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Environmental Characteristics of the Egyptian Mediterranean Coast

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ABSTRACT
In an attempt to evaluate the environmental quality of the Egyptian Mediterranean Sea from El-Dabaa to El-Saloum, environmental parameters as well as amino acids, petroleum hydrocarbons, pesticides and PCBs have been studied in water and sediment samples from seven different locations during the year 2014. Spatial and temporal fluctuations as well as statistical analysis between the analyzed variables were examined.

The results demonstrated a wide range of water temperature (13.50-29.00°C), slightly narrow fluctuations in salinity (37.20-38.78), and well-oxygenated seawaters (6.40–8.96 mg O_2/l), relatively low amounts of oxidizable organic matter (0.10-1.60 mg O_2/l) and the seawater was slightly alkaline (pH range 8.04–8.63). Nutrient characteristics sustained the levels up to 2.45, 5.42, 5.40, 0.28 and 5.36 µM for reactive phosphates, reactive silicates, ammonium, nitrite and nitrate, respectively.

These obtained results signified that water quality from El-Dabaa to El-Saloum is good; within the permissible limits in the majority of monitoring sites, and all stations were generally between Oligotrophic and mesotrophic states, characterized by a relatively low to medium level of nutrients.

Furthermore, seawater from the most sites did not show any levels of pesticides, PCBs and petroleum hydrocarbons. These levels, if any, may have been much lower than the detection limit for the compounds analyzed. In marine sediments, the concentrations of amino acids demonstrated a range of 1884.5-19569.6 µM, while pesticides, PCBs, and petroleum hydrocarbons were below detection limit to 3086, 120, 145 ng/g; respectively. These results are much lower in sediment of the western part of the Egyptian Mediterranean coast compared to other sites and also much lower than permissible levels given by National Academy of Sciences and National Academy of Engineering.

INTRODUCTION

Egypt is in the northern corner of Africa with the entire northern part bordering the Mediterranean Sea. The Egyptian coastline Mediterranean Sea extends over 1,550 km^2 from Rafah in the east to El-Saloum in the west and is one of the longest shores in North Africa. 40% of Egypt's industries are located in the Mediterranean coast, this region is extremely important economically, with substantial capital investment.

However, The Egyptian marine environment along the Mediterranean Coast has been subjected to a substantial increase since the last decades of pollution due to a great number of industrial, agricultural, commercial and domestic waste effluents and emissions as well as hazardous substances (Emara *et al*, 1992; El-Deeb 2007; Fathy *et al*, 2012; Shreadah *et al*. 2014). Marine pollution affects water, sediments and biota. It can be related to oxygen-depleting substances, persistent organic pollutants (POPs), petroleum hydrocarbons, nutrients introduced by human activities or debris. Many different kinds of pollutants enter the Mediterranean Sea from its shores (land-based sources) either by discharge points and dumping grounds (point-source pollution) or from surface fluvial run-off (non-point-source pollution). Pollutants also enter the marine environments by atmospheric deposition, while others are introduced directly by marine activities such as shipping, fishing, mining, and oil and gas exploration.

Water quality is a critical factor significantly affects human and all oceanic organism health. Monitoring of the environmental quality is of great importance to determine effectiveness order of all the adopted governmental steps and if further steps are required to improve the quality of the environment. Water quality parameters that are commonly monitored include temperature, dissolved oxygen (DO), oxidizable organic matter (OOM), pH, salinity and nutrients. Little attention was paid to investigate physicochemical characteristics of coastal waters of the western region of Mediterranean Sea.

Although dissolved free amino acids (DFAA) are present in trace amounts in natural water, there was great interest in studying DFAA in coastal and oceanic waters because these compounds are a good nitrogen source for marine microalgae and bacteria (Tada *et al.,* 1998). Amino acids are the building blocks of protein molecules, making up the largest reservoir of organic nitrogen in most organisms. These compounds account about half of particulate organic nitrogen and one quarter of particulate organic carbon in surface waters. Amino acids are the most studied biochemical classes in organic geochemistry, because they are major constituents of phytoplankton (Wakeham *et al.*, 1997). The studies of distribution of amino acid in water and sediments of the Egyptian Mediterranean Sea from El-Dabaa to El-Saloum is poor; with little known in different regions of the Mediterranean Sea; for example Emara (1983) reported values from 0.81 to 9.37 mg/l for unpolluted and polluted seawater areas, respectively at Alexandria coastal water.

Generally petroleum hydrocarbons have a wide range of industrial, anthropogenic applications. They are of great concern and globally distributed through the environment due to their persistence, high bioaccumulation potential and harmful biological effects (Iwata *et al.* 1993). Once discharged into the marine systems, these chemicals disperse into three phases, water and sediment and biota. Hence, it is important to study the distribution of these compounds in these compartments. The composition of hydrocarbon can be changed due to evaporation, chemical reactions, selective dissolution, biodegradation and photo-oxidation. Simple aromatics and short chain alkanes are rapidly lost, but higher molecules such as hopanes and steranes are little affected and can be particularly useful markers in investigations (Volkman *et al*., 1992).

Persistent organic pollutants (POPs), including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are used to refer to the organic compounds that are found in the environment in very small amounts and can cause significant harm to ecological systems and/or humans. OCPs and PCBs compounds were found widespread in the environmental media, such as in water, air, sediment

and biota; and globally distributed including remote areas where they have never been used (Koziol and Pudykiewicz, 2001). The OCPs could spread into aquatic environments through runoffs from non-point soil sources and have been a major environmental issue, drawing extensive attention to environmental scientists and the public (Jiang *et al*., 2009; Emara *et al.* 2010; El Naggar *et al*., 2013).

PCBs are a class of 209 congeners, each of which consists of two benzene rings and one to ten chlorine atoms (Hutzinger *et al*., 1974). The PCBs are thermally stable, highly lipophilic, and have low flammability (De Voogt and Brinkman, 1989). The PCBs have been shown to bio-accumulate within food chains and they have been detected in different environmental compartments worldwide (Lundgren *et al*., 2002). It is well known that over one hundred PCBs were identified in the technical PCBs mixtures. However, only a part of them could be detected at significant levels in nature. Moreover, it is highly cost-effective to monitor fewer congeners, especially since it may be possible to acquire nearly all desired information from a reduced set of measurements, due to the high correlation of many PCB congeners. The usage of PCBs in Egypt is not well established, but the use of PCBs in electrical equipment, transformers, and other industries is common, owing to their persistence, PCB contaminations are widespread at the Alexandria Harbor (Barakat *et al*., 2002).

Studying of the environmental quality of the environment and focusing on pollutants known to be most harmful to human health (for example OCPs, PCBs, petroleum hydrocarbons) introduced by human activities or debris are of great importance to determine the order of effectiveness of all the adopted governmental steps and to determine if further different steps are required to improve the quality of the environment. Thus, the objectives of the present study were set to study the water quality of the Egyptian Mediterranean Coast from El-Saloum to El-Dabaa by measuring of physical and chemical characteristics of the study area; water temperature, pH, salinity, DO, ammonia, nitrite, nitrate, reactive phosphate and reactive silicate, in addition; investigating the distribution of amino acids, petroleum hydrocarbons, PCBs and OCPs in surface water and sediments to evaluate its environmental quality and put a monitoring and management plan for development this important ecosystem to help support the decision-making processes related to the management of marine and coastal ecosystems.

MATERIALS AND METHODS

Sampling

Samples were collected from seven stations (El-Dabaa E, El-Dabaa W, Alam Elrom, Mrsa Matrouh, El-Negala, Sidi Braani, and El-Saloum) from the Egyptian Mediterranean Coast from El-Saloum in the East to El-Dabaa in the West through four seasonal cruises during the year 2014. The sampling area and location of stations are shown in Fig. (1) and Table (1).

Coastal water samples were collected using Niskin bottles at 2 m depth, while surface sediment samples were collected during winter and summer seasons only using a stainless steel grab sampler. Samples were preserved and moved to the laboratory, where stored at -20°C.

Table 1: Sampling locations of the Egyptian Mediterranean Coast from El-Dabaa to El-Saloum

Station	Locations	Longitude (E)	Latitude (N)
1	El-Dabaa E	28.83016011	30.9245369
2	El-Dabaa W	28.57504837	31.02168065
3	Alam Elrom	27.51303089	31.19583927
4	Mrsa Matrouh	27.30736619	31.31836292
5	El-Negala	26.70262446	31.46451613
6	Sidi Braani	25.90272007	31.62467204
7	El-Saloum	25.13694727	31.54153099

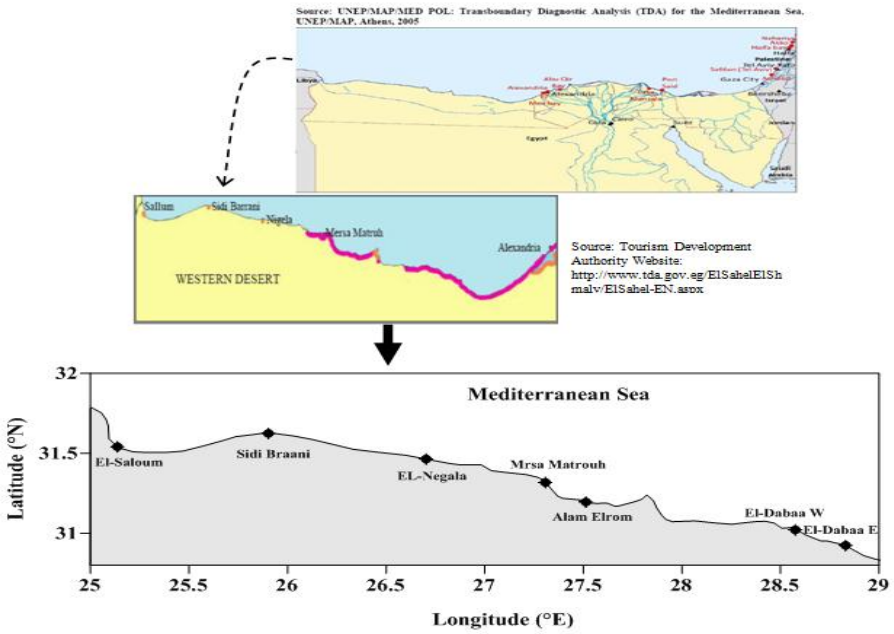

Fig. 1: Sampling stations along the Egyptian western Mediterranean Coast from El-Dabaa to El-Saloum.

Physico-chemical parameters and nutrients

The following physico-chemical variables: temperature, pH and salinity were measured directly in situ using CTD apparatus (Model: YSI 556). Dissolved oxygen (DO) was determined by the modified Winkler method (Grasshoff 1976), oxidizable organic matter (OOM) according to FAO method (FAO 1976). Nutrients (ammonia, nitrite, nitrate, phosphate, and silicate) were analyzed spectrophotometrically by the recent oceanographically methods described by Grasshoff using UV/Visible double beam spectrophotometer (janway Model: 6800). Total phosphorus (TP) and total nitrogen (TN) were determined simultaneously spectrophotometrically according to Valderama (1981). Various statistical analysis of the results occurred using SPSS programme (version 22).

Amino acids Analysis

Hydro1yzable amino acids (AA) were analyzed in sediment during summer season only with Amino Acid Ana1yzer; a Pharmacia LKB (Freiburg, Germany) Alpha Plus 4151, after hydrolysis with 6 N HCl for 22 h at 110 °C. An aliquot hydrolysate was evaporated to dryness, and taken up in distilled water and evaporated to dryness twice again to remove the remaining HCI. The residue in an acidic buffer solution was taken up and injected into the Amino Acid Analyzer. Duplicate analyses resulted in an average variability of 8.2% for AA. Average variability of the major individual amino acids lies in the range of 5-15%. AA concentrations were multiplied by a factor of 1.4 to compensate for losses during hydrolysis (Muller *et al.*, 1986).

Petroleum Hydrocarbons Analysis

Petroleum hydrocarbons in seawater and sediment were sampled during summer and winter 2014. Seawater were extracted on board, stored at -4^{o}C, and transported to the laboratory for aliphatic and aromatic hydrocarbons analysis using well-established techniques (UNEP/IOC/IAEA 1992). Seawater samples were extracted in a separating funnel with 60ml of dichloromethane three times. Sample extracts were combined and concentrated by rotary evaporation to 5ml. Finally, samples were concentrated to a final volume of 1ml under a gentle stream of pure nitrogen. 30g of the sediment samples was mixed with 90g of anhydrous sodium sulfate. From each sediment sample, duplicate samples were taken. Extraction of sediment samples was taken in a Soxhlet extractor with 250ml of hexane for 8h and then re-extracted for 8h into 250 ml of dichloromethane. The extracts were then combined and desulfurized through activated copper powder and then concentrated in a rotary evaporator at low temperature (35°C), followed by a nitrogen gas stream to about 1 ml. Fractionation and clean-up were performed by passing the extract (water and sediment samples) through a silica/alumina column. Silica column was prepared by slurry packing 10g of silica, followed by 10g of alumina and finally 1g of anhydrous sodium sulfate. Elution was performed using 40ml of hexane (F1: aliphatic fractions), then 40 ml of hexane/dichloromethane 90/10 (F2: aromatic fractions), followed by 20ml of dichloromethane/hexane 50/50 (F3: polyaromatic fractions), both of F2 and F3 fractions were combined to give PAHs. Finally, eluted samples were concentrated to about 1ml under a gentle stream of purified nitrogen. Finally analysis of samples was carried out by GC gas chromatograph equipped with a flame ionization detector (FID).

OCPs and PCBs Analysis

OCPs and PCBs in seawater and sediment were sampled during summer and winter 2014. Around 1 liter of the water sample was extracted three times with 100 ml of dichloromethane. The combined extracts were filtered and concentrated in a vacuum rotary evaporator (UNEP/IOC/IAEA 1991). 30g of the sediment samples was treated with 10 g of sodium sulfate and extracted with 250ml of hexane for 8h in a Soxhlet extractor and then re-extracted for 8h into 250 ml of dichloromethane. Dichloromethane (100 ml) was extracted in the same fashion as the sample and used as the blank. The extracted and blanks samples were then concentrated to a volume of 2 ml with a pure nitrogen gas stream. Fractionation and clean-up were carried out by passing the extract (water and sediment) through a silica/alumina column. Silica column was prepared by slurry packing 10g of silica, followed by 10g of alumina and finally 1g of anhydrous sodium sulfate. Elution was performed using 70 ml of hexane for PCBs congeners (F1), followed by elution with a 50ml mixture containing 70% hexane and 30% dichloromethane for pesticide fraction (F2). Finally, eluted samples were concentrated to about 0.2ml using a gentle stream of purified nitrogen, prior to injection into GC/FID for analysis.

RESULTS AND DISCUSSION

Physico-chemical parameters and nutrients

The physico-chemical parameters (water temperature, DO, OOM, salinity and pH) during the year 2014 are illustrated in Table (2). Water temperature varied seasonally from a minimum of 13.5 °C during winter at Sidi Braani to a maximum of 29.0 and 26 °C during spring and summer at Mrsa Matrouh and El-Saloum, respectively (Fig. 2a). Salinity, as temperature, is very important limiting factor,

which affects the biological distribution of the marine environment. Salinity in the present study showed a slightly narrow seasonal variation (Fig. 2b). The lowest salinity value of 37.2 was recorded during spring at El-Dabaa E, while summer represented the highest salinity value of 38.78 recorded at El-Dabaa W. Regionally, the average values of salinity, in general, showed a narrow local variation ranged between 37.62 and 38.37; whereas, the annual salinity average was 38.04.

Hydrogen ion concentration plays an important role in many of the life processes in sea; living organisms are very dependent on and sensitive to it. It is dependent on the interaction of numerous substances dissolved in water, photosynthetic activity of aquatic plants, respiration of aquatic organisms, decomposition of organic matter, precipitation and/or dissolution of CO_2 components and oxidation-reduction reactions (Riley *et al.* 1978). Seawater samples lie in the alkaline side (>7 to <9). The maximum reading of pH value (8.63) was observed during winter at Mrsa Matrouh, while the lowest value (8.04) was recorded at El-Dabaa E and W during spring (Fig. 2c). Negative and positive correlation found between pH and both temperature, salinity, respectively (r= -0.44, 0.44, n= 28, p <0.05).

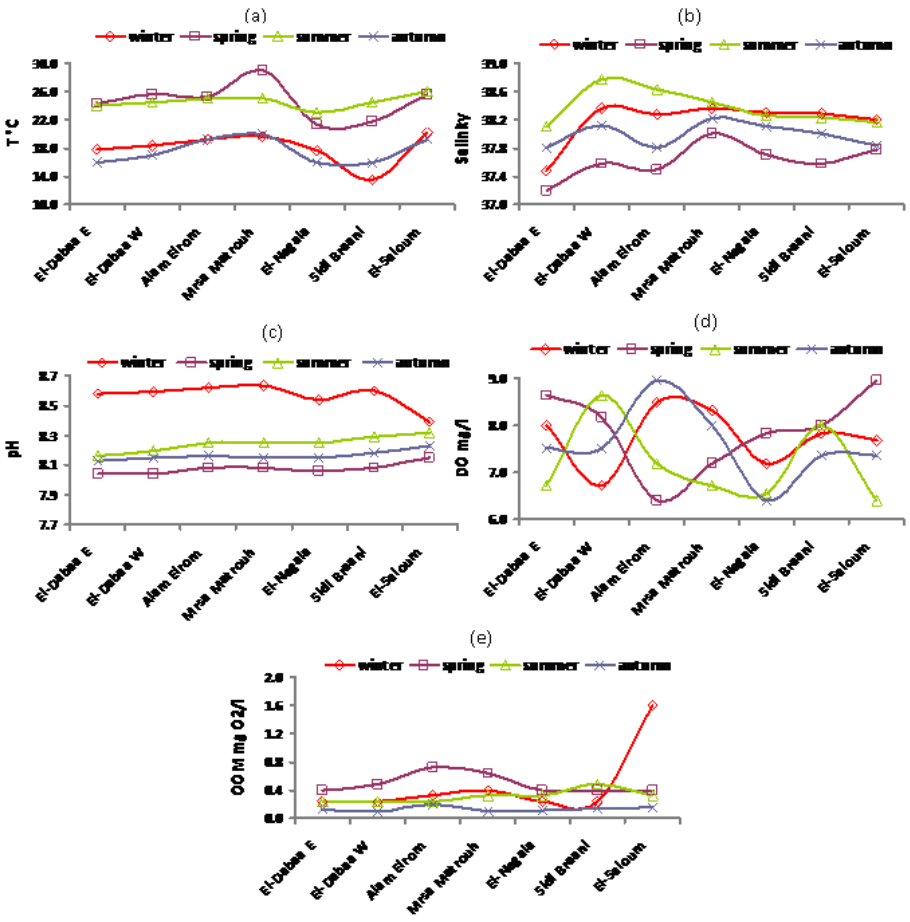

Fig. 2: Seasonal distribution of temperature, pH, Salinity, DO, OOM collected from El-Dabaa to El-Saloum along the Egyptian Mediterranean Sea during 2014.

Table 2: Seasonal values of physical and chemical parameters of water from El-Dabaa to El-Saloum along the Egyptian Mediterranean Sea during the year 2014.

Station		T °C	Salinity	pH	DO	OOM
El-Dabaa E		17.80	37.48	8.58	8.00	0.24
El-Dabaa W		18.40	38.36	8.59	6.72	0.24
Alam Elrom		19.20	38.28	8.62	8.48	0.32
Mrsa Matrouh	Winter	19.60	38.36	8.63	8.32	0.40
El-Negala		17.60	38.30	8.54	7.20	0.24
Sidi Braani		13.50	38.29	8.60	7.84	0.24
El-Saloum		20.20	38.20	8.39	7.68	1.60
El-Dabaa E		24.30	37.20	8.04	8.64	0.40
El-Dabaa W		25.65	37.58	8.04	8.16	0.48
Alam Elrom		25.25	37.50	8.08	6.40	0.72
Mrsa Matrouh	Spring	29.00	38.01	8.08	7.20	0.64
El-Negala		21.40	37.71	8.06	7.84	0.40
Sidi Braani		21.80	37.58	8.08	8.00	0.40
El-Saloum		25.65	37.78	8.15	8.96	0.40
El-Dabaa E		24.00	38.11	8.16	6.72	0.24
El-Dabaa W		24.50	38.78	8.20	8.64	0.24
Alam Elrom		25.00	38.63	8.25	7.20	0.24
Mrsa Matrouh	Summer	25.00	38.44	8.25	6.72	0.32
El-Negala		23.00	38.26	8.25	6.56	0.32
Sidi Braani		24.50	38.23	8.29	8.00	0.48
El-Saloum		26.00	38.17	8.32	6.40	0.32
El-Dabaa E		16.00	37.81	8.13	7.52	0.13
El-Dabaa W		17.00	38.12	8.15	7.52	0.10
Alam Elrom		19.20	37.81	8.16	8.96	0.19
Mrsa Matrouh	Autumn	20.00	38.22	8.15	8.00	0.10
El-Negala		16.00	38.11	8.15	6.40	0.11
Sidi Braani		16.00	38.01	8.18	7.36	0.14
El-Saloum		19.20	37.84	8.23	7.36	0.16

Dissolved oxygen is vital to aquatic life, as it is needed to keep organisms alive. Coastal waters typically require a minimum of 4.0 mg/l and do better with 5.0 mg/l of oxygen to provide for optimum ecosystem function and highest carrying capacity (UNESCO/WHO, 1978) and used as basic water criteria in assessing the degree of pollution in any aquatic environment. The distribution pattern of DO showed a relatively wide seasonally variation and fluctuated between 6.4 mg/l during spring and autumn at Alam Elrom and El-Negala, respectively; and 8.96 mg/l during spring at El-Saloum with an annual average of 7.60 mg/l (Fig. 2d). Available data show that the increase in DO concentrations confirms the good quality of water.

Oxidizable organic matter, (OOM) uses as basic water quality parameter and indicates only the amount of carbonaceous organic matter (Carlberg, 1972) to assess organic pollution, adversely affecting aquatic life, principally through oxygen depletion. A relatively narrow range in seasonal values at the present study was illustrated in (Fig. 6e), 0.10–1.60 mg O_2/l; the lowest value was recorded at stations of El-Dabaa W, Mrsa Matrouh during autumn, while the highest value recorded at El-Saloum station during winter, this is due to sewage from small village. The present annual means at water samples were around 0.13–0.49 mg O_2/l (annual average 0.35 mg O_2/l).

The nutrient salts (ammonium ion, nitrite, nitrate, reactive phosphate and reactive silicate) concentrations during the year 2014 are reported in Table (3). Ammonia is the nitrogenous end product of bacterial decomposition of natural organic matter containing nitrogen (Tadros *et al.*, 2005). Ammonia concentration in water samples reached a maximum value during winter and a minimum value during

autumn being 5.40 and 0.27 µM at stations of Mrsa Matrouh and El-Dabaa E; respectively, with an annual average of 1.39 µM. Most species of phytoplankton utilize the ammonium ion in preference to other inorganic nitrogen forms, which clearly appeared during autumn. Ammonia concentrations were less than permissible limit (0.5 mg/l), but it exceeded this limit at one point in Mrsa Matrouh where its concentration was 0.54 µM. Positive correlation found between ammonia and

salinity ($r= 0.51$, $n= 28$, $p <0.05$). The distribution of ammonia in the study area is illustrated in Fig. (3a).

Table 3: Seasonal values of nutrients in water samples collected from El-Dabaa to El-Saloum along the Egyptian Mediterranean Sea during the year 2014.

Station		NH_4^+	NO_2^-	NO_3^-	DIN	PO_4^{3-}	SiO_4^{2-}
El-Dabaa E		0.45	0.18	2.11	2.74	0.19	2.00
El-Dabaa W		4.50	0.15	2.22	6.87	0.19	3.65
Alam Elrom		2.34	0.15	1.28	3.77	0.10	0.46
Mrsa Matrouh	**Winter**	5.40	0.28	4.35	10.03	0.00	0.23
El-Negala		1.17	0.10	0.24	1.51	0.14	1.65
Sidi Braani		2.57	0.03	0.63	3.22	0.19	1.25
El-Saloum		1.13	0.00	0.26	1.39	0.29	0.40
El-Dabaa E		1.35	0.05	0.31	1.71	0.10	0.23
El-Dabaa W		0.77	0.05	0.13	0.95	0.00	0.17
Alam Elrom		0.36	0.10	0.26	0.72	0.00	3.71
Mrsa Matrouh	**Spring**	1.35	0.08	0.84	2.26	0.05	0.86
El-Negala		0.72	0.08	0.29	1.08	0.05	0.80
Sidi Braani		0.68	0.18	0.01	0.86	0.10	0.23
El-Saloum		1.26	0.18	0.01	1.44	0.24	1.71
El-Dabaa E		1.08	0.08	3.46	4.62	0.72	5.42
El-Dabaa W		2.34	0.13	3.46	5.93	2.45	5.07
Alam Elrom		2.48	0.05	4.86	7.39	1.10	3.31
Mrsa Matrouh	**Summer**	1.53	0.05	5.02	6.60	0.43	2.28
El-Negala		1.04	0.10	5.31	6.44	0.96	1.71
Sidi Braani		0.68	0.10	5.36	6.14	1.44	1.48
El-Saloum		0.59	0.15	4.97	5.71	0.43	1.88
El-Dabaa E		0.27	0.20	1.02	1.49	0.00	0.86
El-Dabaa W		0.68	0.10	0.45	1.22	0.00	1.71
Alam Elrom		0.81	0.18	0.45	1.43	0.00	4.62
Mrsa Matrouh	**Autumn**	1.04	0.15	0.68	1.87	0.00	0.97
El-Negala		0.50	0.15	0.63	1.28	0.00	1.77
Sidi Braani		1.26	0.15	0.29	1.70	0.00	0.68
El-Saloum		0.59	0.10	0.13	0.82	0.00	0.51

Nitrite is the intermediate state between oxidation of NH_4^+ to NO_3^- in nitrification and the reduction of NO_3^- to either N_2O/N_2^- molecules or NH_4^+ in de-nitrification (Grasshoff 1976). Nitrite showed low concentrations for water samples in the study region. The values fluctuated between 0.00 and 0.28 µM determined at stations of Mrsa Matrouh and El-Saloum during winter, respectively, with annual average of 0.12 µM (Fig. 3b). It was observed that the decrease of nitrite could be attributed to assimilation by plants in addition to the de-nitrification process.

Seasonal variation of nitrate content in water samples fluctuated between 0.01 and 5.36 µM determined at El-Saloum and Sidi Braani during spring and summer, respectively with an annual average of 1.75 µM. It was observed that the decrease of nitrate during spring (Fig. 3c) could be attributed to assimilation by plants in addition to the de-nitrification process (i.e. the reduction of nitrate to nitrite before releasing N_2O or N_2 molecules). The data of ammonia and nitrate concentrations (Table 3) showed that the concentrations of nitrate were generally higher in summer, while the opposite trend was recorded for ammonia and nitrite concentrations in winter. This distribution may be due to more oxic conditions in the winter than summer (Table 2).

Based on the annual average, nitrite is a minor constituent if dissolved inorganic nitrogen DIN consists of about 4.99% and nitrite is characterized as the intermediate compound which could be derived either from the reduction of nitrate or oxidation of ammonia and during nitrogen assimilation can be removed from solution by phytoplankton (Schuler *et al.*, 1953). Nitrate comprises the majority of DIN (Fig. 3d) and represents about 53.78% whereas; ammonia comprises about 42.64% of DIN.

Phosphorus is very important element in the aquatic system for primary production. It is important for growth and reproduction of phytoplankton (Riley and Chester, 1971). The distributions of inorganic phosphate were presented graphically in Fig. (3e). The values of inorganic phosphate are depletion at most stations to 2.45 µM at El-Dabaa W. Concentrations of phosphate were always low at most locations of the present study and are principally related to its short residence time in seawater. The seasonal averages of phosphate concentrations were in the following order: winter > summer > spring> autumn (ND).

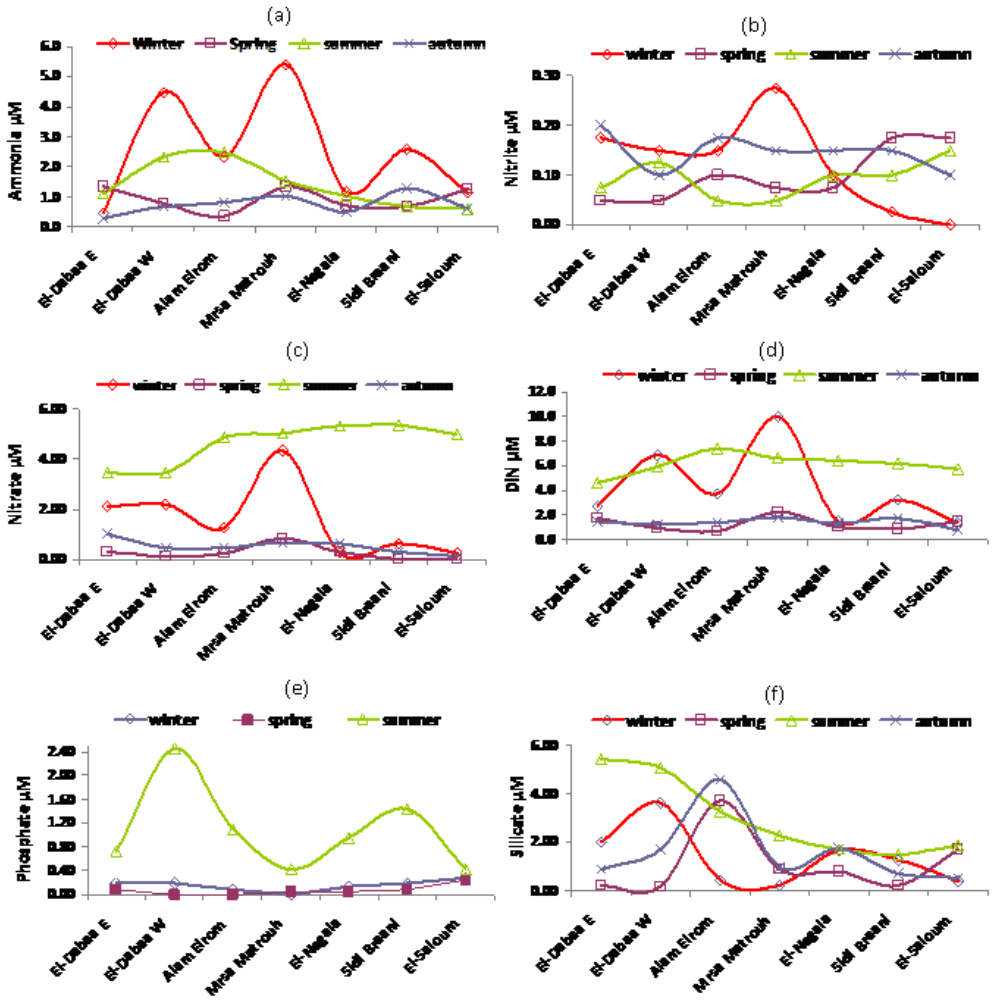

Fig. 3: Seasonal distribution of nutrients collected from El-Dabaa to El-Saloum along the Egyptian Mediterranean Sea during 2014.

Silicate is the major nutrient for diatoms, which are the dominant phytoplankton organisms in the sea (Riley and Chester 1971). The spatial distributions of silicate are presented graphically in Fig. (3f). The minimum absolute

value (0.17 µM) was recorded during spring at El-Dabaa W, while the maximum one (5.42 µM) was observed at El-Dabaa W during summer. The seasonal averages of silicate concentrations were in the following order: summer > autumn > winter > spring.

Therefore, water quality of study area from El-Dabaa to El-Saloum is good; within the permissible limits in the majority of monitoring sites, and results indicated that all stations were generally between Oligotrophic and mesotrophic (low and medium level of nutrients) (Adapted from Vucak, Skrivanic & Strin 1982). This region is not adversely affected by existing development and is accordance with annual report on water quality data from the coastal waters of the Mediterranean Sea.

Amino acids in sediments

The amino acid distributions for the seven stations of the investigated area during summer were reported in Fig. (4). Distribution and composition of amino acids showed variation from a minimum of 1884.5 µM recorded at El-Dabaa E to a maximum of 19569.6 µM at Sidi Braani with an average of 12484 µM. High concentrations were also detected at El-Dabaa W, Sidi Braani and El-Saloum, while Alam Elrom and Mrsa Matrouh were relatively depleted in amino acids.

Aliphatic amino acids (alanine, serine, glycine and isoleucine) were detected at very low levels (0.06%-2.78%), while threonine was at wide range of concentrations (3.8%- 83%); in contrast, leucine was not detected. Amino acids containing sulphur; cysteine was found at El-Saloum station with concentration of 3974.6 µM (22%), but methionine was not detected. Mono-aminodicarboxylic acids and their amide glutamic and aspartic acids were detected at El-Saloum station (2.26%); El-Negala and El-Saloum (1.45- 13.4%). Basic amino acids arginine and lycine were present at low concentrations not exceeding 1.93% at El-Dabaa W, Negala, El-Saloum stations.

Aromatic amino acids phenylalanine and tyrosine were present at considerable levels 4.6-56.2% and 0.3-72.5% respectively. This reflects that on an average scale, aromatic amino acids in sediments of the Egyptian coast are higher than the aliphatic by a factor of 3.4 and also strong predominance of aromatic tyrosine (72.5 %) and phenylalanine (56.2%) at El-Dabaa W and El-Saloum stations respectively. Leucine, histidine and methionine were not detected in the sediments of this area.

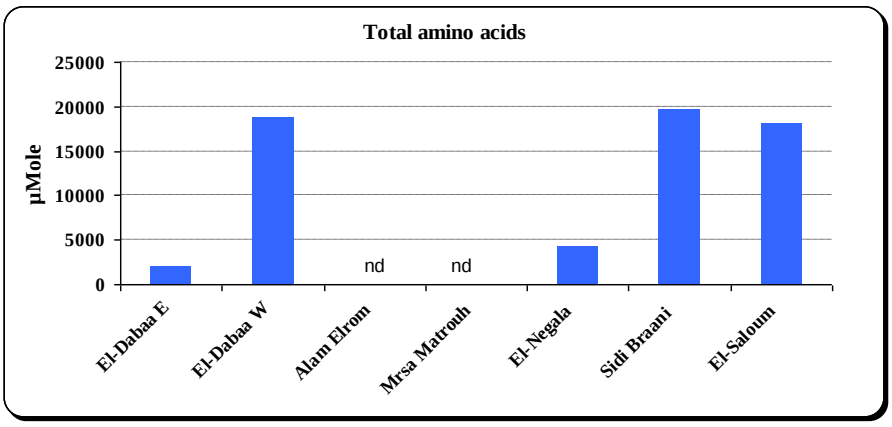

Fig. 4: Total amino acids in sediment collected from El-Saloum to El-Dabaa along the Egyptian Mediterranean Sea during summer 2014.

Linear regression equation between concentrations of amino acids and their molecular weight (MW) showed that amino acids increase with increasing their molecular weight (Fig. 5), according to the formula:

Amino acid concentrations = -5.25 M W + 53.05 r=0.50, n= 32, P {0.01}

The effects of physico-chemical parameters of seawater: temperature (T), salinity (S), pH, DO, NO_2^-, NO_3^-, PO_4^{3-}, DIN, TN and SiO_4^{2-} on the concentration of total amino acids showed that during summer 2014, these compounds increase by increasing temperature (r =0.69), pH (r=0.58), DO (r= 0.59), and NO_2^- (r= 0.706), while the effects of other environmental conditions were negligible. However, no significant correlation were found between amino acids and both TN and TOC in sediment.

The results of amino acids in the investigated area is comparable with total amino acids of the Eastern Harbor that is varied widely between 1021 µg/g in winter and 11843 µg/g in spring (Gouda et al., 2006).

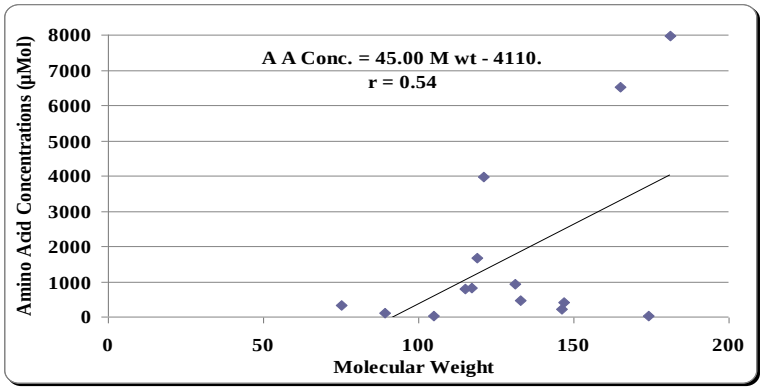

Fig. 5: Amino acids-Molecular weight relationship in sediments of study area during summer 2014.

Petroleum Hydrocarbons

Aliphatic and aromatic hydrocarbons in water

Aliphatic hydrocarbons concentrations in seawater were below the detection limit during winter and summer seasons; Excepting only C_{14} (10 ng/l), C_{29} (31.2 ng/l) were detected at El-Dabaa E and Mrsa Matrouh, respectively in winter, and C_{17}, C_{18}, C_{19}, C_{23}, C_{25}, C_{26} (3-6 ng/l) at Sidi Braani in summer; revealing high values by 14.5 times during summer season than winter. For aromatic fraction, the concentrations were also below the detection limit except naph (39 ng/l) was detected at El-Dabaa E station in winter, Flu, Pyr, BaA, BaP (1.5-4 ng/l) were detected at Sidi Braani station in summer; revealing the same trend for aliphatic one.

Aliphatic and Aromatic hydrocarbons in sediments

Values of total petroleum hydrocarbons were presented graphically in Fig. (6). The highest concentrations (3086, 469.7ng/g), observed at El-Dabaa E and Alam Elrom during winter and summer season, respectively, with depletion in TPH concentrations at El-Dabaa W, El-Negala in winter, Sidi Braani in summer, respectively. The average value of petroleum hydrocarbons were in the following order: winter > summer.

The concentrations of aliphatic fraction in sediments during winter season for El-Dabaa E station exhibited the following values, C_{14} (26 ng/g), C19 (11 ng/g), C_{21} (24.7 ng/g), C_{23} (6.7 ng/g), C_{29} (32.5 ng/g), C_{30} (135 ng/g) and C_{31} (1034 ng/g), representing a total concentrations of 1269.9 ng/g in winter. In addition, the concentrations determined at Alam Elroom, Mrsa Matrouh, Sidi Braani and El-Saloum being 478.1 ng/g. Thus for the winter, total concentrations were found to be 1748 ng/g for the study area.

During summer, aliphatic hydrocarbons represent 153.4 ng/g for El-Dabaa W, Alam Elrom, Mrsa Matrouh, El-Negala and El-Saloum, reflecting higher

concentrations in winter by 11.4 times than summer; showing the same trend for seawater. In addition, the highest concentrations were recorded for higher carbon number C_{29}, C_{31} of both seawater and sediments. Similar results were reported by El-Deeb and Emara (2005) for aliphatic hydrocarbons of Mediterranean seawater west of Alexandria.

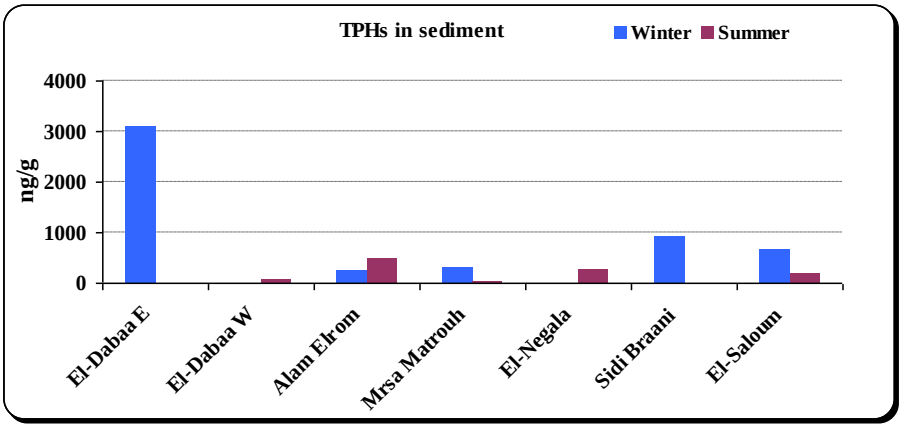

Fig. 6 Total petroleum hydrocarbons (ng/g) in sediment collected from El-Dabaa to El-Saloum along the Egyptian Mediterranean Sea.

Generally, the aromatic hydrocarbon concentrations of sediments ranged from ND to 3602.3 ng/g in winter with a decreasing order for the stations, El-Dabaa E > Sidi Braani > El-Saloum > Mrsa Matrouh > Alam Elrom, while in summer, the total concentration was found to be 856.1 ng/g; showing the following trend stations: Alam Elrom > El-Negala > El-Saloum > El-Dabaa W > Mrsa Matrouh > El-Dabaa E, with a winter/summer ratio of 4.2 (Table 2). In addition; the concentrations of aromatic hydrocarbon compounds in a decreasing order were BaA > B (ghi) P > InP > Acthy > Chr > Ace > Pyr > BbF > Phe > BaP > BkF > Flu > AnT. For aromatic fractions in seawater the concentration was in the order Naph > Pyr > BaP > BaA > Flu. For aliphatic hydrocarbons, concentration factor of sediments/water during winter and summer being 5.4 and 6.9 respectively, while for aromatic fractions; the ratios were 11.2 and 10.3 nearly two times higher respectively.

On the concentration of TPHs showed that these compounds increase by decreasing S‰ ($r = -0.78$, $P < 0.05$), T° C ($r = -0.53$ $P < 0.05$) and TOC% ($r = -0.77$, $P < 0.05$), according to the equations: TPHs concentrations $y = -0.2937$ S‰ + 38.438, $y = -2.348$ T + 22.942, $y = 0.0257$ TOC + 0.1422 (Fig. 7); while the effect of other environmental parameters are negligible. This is most probably attributed to the ability of petroleum hydrocarbons to be adsorbed onto bottom.

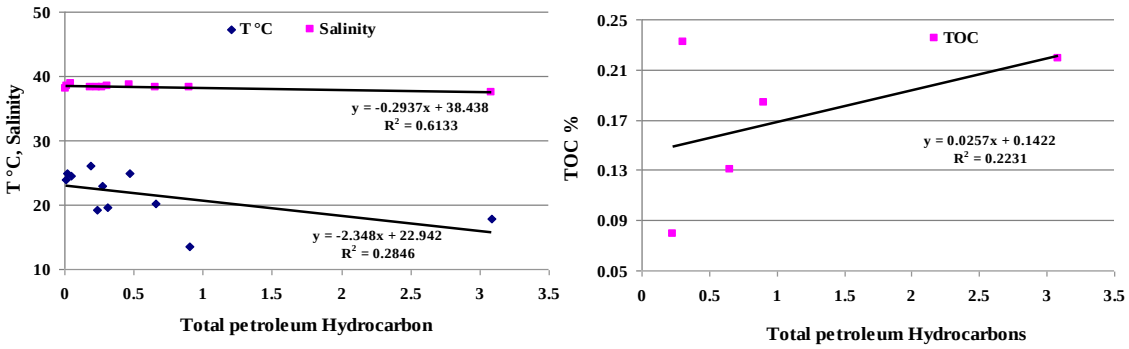

Fig. 7: Correlation between TPHs and each salinity, temperature and TOC% in the area of study

OCPs and PCBs in the seawater and sediments

There is complete depletion of OCPs and PCBs in the seawater samples of the study area during summer and winter seasons; except ß-HCH was detected with very low concentration 0.141ng/l at El-Dabaa E. For sediment samples; the sum of total pesticides varied from below detection to 120 ng/g (Table 4). High value (120ng/g) was observed only at El-Saloum at summer season. The order of decreasing concentrations in sediment samples during winter season was: El-Dabaa W > El-Dabaa E > Mrsa Matrouh with complete depletion of OCPs in the other stations. HCHs were below detection limits in the sediment and this may attributed to higher vapor pressure of these compounds which facilitate relatively rapid atmospheric dissipation in the tropics, leaving fewer residues in soil and water.

Table 4: Concentration of chlorinated pesticides, PCBs, TPHs (ng/g) measured in sediment samples collected from El-Dabaa E to El-Saloum of the Egyptian Mediterranean Coast.

Name		El-Dabaa E	El-Dabaa W	Alam Elrom	Mrsa Matrouh	El-Negala	Sidi Braani	El-Saloum
HCHs	Winter	ND	ND	ND	ND	ND	ND	ND
TCs		ND	3.58	ND	ND	ND	ND	ND
DDTs		0.64	ND	ND	0.635	ND	ND	ND
TP		0.64	3.58	ND	0.635	ND	ND	ND
PCBs		60.1	ND	64.1	ND	6.3	4.69	9.8
TArHC		1817	ND	209	ND	ND	822.3	597
TAlHC		1269	N D	25	312.2	ND	81.4	59.5
TPHs		3086	N D	234	312.2	ND	903.7	656.5
HCHs	Summer	ND	ND	ND	ND	ND	ND	ND
TCs		ND	ND	ND	ND	ND	ND	15.6
DDTs		ND	ND	ND	ND	ND	ND	104.6
OCPs		ND	ND	ND	ND	ND	ND	120.1
PCBs		ND	ND	ND	ND	ND	ND	8.12
TArHCs		9.8	38	411.9	10.3	233.9	ND	152.2
TAlHCs		ND	8.9	57.8	6	41.5	ND	39
TPHs		9.8	46.9	469.7	16.3	275.4	ND	191.2

ND: below detection limit, HCHs=α-HCH + β-HCH + γ-HCH, TCs = aldrin + dieldrin + endrin, DDTs=o,p'-DDE + p,p'-DDE + o,p'-DDD + p,p'-DDD + o,p'-DDT + p,p'-DDT, OCPs =ΣHCHs + ΣCs + ΣDDTs, ΣPCBs= PCB 28 + PCB 52 + PCB 101 + PCB 118 + PCB 153 + PCB 138 + PCB 180, TArHCs= total aromatic hydrocarbons, TAlHCs= total aliphatic hydrocarbons.

Cyclodienes also not detected in the sediment, except at El-Dabaa W (3.58 ng/g) in the winter and at El-Saloum (15.6 ng/g) in the summer. The presence of Dieldrin values of 3.58, 1.9 ng/g at El-Dabaa W and El-Saloum in winter and summer; respectively, and 13.7 ng/g of Endrin in summer; declared that Aldrin is converted into its epoxide form; Dieldrin and then rearrangement to endrin (GESAMP, 1993) in sediment of the study area.

DDTs compounds, in particular its metabolite p,p –DDT was only detected at El-Dabaa E and Mrsa Matrouh in winter with values of 0.64 and 0.635 ng/g respectively. Total concentration of DDTs was found to be 104.6 ng/g at El-Saloum in summer.

Concentrations of PCBs in winter showed the following congeners PCB 28 (6.3 ng/g, El-Negala), PCB52 (64.1 ng/g, Alam Elrom), PCB 101 (4.69 ng/g, Sidi Braani), (9.827ng/g, El-Saloum). While, in summer showed the following congeners PCB101 (3.8 ng/g, El-Saloum), PCB 153 (0.5ng/g, El-Saloum), PCB 138 (60.1 ng/g, El-Dabaa E). Total concentrations of PCBs in winter and summer were found to be 145 ng/g and 8.12 ng/g respectively; with ratio of 18.08.

In marine sediments, the average concentrations of pesticides, PCBs, TPHs were much lower in sediment of the western part of the Egyptian Mediterranean

coast compared to other study sites. These data are in agreement with the data recorded in Western Mediterranean Sea coastal sediments (Shreadah *et al*. 2016) and lower than data previously measured in the Western coast of Alexandria, Egypt (Said, 2007) and Mediterranean Sea sediments (Guitierrez *et al*. 2007). Generally, it was observed that seawater from most sites did not show any levels of pesticides, PCBs and TPHs. These levels, if any, may have been much lower than the detection limit for the compounds analyzed. The present study indicated that all measured concentrations of pesticides, PCBs and petroleum hydrocarbons in the Egyptian coast of Mediterranean Sea were much lower than those reported as permissible levels. The maximum permissible levels recommended by the National Academy of Sciences and National Academy of Engineering [NAS-NAE, 1972] for organochlorine pollutants are 1000-5000 ng/g for PCBs and 100 ng/g for cyclodienes. The recommended levels by Swedish Food Regulation are 5000 ng/g for DDTs, 2000 ng/g for PCBs (SFR, 1983).

CONCLUSION

This study represent an important data regarding environmental parameters as well as amino acids, petroleum hydrocarbons, pesticides and PCBs in water and sediment of the western section of the Egyptian Mediterranean Sea from El-Dabaa to El-Saloum during the year 2014. The measurements of physico-chemical parameters and nutrients in water collected from the study area indicated that water quality from El-Dabaa to El-Saloum is good; within the permissible limits in the majority of monitoring sites, and all stations were generally between oligotrophic and mesotrophic (low and medium level of nutrients), and this area is not adversely affected by existing development. Furthermore, Seawater from most sites did not show any levels of pesticides, PCBs and TPHs. These levels, if any, may have been much lower than the detection limit for the compounds analyzed. In marine sediments, the average concentrations of amino acids is similar to other comparable areas, while pesticides, PCBs, TPHs were much lower in sediment of the western part of the Egyptian Mediterranean coast compared to other study sites.

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