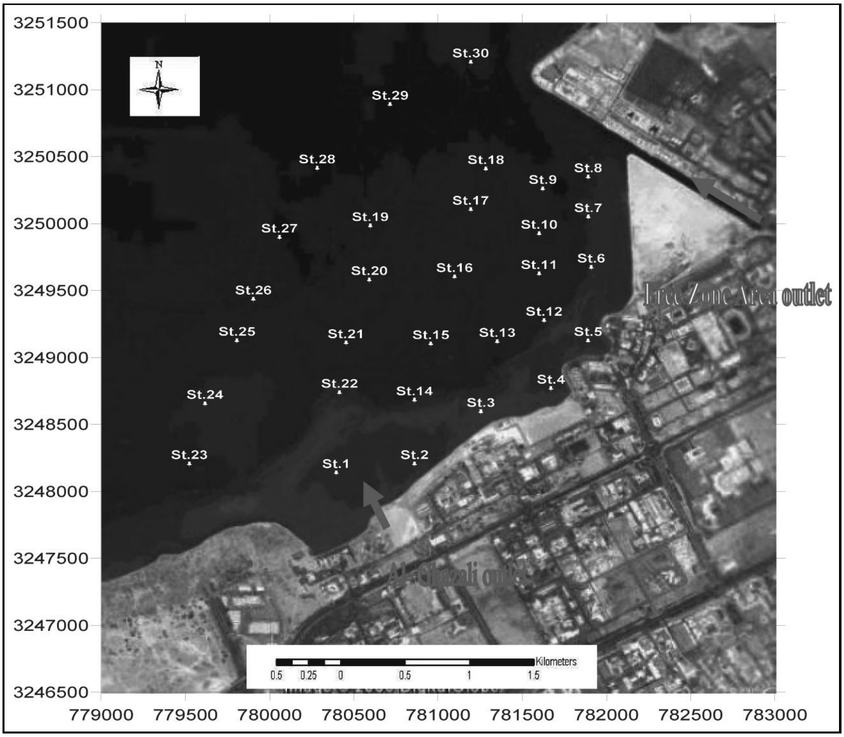

Figure 4: Locations of the sampling stations (Satellite image) Source: Google image

ANALYSIS

Total organic carbon analysis

Organic carbon was determined following the method of Gaudette *et al*., (1974). This method provides an excellent agreement with the LECO combustion method of organic carbon analysis. The method was as followed as:- 49.04 g of potassium dichromate was dissolved in 500 ml of distilled water, and the solution was diluted to 1L. 40 ml of 98% concentrated H_2SO_4 was diluted to 500 ml with distilled water, and 159.6g of ferrous ammonium sulfate was dissolved in 98% concentrated H_2SO_4 solution and the mixture was shaken until a clear solution was obtained. The solution was cooled and diluted to 1L by water, and stored in dark colored bottles (opaque bottle) to a void exposure from direct sun light. In a 500 ml Erlenmeyer flask, 0.2 g-0.5 g of air dried sediment samples, sieved through 0.63 mm (230) mesh were mixed with 10 ml of 1N$K_2Cr_2O_7$ (294.19 M.W. dissolve 49.04 g of 1N$K_2Cr_2O_7$ in water then dilute to 1 L) solution and 20 ml of 98% concentrated H_2SO_4 with Ag_2SO_4 (dissolve 2.5g Ag_2SO_4 in 1L of H_2SO_4) were mixed and added gently by rotating the flask for about 1 minute. The mixture was kept for 30 minutes at room temperature. A Standardized blank without sediment was ran with the samples (dextrose $C_6H_{12}O_{16}$ is used as standard which contain 39.99% carbon). After 30 minutes, 200 ml distilled water, 10 ml of 85% H_3PO_4, and 0.2 g solid NaF were added. Diphenylamine indicator (15 drops, dissolve approximately 0.5 g of reagent grade diphenylamine in 20 ml of water and 100 ml of 98% concentrated H_2SO_4) was added to the sample flask, and the solution was titrated with the 0.5 N Ferrous ammonium sulfate solution (dissolve 196.1 g of Fe $(NH_4)_2SO_46H_2O$ (392.13 M.W.) in 800 ml of water containing 20 ml of 98% concentrated H_2SO_4; diluted to 1 L) to one drop end point brilliant green (ROPME, 1999).

The percentage of organic matter was calculated by using the following equation:

% organic matter = 10 (1-T/Ś) x F

Where T is sample titration ml of ferrous solution, Œ is Standardization blank titration in ml of ferrous solution, and F is a factor derived as follow:

(1.0N) x 12/4000x 1.72 x 100/sample weight = 1.03 when the sample weight is exactly 0.5 g. Where 12/4000 = meq wt. Carbon and 1.72 = factor of organic matter from carbon.

Trace metals in sediment analysis

Following ROPME, 1999 manual procedures, a maximum 200 mg dried sample was used for trace metal analysis in teflon bombs. One ml of aqua regia (70% of HNO_3: 37% of HCl, 1:3 v/v) and 6 ml of concentrated hydrofluoric acid (48% of HF) were slowly added. The samples were left at room temperature for at least one hour. The Teflon bombs were closed tightly and placed in a microwave oven for 1 min and 50 sec at 100% of power (180^o).

Weigh 3.70 g of boric acid into 50 ml polypropylene graduated tubes and add to it 20 ml of Milli-Q water and shake it well. The samples were allowed to cool at room temperature, and then transferred into the polypropylene graduated tubes containing boric acid (61.83 M.W.). The teflon bombs were rinsed with Milli-Q water at least 3 times by adding the wash to the polypropylene tubes. In a shaker machine, the tube was shaken to complete the dissolution of H_3BO_3, and diluted to the mark (50ml) with Milli-Q water. The particles were allowed to settle overnight, and then analyzed by Atomic absorption spectrometry (ROPME, 1999). Three Blanks were prepared for each batch of analysis following the same procedure except that no sediment sample was added to the digestion vials. Concentration of trace metals in sediment was calculated by using the following equation:

Concentration of trace metals in sediments =

$$\frac{(\text{Concentration of trace metals in solution } \times \text{ volume in ml})}{\text{Original weight of the sample}}.$$

RESULTS AND DISCUSSION

1 - Total Organic Carbon in sediments

A total of 60 samples of sediments were taken during the winter and summer of 2006 for the analysis of Total Organic Carbon content (TOC). TOC is an important environmental factor used to indicate oil and non-oil pollution (Al-Abdul Razzaq *et al.,* 1983). TOC percentage is considered a good indicator for pollution which has positive correlation to trace metal contaminations (Khalaf *et al.,* 1982 and Al-Abdali *et al.,* 1996).

In the study area and during the winter season, the concentration of TOC in sediments ranged between 1.45 and 8.42% and averaged 4.32% ± 1.96. High TOC concentration was found in areas close to Al-Ghazali outlet, the Free Zone outlet, and Shuwaikh harbor.

During the summer season, TOC concentrations in sediment ranged between 0.41 and 8.76% and averaged 4.64% ± 2.44 (Tables1-2). High TOC concentrations were recorded in the study area close to Al-Ghazali outlet, the Free Zone outlet, Shuwaikh harbor, and north of the study area. Sources of TOC concentration during the summer season are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area, and the Free Zone outlet. Also, discharge from Shuwaikh harbor and high river influx from Shatt Al-Arab.

Literathy *et al.,* (1992) determined the background level of TOC in Kuwait's marine bottom sediment to be in the range of 0.50% to 0.80%. It is concluded that TOC concentration in the study area is higher than the background level and the area is exclusively contaminated with TOC.

Table 1 Descriptive statistics of Total Organic Carbon during the two seasons

Variable	Valid N	Average	Minimum	Maximum	Std.Dev.%
TOC - February 2006	30	4.32	1.45	8.42	1.96
TOC - June 2006	30	4.64	0.41	8.76	2.44

Table 2: Percentages of Total Organic Carbon (%)
in the study area during the two seasons

St.N	TOC - February 2006	TOC - June 2006
St. 1	4.18	4.84
St. 2	2.79	0.72
St. 3	6.73	2.58
St. 4	3.57	2.27
St. 5	6.00	5.77
St. 6	6.73	7.00
St. 7	2.91	8.65
St. 8	7.03	8.45
St. 9	6.06	4.94
St. 10	8.42	7.42
St. 11	7.88	6.28
St. 12	4.91	0.41
St. 13	4.36	4.94
St. 14	3.76	3.81
St. 15	3.15	7.42
St. 16	2.42	3.81
St. 17	2.30	7.21
St. 18	6.30	8.03
St. 19	6.48	4.43
St. 20	3.03	2.16
St. 21	3.39	3.91
St. 22	4.67	5.25
St. 23	2.36	1.55
St. 24	3.21	1.85
St. 25	2.30	4.22
St. 26	1.45	4.43
St. 27	2.42	3.50
St. 28	2.67	1.75
St. 29	6.06	8.76
St.30	2.06	2.88
Average	4.32	2.88

2 - Trace metals in sediments

Eleven trace metals were selected and determined for the present study. These metals are: iron (Fe), lead (Pb), mercury (Hg), silicon (Si), manganese (Mn), zinc (Zn), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni), and vanadium (V). All the trace metal concentrations in the study area were measured and analyzed and compared during the two seasons to find the correlations and understand the behavior of these elements in the study area (Table 3).

Table 3: Statistical distribution of trace metals in the study area during the two seasons

Variables		sample N	Mean	Minimum	Maximum	Std.Dev.%
Fe (ppm)	February 2006	30	19452.26	1073.48	27350.52	5683.17
	June 2006	30	19854.49	2450.75	29339.00	8233.36
Pb (ppm)	February 2006	30	19.45	16.90	44.30	4.87
	June 2006	30	18.30	16.77	23.20	1.42
Hg (ppm)	February 2006	30	18.28	16.90	19.29	0.64
	June 2006	30	18.00	16.77	20.00	0.92
Si (ppm)	February 2006	30	109935.92	30978.47	138039.07	21243.45
	June 2006	30	139278.20	49281.31	200400.00	33852.14
Mn (ppm)	February 2006	30	290.84	48.55	399.42	83.24
	June 2006	30	320.88	45.35	512.45	126.22
Zn (ppm)	February 2006	30	119.15	9.21	389.43	87.70
	June 2006	30	116.79	10.78	294.48	78.59
Cd (ppm)	February 2006	30	9.29	8.40	10.34	0.42
	June 2006	30	9.00	8.38	10.00	0.46
Cu (ppm)	February 2006	30	35.89	17.69	93.26	18.75
	June 2006	30	38.74	17.11	77.95	19.51
Cr (ppm)	February 2006	30	89.05	18.41	124.91	24.77
	June 2006	30	90.49	16.98	170.32	42.21
Ni (ppm)	February 2006	30	78.98	18.41	108.11	20.07
	June 2006	30	84.75	15.49	115.76	32.49
V (ppm)	February 2006	30	275.98	61.39	372.50	67.89
	June 2006	30	282.15	37.73	423.14	103.14

2.1 Iron (Fe)

The concentration of Fe in sediments during the winter season ranged between 1073.48 and 27350.21 ppm, and averaged 19452.26 ppm ± 5683.17. High Fe concentration was distributed equally among all the study area sediments.

During the summer season, Fe concentration ranged between 2450.75 and 29339.00 ppm and averaged 19854.49 ppm ± 8233.36. High Fe concentration was recorded in an area close to the shoreline, Al-Ghazali outlet, the Free Zone outlet, the sand-filled triangle rehabilitated, and in the northern part of the study area (Table 3).

Possible sources of Fe in the study area sediments were Al-Ghazali outlet that discharges sewage water from Shuwaikh industrial area, discharge from the Free Zone outlet, suspended solid materials rich in trace metals from Shatt Al-Arab related to high sediment influx during the summer season, discharge from industrial and commercial activities in the north of Sulaibikhat Bay as well as Fe rich sediments in areas close to the triangle rehabilitated related to the naturally oxy(hydr)oxides of shipwrecks. The back ground level of Fe in Sulaibikhat Bay sediment was 16000 ppm (Anderlini *et al.,* 1986). It is concluded that Fe concentration in the study area is higher than the background level.

2.2 Lead (Pb)

The concentration of Pb in sediments during the winter season ranged between 16.90 and 44.30 ppm while the average was 19.45 ppm ± 4.87. High Pb concentration was recorded in areas close to the Free Zone outlet.

During the summer season, Pb concentration in sediments ranged between 16.77 and 23.20 ppm while the average was 18.30 ppm ± 1.42. High Pb concentration was recorded in areas close to the sand-filled rehabilitated triangle and the Free Zone outlet as well as in the west (Table 3).

Pb concentration was higher during the summer than the winter season. A possible source of Pb in the study area was discharge from the Free Zone outlet. The back ground level of Pb in Sulaibikhat Bay sediment was 27.00 ppm (Anderlini *et al.,* 1986).

2.3 Mercury (Hg)

Mercury (Hg) concentration in sediments during the winter season ranged between 16.90 and 19.29 ppm while the average was 18.28 ppm ± 0.64. High Hg concentration was recorded in areas close to Al-Ghazali outlet, the Free Zone outlet, and in the northern part of the study area.

During the summer season, Hg concentration in sediments ranged between 16.77 and 20.00 ppm, while the average was 18.00 ppm ± 0.92 (Table 3). High Hg concentration was recorded in areas close to the Free Zone outlet as well as in the west and north of the study area. Higher concentrations of Hg were recorded during winter season than summer season.

Possible sources of Hg in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area, discharge forms the Free Zone outlet, discharge from the emergency outlet close to Kuwait University, and discharge from different activities in the northern part of Sulaibikhat Bay as Doha power plant. There was no study for back ground level of Hg in Sulaibikhat Bay sediment.

2.4 Silicon (Si)

Silicon (Si) concentration in sediments during the winter season ranged between 30978.47 and 138039.07 ppm, while the average was 109935.92 ppm ± 21243.45. High Si concentration was recorded in areas close to Shuwaikh harbor, as well as in the north and west of the study area.

During the summer season, silicon concentration in sediments ranged between 49281.31 and 200400.00 ppm, while the average was 139278.20 ppm ± 33852.14. High Si concentration recorded in areas close to Shuwaikh harbor, Al-Ghazali outlet, the Free Zone outlet, Kuwait University as well as in the north and west of the study area. Higher Si concentration was recorded during the summer than the winter season (Table 3).

Possible sources of high Si concentration in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area which increases during the summer season, discharge from the Free Zone outlet, discharge from the emergency outlet close to Kuwait University, high suspended sediment influx from Shatt Al-Arab during the summer season as well as the silty sediments in the study area. There was no study for back ground level of Si in Sulaibikhat Bay sediment. The high Standard deviation for Si concentration in the study area related to the different between high and low parameters that have recorded.

2.5 Manganese (Mn)

Manganese (Mn) concentration in sediments during winter season ranged between 48.55 and 399.42 ppm, while the average was 290.84 ppm ± 83.24. High Mn concentration was recorded in all the study area which makes it difficult to predict its source.

During the summer season, Mn concentrations in sediments ranged between 45.35 and 512.45 ppm, while the average was 320.88 ppm ± 126.22. High Mn was recorded in areas close to Al-Ghazali outlet as well as in the north and the west of the study area (Table 3).

Possible sources of Mn concentration in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area and high sediment influx carried by rivers to Shatt Al-Arab and then to the area during the summer season. The back ground level of Mn in Sulaibikhat Bay sediment was 470.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for Mn concentration in the study area related to the different between high and low parameters that have recorded.

2.6 Zinc (Zn)

Zinc (Zn) concentration in sediments during the winter season ranged between 9.21 (in areas faraway from the sewage outlets) and 389.43 ppm while the average was 119.15 ppm ± 87.70. High Zn concentration was recorded in areas close to the Free zone outlet.

During the summer season, Zn concentration in sediments ranged between 10.78 and 294.48 ppm, while the average was 116.79 ppm ± 78.59. High Zn concentration was recorded in areas close to the Free zone outlet (Table 3). The back ground level of Zn in Sulaibikhat Bay sediment was 57.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for Zn concentration in the study area related to the different between high and low parameters that have recorded. It is concluded that Zn concentration in the study area is higher than the background level.

2.7 Cadmium (Cd)

Cadmium (Cd) concentration distribution showed similar tends in the study area during summer and winter and did not show any seasonal variation.

During the winter season Cd concentration in sediment ranged between 8.40 and 10.34 ppm while the average was 9.29 ppm ± 0.42. High Cd concentration was recorded in areas close to Al-Ghazali outlet, the Free zone outlet, Kuwait University, Shuwaikh harbor, and north of the study area.

Similarity, Cd concentration in sediments during summer ranged between 8.38 and 10.00 ppm while the average was 9.00 ppm ± 0.46 (Table 3). High Cd concentration was recorded in areas close to Al-Ghazali outlet, Free zone outlet, Kuwait University, Shuwaikh harbor, and in the north and west of the study area.

Possible sources of Cd high concentration in the study area were Al-Ghazali outlet that discharges sewage from the Shuwaikh industrial area, discharge from the Free Zone outlet, discharge from an emergency outlet close to Kuwait University, oil spills from Shuwaikh harbor, discharge from industrial and commercial activities in the northern part of Sulaibikhat Bay, as well as high suspended sediment influx from Shatt Al-Arab during the summer season. The back ground level of Cd in Sulaibikhat Bay sediment was 5.75 ppm (Bou Olyan *et al.,* 1998). It is concluded that Cd concentration in the study area is higher than the background level.

2.8 Copper (Cu)

Copper (Cu) concentration in sediments during winter season ranged between 17.69 and 93.26 ppm while the average was 35.89 ppm ± 18.75. High concentration of Cu recorded in areas close to the Free Zone outlet and Shuwaikh harbor.

During the summer season, Cu concentration in sediments ranged between 17.11 and 77.95 ppm while the average was 38.74 ppm ± 19.51. High concentration of Cu recorded in areas close to the new Chest Hospital, the Free Zone outlet, and Shuwaikh harbor (Table 3).

Possible sources of Cu concentration in the study area are discharge from the new Chest Hospital, discharge from the Free Zone outlet, and oil spills from Shuwaikh harbor. The back ground level of Cu in Sulaibikhat Bay sediment was 23.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for Cu concentration in the study area related to the different between high and low parameters that have recorded. It is concluded that Cu concentration in the study area is higher than the background level.

2.9 Chromium (Cr)

Chromium (Cr) concentration in sediments during the winter season ranged between 18.41 and 124.91 ppm, while the average was 89.05 ppm ± 24.77. High Cr concentrations were recorded during the winter season, which was difficult to predict its source.

During the summer season, Cr concentration in sediments ranged between 16.98 and 170.32 ppm, while the average was 90.49 ppm ± 42.21. High Cr concentration was detected in areas close to Al-Ghazali outlet, Kuwait University, Kuwait Institute for Scientific Research as well as in the northern and western part of the study area (Table 3).

Possible sources of Cr concentration in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area, discharge from emergency outlet closed to Kuwait University and Kuwait Institute for Scientific Research, and high sediment influx from Shatt Al-Arab during the summer season. The back ground level of Cr in Sulaibikhat Bay sediment was 80.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for Cr concentration in the study area related to the different between high and low parameters that have recorded. It is concluded that Cr concentration in the study area is higher than the background level.

2.10 Nickel (Ni)

Nickel (Ni) concentration in sediments during the winter season ranged between 18.41 and 108.11 ppm, while the average was 78.98 ppm ± 20.07. High Ni concentration was recorded in all the study area which makes it difficult to predict its source.

During the summer season, Ni concentration in sediments ranged between 15.49 and 115.76 ppm while the average was 84.75 ppm ± 32.49. High Ni concentration was detected in areas close to Al-Ghazali outlet, the Free Zone outlet, and Kuwait University (Table 3).

Possible sources of Ni concentration in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area, discharge from the Free Zone outlet, and discharge from the emergency outlet close to Kuwait University campus. The back ground level of Ni in Sulaibikhat Bay sediment was 91.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for Ni concentration in the study area related to the different between high and low parameters that have recorded.

2.11 Vanadium (V)

Vanadium (V) concentration in sediments during the winter season ranged between 61.39 and 372.50 ppm, while the average was 275.98 ppm ± 67.89.

During the summer season, V concentration in sediments ranged between 37.73 and 423.14 ppm, while the average was 282.15 ppm ± 103.14. High concentration of V was detected during the two seasons in areas close to Al-Ghazali outlet, the Free Zone outlet, Kuwait University, and Shuwaikh harbor (Table 3).

Possible sources of V in the study area are Al-Ghazali outlet that discharges sewage from Shuwaikh industrial area, discharge from the Free Zone outlet, oil spills from Shuwaikh harbor, and discharge from the emergency outlet close to Kuwait University. The back ground level of V in Sulaibikhat Bay sediment was

43.00 ppm (Anderlini *et al.,* 1986). The high Standard deviation for V concentration in the study area related to the different between high and low parameters that have recorded. It is concluded that V concentration in the study area is higher than the background level.

3 - Statistical correlations

Eleven trace metals and total organic carbon were studied and analyzed statically. Person correlation test were used to determine the degree of association between the parameters. The correlations results for each element are shown in Table 4.

Table 4: Statistical correlation of trace metals in the study area during the two seasons

trace metal elements	Fe - S	Si - S	Zn - S	Cu - S	Cr - S	Ni - S	V - S	TOC - S
Fe - W	.411*	.451*	.504**	.457*		.449*	.363*	.364*
Pb - W			.375*					.368*
Si - W		.418*						
Zn - W			.816**	.712**		.465**		.730**
Cd - W	0.365*							
Cu - W	.385*		.826**	.744**		.471**		.719**
Ni - W	.406*	.389*	453*	.403*		.433*	.367*	
V - W			.406*			.385*		
TOC - W	.494**	.477**	.721**	.762**	.375*	.491**	.429*	.452*

* $P < 0.05$

** $P < 0.001$

Between summer and winter the study show:- iron in summer had high correlation with TOC and low correlation with Fe, Cd, Cu and Ni in winter. Iron in winter had high correlation with Zn and low correlation with Fe, Si, Cu, Ni, V and TOC in summer. Lead in winter had low correlation with Zn and TOC in summer. Silicon had high correlation with TOC and low correlation with Fe, Si and Ni in winter. Silicon in winter had low correlation with Si. Zinc had high correlation with TOC and low correlation with Pb, Ni and V. Zinc in winter had high Zn, Cu, Ni, and TOC in summer. Cadmium in winter had low correlation with Fe. Cooper in summer had high correlation with Cu, Zn and TOC and low correlation with Fe and Ni in winter. Cooper in winter had high correlation with Zn, Cu, Ni and TOC and low correlation with Cr, V and TOC in summer. Chromium in summer had low correlation with TOC in winter. Nickel in summer had high correlation with Zn, Cu, and TOC and low correlation with Fe, Ni and V in winter. Nickel in winter had low correlation with Fe, Si, Zn, Cu, Ni and V in summer. Vanadium in summer had low correlation with Fe, Ni and TOC in winter. Vanadium in winter had low correlation with Ni and Zn in summer. TOC in summer had high correlation with Zn and Cu and low correlation with Fe, Pb and TOC in winter. TOC in winter had high correlation with Fe, Si, Zn, Cu and Ni and low correlation with V, Cr and TOC in summer (Table 4).

From the study it had shown that elements as Fe, Si, Mn, Zn, Cu, Cr, Ni, V and TOC had high correlation with each other, they are present in the same areas which are around the two outlets and close to the Shuwaikh harbor. Trace elements like Mn, Zn, Cu, Cr, Ni, V and TOC increase and decrease together in different stations which mean that they come from the same sources and affect the same areas where they present. Silicon is present in the area normally related to the type of the sediment in the area which is muddy and rich in silt. Iron is present in the area for long time related to the wrecked ships that present from1990 until 2002.

The main sources of trace metals in the study area are Al-Ghazali outlet discharges sewage from Shuwaikh industrial area, Free Zone outlet discharges sewage from the commercial area, and oil spills from the main Shuwaikh harbor in Kuwait city.

CONCLUSION

In summary, sediments are known as final hosts for marine contaminations, and are considered good indicators for pollution (Al-Abdul Razzaq *et al.,* 1983). There are other confounding factors affect the concentrations of trace metals in sediments as temperature, salinity, pH, dissolved oxygen turbidity and depth. The physical properties of the sediments in the study area are muddy, dark grey color and rich in organic matter.

Organic matter refers to substances of living and nonliving organisms and their byproducts. The major sources of TOC in the study area are discharges from Al-Ghazali outlet, Free Zone outlet, Shuwaikh harbor, and high influxes from Shatt Al-Arab river during the summer season (Abel, 1989; Montgomery, 2006).

Trace metals are natural elements found in sea water, sediments, and marine organisms. Metal speciation is influenced by many factors, such as: source of the trace metal, physiochemical parameters, currents and tides, type of grain size of sediments, presence of organic matters, and the behaviors of trace metals in the environment (Burden *et al.,* 2002). Rivers are major sources of trace metals present in the sea, and small quantities of many metals are added to the sea by direct discharge, and by the atmosphere (Clark *et al.,* 2001).

There are many other sources of trace metals in the study area, such as: Al-Ghazali outlet that discharges raw sewage from Shuwaikh industrial area, discharges from the Free Zone area and emergency outlets close to Kuwait Institute for Scientific Research and Kuwait University, discharges from the industrial and commercial activities in the north of Sulaibikhat Bay, oil spills and accidents from Shuwaikh harbor, as well as high sediment influx from Shatt Al-Arab during the summer season where high levels of heavy metal were observed (Montgomery, 2006).

Comparing the concentration of trace metals in the two seasons it was found that levels of trace metals in the study area were high close to the two outlets (Al-Ghazali outlet, Free Zone outlet) and Shuwaikh harbor. Trace metals were observed to behave differently in winter and summer seasons. Iron, silicon, zinc, cadmium, copper, chromium, nickel, vanadium and total organic carbon were highly correlated with each other. TOC and trace metal concentration increases during the summer season may be due to the river influx and high sewage discharge. Another source of trace metal contamination in Sulaibikhat Bay sediments are mainly river input from Shatt Al-Arab, Shuwaikh harbor, or via the atmosphere (Abayachi and Douabul 1985; Al-Shemmari 2000; Al-Sarawi *et al.,* 2002). Sulaibikhat Bay is considered to be a fragile marine environment because of the presence of several commercial and industrial activities and many emergency outlets on its shores. As a result trace metals accumulated in the area for long periods, and some elements had increased gradually in the area (Khan *et al.,* 1999 and El-Sammak *et al.,* 2005).

The concentration of zinc, chromium, nickel, cadmium, and vanadium in sediments was high in the area and they came from the same sources. The sources of these four elements were found in areas close to the shoreline where a lot of emergency outlets are present (Al-Ghazali outlet discharge sewage water from Shuwaikh industrial area, and free zone outlet discharge sewage water from commercial and industrial area). Furthermore, oil spills from Shuwaikh harbor could be another source of these metals. Silicon is an element that is found in the sediment naturally, but also may be observed in the area from the two sewage outlets discharges. Iron is not considered a contaminating element in the sea; however in the study area the high levels recorded is related to the oxy(hydr)oxides acting on the sunken boats that had been present in the area closed to the rehabilitated triangle region set after Gulf War,and from the increase of transportation process in Shatt Al-Arab (Al_ Abdali *et al.,* 1996; Clark *et al.,* 2001; Al-Sarawi *et al.,* 2002).

To minimize the pollution level in Sulaibikhat Bay, the following recommendations could be adopted: adequate treatment of sewage water before discharge into the marine environment. Sewage from Shuwaikh industrial area has to be isolated. Find the best environmental techniques that can help control oil spills from Shuwaikh port. Open a channel under Shuwaikh port through the study area to increase water circulation in the area and avoid precipitation and accumulation of pollutants in the sediments. Activate Kuwaiti Law 12 of 1964 regarding the prevention of pollution in navigable waters by oil spills from marine-based sources such as marine vassals or industrial activities from urban areas that can cause danger to the ecosystem (Al-Kandari, 2003). Further study in the area to find the effect of trace metals pollution on the marine organisms is recommended.

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تركيز المعادن النذرة و المواد الهيدروكربونيه في الشريط الساحلى لمنطقة الشويخ - دولة الكويت

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خلاصة

تقع منطقة الدراسة في الجهة الشرقية من جون الصليبيخات مقابل جامعة الكويت في منطقة الشويخ. تعتبر المنطقة ضحلة موحلة وداكنة اللون وضعيفة في حركة التيارات والأمواج متأثرة كثيرا بالملوثات. جزء من منطقة الدراسة تم إعادة تأهيلها خلال إزالة السفن المعطوبة والرسوبيات الملوثة.

الهدف من هذه الدراسة هو إيجاد تراكيز المعادن النذرة في المنطقة والبحث عن الارتباطات بين مختلف هذه العناصر بين موسمي الصيف والشتاء.

ثلاثون محطة رصد تم تجميع ستون عينة ماء وستون عينة رسوبيات خلال موسمي الشتاء والصيف من عام 2006. جميع الرسوبيات تم تحليلها لمعرفة تراكيز المعادن النذرة. تراكيز أحد عشر عنصر من المعادن النذرة (الحديد، الرصاص، الزئبق، السيلكون، المنغنيز، الزنك، الكادميوم، النحاس، النيكل، والفانيديوم) بالإضافة إلى تركيز المواد الكربونية العضوية تم تحليلها ودراستها كيميائيا.

تبين من الدراسة أن خلال تحليل الرسوبيات وجد أن المنطقة ملوثة بمعادن الزنك والكروميوم والكادميوم والنيكل والفانيديوم. أما الرصاص والمنغنيز والنحاس تعتبر من العناصر التي زاد معدل تراكيزها عن الدراسات الأوليه للتربة في جون الصليبيخات. المنطقة الساحلية في منطقة الدراسه ملوثة جدا بالمعادن النذرة وتركيز المواد الكربونية العضوية. السبب الرئيسي لارتفاع ارتباط بين السيليكون والحديد والعناصر المختلفة هو نوع من الرواسب في المنطقة الموحلة من الطمى ووجود الحديد في منطقة الدراسة في الفترة من عام 1990 حتى بعد إزالة السفن الغارقة.

أوضحت الدراسة أن منطقة الدراسه والتي تقع ضمن جون الصليبيخات واقعة تحت ضغوطات بيئية عالية ناتجة عن إرتفاع تراكيز المعادن النذرة والمواد العضوية. لتجنب المزيد من المشاكل البيئية في المستقبل توصي هذه الدراسه بعزل مخلفات المجاري الناتجة من منطقة الشويخ الصناعية ومعالجة مياه المجاري بكفاءة عالية قبل صرفها إلى البيئة البحرية وتوفير التكنولوجيا البيئية لمكافحة التسرب النفطي وتفعيل قانون رقم 12 لعام 1964 والذي يحث على مكافحة التلوث النفطي الظاهر في المياه البحرية.