

Impact of Heavy Metals and Petroleum Hydrocarbons Contamination of the East Port Said Port area, Egypt

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Abstract: The concentration of total organic carbon (TOC), total petroleum hydrocarbons (TPH), and petroleum related heavy metals beside the grain size distribution of East Port Said Port area, Egypt were determined in the bottom sediment. Copper, zinc, nickel, lead, cadmium and vanadium concentration were found above the accepted level. The contamination levels were found due to anthropogenic origin. These include intensive maritime activities, disposal of wastes from anchorage vessels that are waiting the crossing of the Suez Canal, lubricating oil, wastes from the ships yard at the entrance of the Suez Canal and wastes from the urban centers (Port Said and Port Fouad cities). The study area is subjected to environmental stresses due to the occurrence of different pollution sources. The latter may include ship wastes, leaching of ship paints, waste disposal from the Suez Canal Authority ship yard at Port-Fouad, Port-Said harbor, municipal waste from two major urban areas (Port-Said and Port Fouad cities). In addition the offshore area is considered as an important fishing ground.

Key words: heavy metals, contamination, TOC, TPH, TKN, Port Said, and Egypt

INTRODUCTION

The study area lies between latitudes 31° 13' to 31° 27' N and longitudes 32° 15' to 32° 29' E. It represents a part of the Egyptian Mediterranean coast lying to the north of the Nile Delta east of Port Said. The area under consideration covers about 400 km² to the north of Port Fouad city (Fig. 1). The seabed slopes gradually from the coastline towards the open sea with overall average gradient of 1m/km. The depth reaches about 25 m at the northern limit of the study area. Sandy sediments mostly cover the coastal and nearshore area while the seabed of the deeper zone is generally muddy. The study area is located within the eastern fringe of the Damietta Nile Branch offshore sediment lobe. The area is characterized by a long shore littoral drift from SW to NE with average velocity of 17 cm /sec. Hydrodynamic processes are of prime importance for the understanding of the magnitudes and pattern of sediments movements and associated pollutants. The study area is very busy with diversified maritime activities due to its location close to the entrance of the Suez Canal. Two anchorage areas are located within the northwestern corner of the study area. The present article was aimed to determine the source and the level of pollution in the bottom sediment of East Port Said Port area. These data are of valuable importance for the construction of the new port recently occurred.

Geologic Setting of the Study Area: The Sinai subplate is located between the Nubian – Arabian shield in the southeast and the eastern Mediterranean basin. A generalized lithostratigraphic column for North Sinai is illustrated in (Fig. 2). According to surface and subsurface data, facies change occurred during the Jurassic and cretaceous along the hinge zone^[7]. A regional stratigraphic gap and unconformity underlies the basal fluvio – continental deposits of the lower cretaceous represented by the Nubian strata. During the middle cretaceous, ruelistid fining reefs developed all along the pre-existing hinge zone^[1]. During the upper cretaceous, the Sinai shelf platform was uniformly covered by a chalky marly sequence. The Eocene “plateau limestone “is 300 to 400 m thick and is made up of two units, limestone with flint of lower Eocene Egma or Thebes formation. Northern Sinai known from borehole drilled in extreme north of Sinai and offshore area is related to the relationship of three geological components^[4]. Transgression from the Tethys began, which invaded the Suez graben. It was followed by the late Miocene generation regression. Quaternary sediments are well represented, thus the real distribution of Miocene platform carbonates and the coral sand / shale, mainly supplied by the Nile Delta. The plio–Quaternary sequence is represented on shore by tin continental to littoral sediments, which are approximately 300m, consists mainly of sandstone, shell breccia, bioclastic limestone and conglomerates^[5]. The study area was the subject of intensive surface and

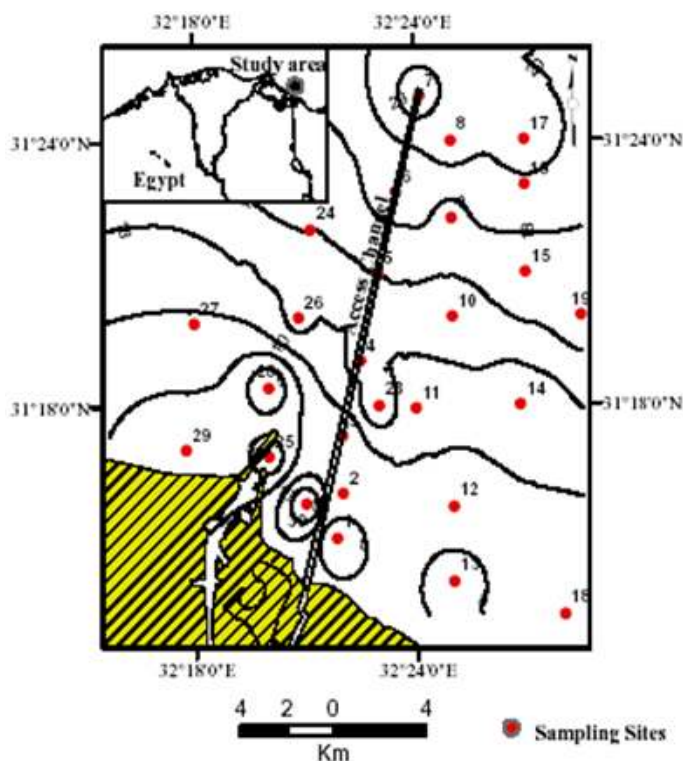


Fig. 1: Location Map of the bottom sediments sampling sites.

subsurface geological investigation during hydrocarbon and tectonic evolution of north Sinai area has been subdivided into four phases. Phase I is the break up of north Arabia in Late Triassic time and the opening of the Tethys. Phase II during the Late Cretaceous to Early Tertiary time, Africa moved West–north west relative to Eurasia, which closed the Tethys Sea and produced a right lateral shear couple between north Africa and Eurasia. Phase III the rifting of the Gulf of Suez started between 24 and 21 Ma during the latest Oligocene to the Earliest Miocene. Phase IV This phase is represented by the Late Miocene to Recent Gulf of Aqaba rifting, which was formed by left lateral oblique slip movement a long the Dead Sea. The structures of the north Sinai have been studied by several authors. The Sinai Peninsula is one of several semi–independent blocks, which have been interacting with other plates in the eastern Mediterranean in recent geologic times. The Sinai sub-plate is through to extend between the Aqaba/Dead Sea Jordan shear in the east and Gulf of Suez rift and the north–north west shear zone which represents the extension of the Suez rift to the west. The pelusium line is an east-north east to west–south west trending lineation. The eastern extension of the pelusium line cuts east north east across the continental shelf of north Sinai. Before binding north wards forming a series of north–north east to south west striking faults that follow the

continental shape of Palestine. In north Sinai and south east Mediterranean a major feature affecting the evolution of the area is the east – north east trending Hinge zone across which marked facies and thickness change in Jurassic and cretaceous sediments .

MATERIALS AND METHODS

Some physicochemical parameters e.g., pH, dissolved oxygen, salinity temperature and depth were measured in situ using the water quality logger (3800), where locations were determined by a GPS. The study area represents a part of the Egyptian Mediterranean coast lying to the north of The Nile Delta east of Port Said. Thirty–one sites were selected for the collection of the seabed samples. These sites are distributed to cover the offshore study area that extends from 3.0 m to 24.0 m depth, and about 12 km and 8 km to the west and to the east of the Suez Canal Bypass access channel, respectively Table 1. Professional divers were used to collect these seabed samples and provided general description of the bottom nature. Samples were put into plastic bags and subdivided for the various laboratory analyses. Six samples representing the top layer penetrated by boreholes were also collected. Due to the fact that most of the collected seabed sediment samples are muddy, grain size analysis was carried out using the hydrometer technique.

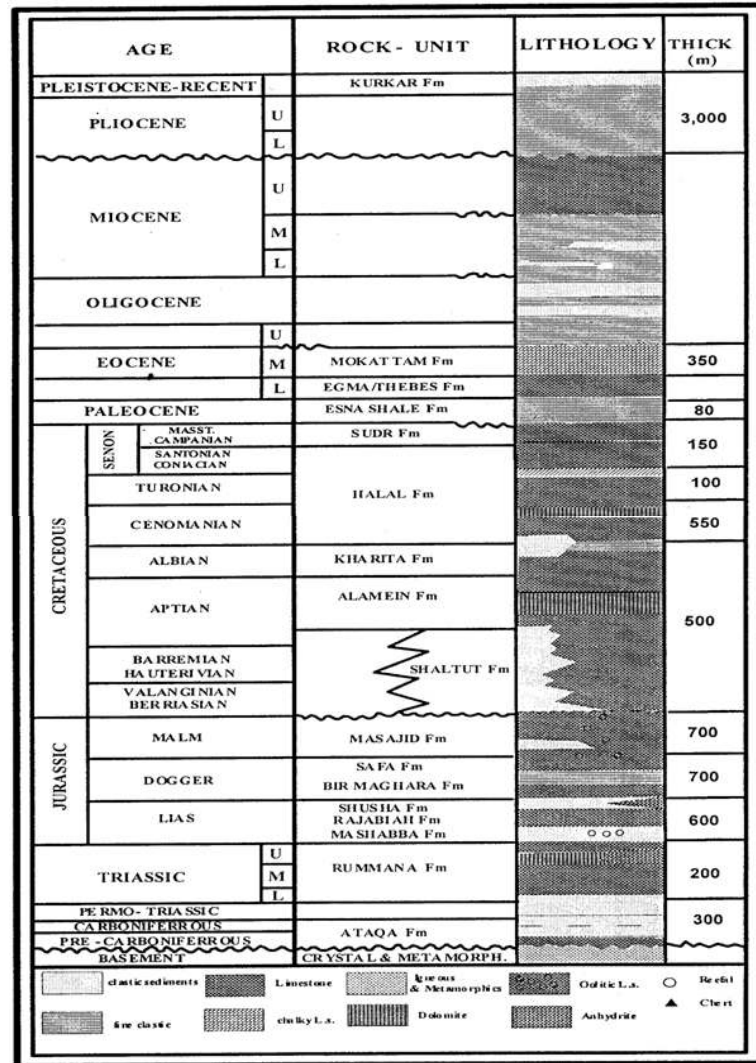


Fig. 2: Generalized Litho-Stratigraphic Column North Sinai after Schlumberger^[8].

The cumulative curves were prepared, the percentages of the main size fractions (gravel, sand and mud) and the statistical size parameters for all analyzed samples were critically computed. Carbonate content was determined by digesting the sediment with 10% HCl. The weight of acid soluble (carbonate) material was expressed as a percentage of the sample total weight. One gram of air dried sample was mixed with 3 ml HNO₃, 5 ml H₃ ClO₄, and 20 ml HF in wide-mouth crucible using a microwave mixer. The mixture heated to dryness. Few drops of concentrated HCl were then added and heated to dryness. 20 ml of HCl (5N) was added and heated to boiling and then transferred to 50 ml measuring flask. Heavy metals were measured by using Atomic Absorption (Apparatus (GBC, Avantar). Thirty samples of dried sediments were extracted in a soxhelt with methylene chloride. The siphon cycle was

around 20-30 minutes and it was repeated at least ten times. After complete extraction the solvent was evaporated over low heat (40° C) to a volume of lees than 20 ml. The extract was then transferred to a 25 ml measuring flask. The soxhelt extraction flask was rinsed with ethylene chloride and the rinse was used to make the volume up to 25 ml. Three ml of the extract were transferred to a ten ml measuring flask and the volume was made-up to the ten ml mark with n-hexane. The total hydrocarbon concentrations ug / g were calculated using the following formula:

- $A = BC / D$
- A = concentration of hydrocarbons in the original samples in ug / g.
- B = Concentration of hydrocarbons in the sample extracted in ug / l.

Table 1: Geographic coordination, salinity, and the depth of the sampling stations.

Sampling stations	Geographic coordination		Salinity mg/L	Depth of water (m.)
	N	E		
1	31o15' 00"	32o 21' 50"	41.0	05.5
2	31o 16' 00"	32o 22' 00"	41.0	08.0
3	31o 17' 18"	32o 22' 00"	39.5	08.0
4	31o 19' 00"	32o 22' 30"	39.0	13.0
5	31o 21' 00"	32o 23' 00"	41.5	15.0
6	31o 22' 50"	32o 23' 30"	41.5	19.0
7	31o 25' 00"	32o 24' 10"	40.5	24.0
8	31o 24' 00"	32o 25' 00"	41.5	21.0
9	31o 22' 15"	32o 25' 00"	41.5	17.0
10	31o 20' 00"	32o 25' 00"	40.5	13.0
11	31o 17' 55"	32o 24' 00"	39.0	10.0
12	31o 15' 42"	32o 25' 00"	39.5	08.0
13	31o 14' 00"	32o 25' 00"	40.0	06.5
14	31o 18' 00"	32o 26' 50"	40.0	10.5
15	31o 21' 00"	32o 27' 00"	41.0	16.0
16	31o 23' 00"	32 o 27' 00"	42.5	20.0
17	31o 24' 00"	32o 27' 00"	41.0	21.5
18	31o 13' 15"	32o 28' 00"	41.0	08.0
19	31o 20' 00"	32o 28' 30"	41.0	15.5
20	31o 26' 00"	32o 20' 00"	41.0	20.0
21	31o 25' 00"	32o 15' 40"	41.0	16.0
22	31o 23' 20"	32o 21' 00"	41.5	16.0
23	31o 18' 00"	32o 23' 00"	41.0	15.0
24	31o 22' 00"	32o 21' 10"	41.0	15.0
25	31o 16' 50"	32o 20' 00"	39.5	03.5
26	31o 20' 00"	32o 20' 50"	41.5	13.0
27	31o 19' 52"	32o 18' 00"	40.5	10.0
28	31o 18' 25"	32o 20' 00"	39.5	03.0
29	31o 17' 00"	32o 17' 45"	39.0	05.0
30	31o 15' 45"	32o 21' 00"	39.5	15.0
31	31o 23' 00"	32o 20' 00"	41.0	15.0

- C = Volume of the extract in ml.
- D = Weight of the original sediments in g.

A rapid dichromate oxidation technique was used to determine the organic carbon^[9] ten ml of 1 N Potassium dichromate was mixed with about 0.5 g of sediment in a 500 ml flask. 20 ml of concentrated sulfuric acid was added to this mixture, then was swirled for 1 minute and allowed to stand for 30 minutes. 200 ml deionized water, 10 ml conc. phosphoric acid and 4 drops of phenanthroline-ferrous complex were added to the cold mixture. The mixture was then filtered before titration with 0.5N ferrous sulfate. Total nitrogen was determined by the Kjeldahl method. The sulfuric – peroxide digestion method was used for the determination of the total phosphate in the studied sediments.

RESULTS AND DISCUSSION

Grain Size Distribution: Results of grain size analysis of selected bottom sediment samples are presented in Table 2, while the general description of these samples is given in Table 3. It was noticed that these sediment are much diversified in their grain size characteristics. Four textural classes were identified. These are, arranged from the coast towards offshore: sand, muddy sand, sandy mud, and mud. Correlation of the regional distribution of these textural classes with the offshore bathymetry indicates that the limit of the sand class is 5 m depth, while the area limited between 5 m and 10 m depth is mostly covered with muddy sand. Mud sediments occur at depths of 15 m and more. The sandy mud sediments are transitional between the muddy sand and mud and are mostly located at the western side of the studied area.

Sediment Density: Eight samples were selected for the determination of the sediment minimum and maximum unit weight in Mg / m³. The results are given in Table 4. Three types of sediments were measured, namely, sand, muddy sand and mud. The sand samples range between (1.362 to 1.261 and 1.641 and 1.572) in minimum and maximum density, respectively. On the other hand muddy sand samples range between 1.186 and 1.131 and 1.520 and 1.460 in minimum and maximum densities, respectively. Only one mud sample was measured where its minimum density is 1.264 and its maximum density is 1.592.

Total organic Carbon and Carbonate Content: Table (5) presents the percentage of carbonate content in the studied sediments. It was noticed that the bottom sediments in the study area are relatively low in carbonate content. The latter varies between 2.5 % to

10.4 %. The distribution pattern of the carbonate content of the studied bottom sediments generally increases with depth. It was also noticed that the muddy sediments are more calcareous than the sandy ones. Thirty-one samples from the bottom sediments and 6 samples from the top 0.5 m of 6 boreholes were selected for the determination of the total organic carbon (TOC) content. Results are presented in Table 5. TOC varies between 0.30 % and 2.82 %. Close correlation was found between the sediment texture and the TOC content, the finer the sediments the higher the TOC %. Figure 3 presents the general frequency distribution percentage of the TOC in the studied bottom sediments. It shows one anomaly in the anchorage zone located to the northwest of the Suez Canal entrance. This is mostly attributed to the pollution of the bottom sediments by the illegal discharge of oily wastes from anchored vessels. It has to be noted that the seabed sediments within the southern reach of planned access channel (from the shoreline till bathymeter 10 m) has a relatively low organic content (less than 1 %). On the other hand, the seabed sediments within the deeper reach (deeper than 10 m) are relatively rich in organic carbon.

Total Nitrogen TN and Total Phosphorous TP: Thirty-one samples from bottom sediments were selected for the determination of the total nitrogen and phosphorous contents. Results are presented in Table 5. It was found that the total nitrogen in the bottom sediments varies from 0.33 % to 1.56 %. Spatial distribution of the total nitrogen % indicated that it increases with depth. Total phosphorous varies between 0.4 and 16 mg/100 gm. It was found that phosphorous content is relatively high in the near shore area of both Port-Said and Port-Fouad cities (Fig. 3). It is expected that the dredged material from the planned access channel close to the shore will be relatively rich in both phosphorous and nitrogen content.

Total Petroleum Hydrocarbons (TPH): The importance of measuring the petroleum hydrocarbons in sediments may arise from different reasons. These may include the desire to establish background values prior to offshore drilling, assessing pollution from heavy traffic, assessment of fishing grounds subjected to oil spills, and if an area is subjected to dredging activities and therefore contaminants will be released in the water column. All these conditions may significantly impact the marine life and fisheries. It is therefore of paramount importance to assess the petroleum hydrocarbon residues and their potential impacts on marine life. So the analysis of sediments can provide results of baseline values before any activities leading to the discharge or release of petroleum hydrocarbon

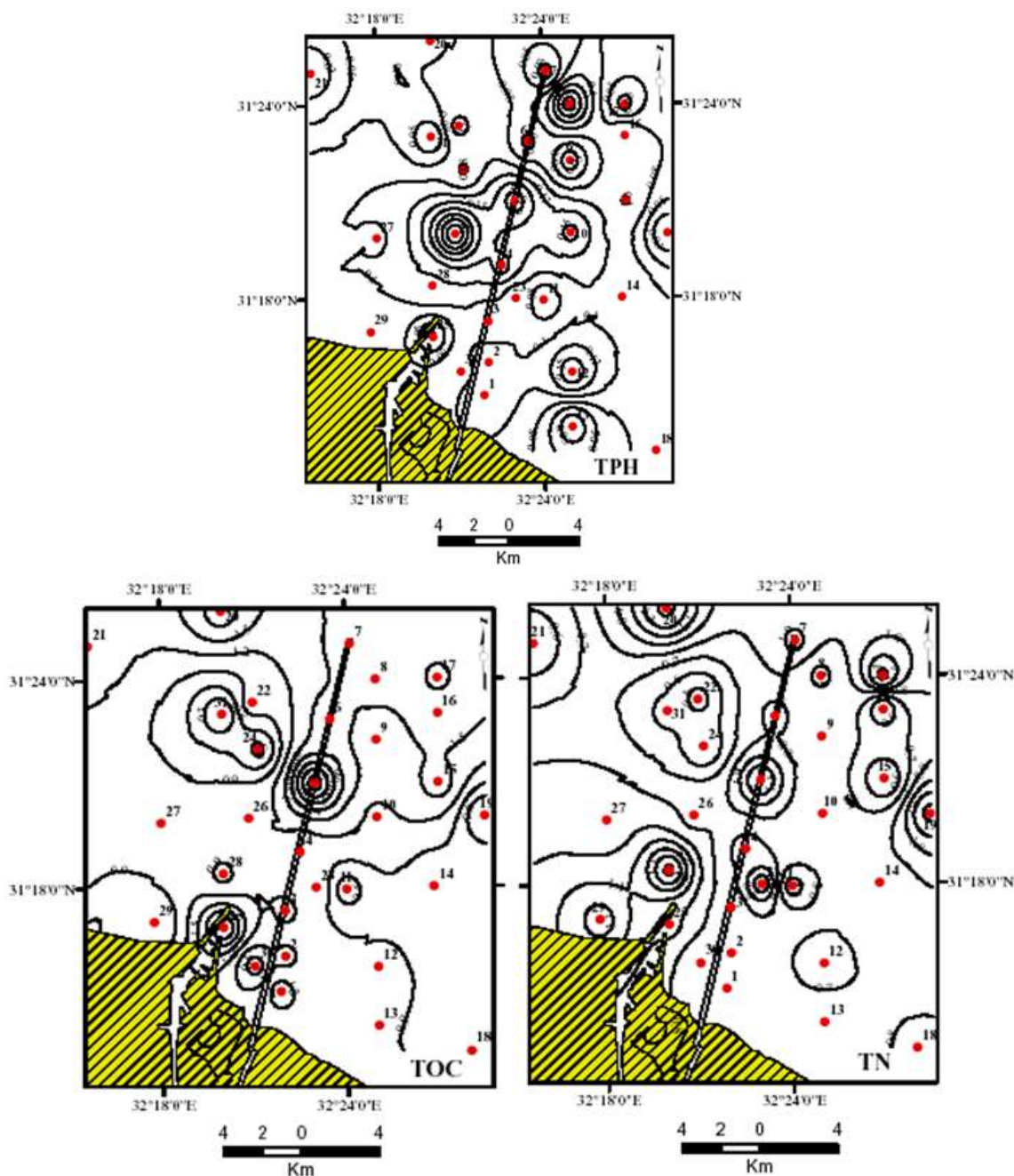


Fig. 3: Distribution of total petroleum hydrocarbons (TPH), total organic carbon (TOC) and total nitrogen (TN) in the investigated bottom sediments.

pollutants. The Mediterranean and the Suez Canal have almost the highest traffic density of oil tanker relative to other regional seas. Because of this fact the potential risk of oil pollution is considered serious. A relatively high value of accumulated hydrocarbons (2.45 mg/kg dry wt. sediments) was measured in the sediments at Port Said (Fig. 3), compared with 0.04 mg/kg dry wt. in the sediments

at Port Tawfik^[2]. Thirty samples from the bottom sediments were selected for the determination of total petroleum hydrocarbon concentration (TPH). Table 5 presents the results of analysis. TPH levels in the study area ranges from 1.86 ppm to 32.25 ppm. It was found that the TPH of the most of the bottom sediments are within high levels (4 to 26 ppm).

Table 2: Relative frequency percent of the main size fractions and textures of the studied samples.

Sample No	Sand %	Silt %	Clay %	Texture
1	95	5	00	Sand
2	40	40	30	Muddy sand
3	40	25	35	Muddy sand
4	35	30	35	Sandy mud
5	10	40	50	Mud
6	00	50	50	Mud
7	00	40	60	Mud
8	10	40	50	Mud
10	00	50	50	Mud
12	45	25	30	Muddy sand
14	70	20	10	Muddy sand
16	00	45	55	Mud
18	40	35	35	Muddy sand
20	05	45	50	Mud
23	20	55	30	Sandy mid
24	05	65	30	Mud
27	35	40	25	Sandy mud
28	55	20	25	Muddy sand
29	75	15	10	Muddy sand
30	95	5		Sand

Table 3: Grain size description of the studied samples

Sample No	Samples Description
1	Dark Brown slightly micaceous slightly calcareous silty fine to medium sand with little broken shells
2	Dark Brown slightly micaceous slightly calcareous very silty clayey fine sand with little broken shells
3	Dark Brown slightly micaceous slightly calcareous very silty clay / sand with little broken shells
4	Dark Brown slightly micaceous slightly calcareous very silty very sandy clay
5	Dark Brown slightly micaceous slightly calcareous sandy silt / clay with little shells
6	Dark Brown slightly micaceous slightly calcareous sandy silt / clay
7	Dark Brown slightly micaceous slightly calcareous sandy silt / clay
8	Dark Brown slightly micaceous slightly calcareous sandy silt / clay
10	Dark Brown slightly micaceous slightly calcareous very sandy very silty clay
12	Dark Brown slightly micaceous slightly calcareous silty very clayey fine sand
14	Dark Brown slightly micaceous slightly calcareous silty very clayey fine sand
16	Dark Brown slightly micaceous slightly calcareous silty / clay

Table 3: Continued

18	Dark Brown slightly micaceous slightly calcareous very clayey very silty fine sand
20	Dark Brown slightly micaceous slightly calcareous sandy silt / fine
23	Dark Brown slightly micaceous slightly calcareous very sandy clay / silt
24	Dark Brown slightly micaceous slightly calcareous sandy very clayey silt
27	Dark Brown slightly micaceous slightly calcareous very clayey very sand silt
28	Dark Brown slightly micaceous slightly calcareous very silty very clayey fine sand
29	Dark Brown slightly micaceous slightly calcareous silty clayey fine sand
30	Dark Brown slightly micaceous slightly calcareous silty fine to medium sand , with little broken shells

Table 4: Minimum and maximum dry unit weight (Mg / m^3)

Sample No	Size Class	Minimum unit Wt.	Maximum unit Wt.
1	Sand	1.262	1.621
30	Sand	1.362	1.641
14	Muddy sand	1.180	1.482
18	Muddy sand	1.131	1.460
29	Muddy sand	1.142	1.471

Table 5: Weight percentage of Carbonate content, Concentration of total organic carbon (TOC), total nitrogen (TN), total phosphorous (TP) and total petroleum hydrocarbons (TPH).

Sample No.	C%	TOC wt %	TN %	TP mg/100g	TPH ppm
1	02.53	1.32	0.812	02.0	11.87
2	06.05	0.84	0.756	00.8	11.89
3	07.04	1.26	0.784	01.0	07.93
4	06.08	1.02	0.644	00.6	15.80
5	08.08	2.82	1.260	00.4	18.68
6	09.21	1.62	0.868	02.0	04.61
7	10.42	1.56	1.008	02.0	01.86
8	10.00	1.62	0.672	01.0	18.57
9	09.18	1.20	0.728	01.0	-
10	07.32	1.15	0.700	00.4	15.55
11	04.22	0.42	1.036	06.0	04.93
12	07.54	0.96	0.588	02.0	16.48
13	06.56	0.90	0.812	01.0	-
14	07.20	0.60	0.812	02.0	09.53
15	08.70	1.62	0.420	00.8	10.06
16	08.32	1.68	0.448	00.8	09.91
17	08.64	1.86	1.288	00.4	-

Table 5: Continued

18	03.33	0.84	0.868	01.0	07.59
19	08.39	0.30	1.288	04.0	-
20	09.85	1.92	1.428	02.0	07.35
21	06.87	1.38	0.476	00.2	-
22	08.02	1.02	0.364	01.0	10.51
23	07.04	1.08	0.336	00.2	08.53
24	07.54	0.24	0.420	04.0	07.34
25	02.64	2.36	1.008	06.0	-
26	06.39	1.14	0.812	04.0	26.98
27	07.04	0.96	0.896	02.0	09.71
28	05.20	0.84	1.568	05.0	12.33
29	05.92	0.60	1.316	04.4	08.39
30	04.78	0.48	0.700	16.0	09.43
31	06.73	2.82	0.532	00.8	-

Table 6: Concentration of Heavy Metals (ppm)

Sample No.	Cu	Pb	V	Cd	Zn	Ni
1	11.75	129.0	137.0	04.00	105.2	062.2
2	34.70	122.5	307.0	06.25	207.7	102.7
3	62.00	109.7	267.0	10.30	159.0	106.0
4	61.70	296.2	107.0	17.00	199.0	160.5
5	77.70	292.5	277.0	18.20	234.7	187.0
6	77.50	355.0	222.0	17.25	211.0	149.2
7	99.70	090.5	247.0	08.10	292.0	112.0
8	83.50	078.5	285.0	08.10	250.0	066.0
10	64.00	245.0	250.0	15.00	240.0	127.0
11	31.00	205.0	172.0	17.30	175.7	042.0
12	64.00	273.0	237.0	16.00	206.0	051.5
14	58.50	290.0	250.0	16.20	184.5	065.7
15	74.70	112.5	285.0	10.50	222.5	094.4
16	64.00	079.0	277.0	08.10	197.5	080.1
18	52.0	277.5	300.0	16.30	187.0	058.2
20	84.00	270.0	250.0	14.50	205.0	064.0
22	84.50	205.0	250.0	12.00	199.5	075.2
23	63.00	235.0	277.0	10.70	189.0	058.5

Table 6: Continued

24	65.00	155.0	278.0	06.00	163.0	069.0
26	57.00	109.7	250.0	06.50	121.7	064.0
27	44.00	262.5	277.0	11.80	184.5	052.0C
28	43.25	172.5	285.0	09.00	192.20	067.0
29	33.00	267.0	245.0	11.50	169.5	054.2
30	12.20	187.0	185.0	08.00	111.5	041.5

Heavy Metals: Thirty samples from the collected bottom sediments were analyzed for the determination of the concentration of six heavy metals, namely: Cu, Pb, V, Cd, Zn and Ni, Results are presented in Table 6. The concentration of Cu ranges from 11.7 to 99.7 ppm, Cu level in most of the offshore sediments is more than 30 ppm which above the accepted level. The area at the entrance of the approach channel of the Suez Canal is significantly polluted, where the concentration is more than 90 ppm (Fig. 4).

The concentration of Pb varies between 78.5 and 700 ppm. Such concentrations indicate significant pollution. The level of Pb in the planned approach channel site ranges from 300 to 500 pm which is considered heavily polluted (Fig. 4). The concentration of Zn varies between 99 and 292 ppm. The majority of the studied sites are considered polluted with Zn. Concentration of Ni ranges between 41.5 and 287 ppm. The highest concentration is more than 150 ppm (Fig. 4). The V levels ranges from 107 to 300 ppm which is way above the accepted levels. These V levels are relatively high in anchorage area as well as to the east of the Suez Canal entrance. The concentration Cd varies between 4 and 18.2 ppm. The studt area is considered severely polluted with Cd, in particular the areas of the ship anchorage and the entrance of the Suez Canal (Fig. 5).

The V levels ranges from 107 to 300 ppm which is way above the accepted levels. These V levels are relatively high in anchorage area as well as to the east of the Suez Canal entrance. The concentration Cd varies between 4 and 18.2 ppm. The studt area is considered severely polluted with Cd, in particular the areas of the ship anchorage and the entrance of the Suez Canal (Fig. 5). The above mentioned concentrations indicate that the studied offshore area is significantly polluted by heavy metals. This is mostly due to the ship traffic and maritime activities. Also the anchorage of vessels at the waiting area, lubricating oil and the urban activity centers (Port Said and Port Fouad cities). These high values are considered to be toxic and have a negative impact to the surrounding marine environment.

Conclusions: The sedimentological investigation revealed that the seabed sediments are generally sandy close to the shore line and the mud content increase in depth, until they become completely muddy at depths of 15 meters and deeper. The dry maximum unit weight of the sand and muddy sand ranges between 1.57 and 1.64 Mg / m³ and 1.46 and 1.52 Mg/m³ respectively. The bottom sediments are mainly terrigenous where the carbonate content does not exceed 10 %. Geochemical analyses indicate that the study bottom sediments are generally very rich in nutirents namely, total organic carbon, total nitrogen and total phosphorous. It was also found that these sediments are heavily polluted with heavy metals (Cu, Ni, V, Pb, Zn and Cd) and petroleum hydrocarbons. The sources of these pollutions are mostly anthropogenic. These include but not limited to intensive maritime activities, disposal of wastes from anchorade vessels that are waiting the crossing of the Suez Canal, wastes from the ship yard at the entrance of the Suez Canal and wastes from the urban centers (Port Said and Port Fouad cities).

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