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ORIGINAL ARTICLE

Distribution of total carbohydrates in surface sediments of the Egyptian Mediterranean coast, in relation to some inorganic factors

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Abstract The interrelation between calcium, magnesium, carbonate, fluoride and total carbohydrates (THCO) distribution was investigated for surface sediments collected from three sectors (A–C) along the Egyptian Mediterranean coast during the summer of 2008. The recent ultrasound-acetic acid technique was used for the simultaneous extraction and hydrolysis of total carbohydrates. Based on the average values, the sandy sediments of sector (C) exhibited the highest THCO levels (163.78 ± 53.28 μg/g). In contrast, the silty sand sediments of sector (A) had the lowest average THCO level (8.56 ± 2.60 μg/g). Linear regression model with one predictor showed that there are significant correlations between total carbohydrates, carbonate and fluoride suggesting the common origin of these components. Neither calcium nor magnesium has correlation with THCO. This study revealed that carbonate is the dominant factor affecting the distribution of carbohydrates in the sediments. The spatial distribution of THCO was not affected by the potential sources of runoff, but varied according to the sediments mineralogy.

1. Introduction

In the biosphere, carbohydrates are the major organic compounds produced photosynthetically by autotrophic organisms. They have a substantial amount of the dissolved and particulate organic carbon in water and sediments of marine environments (Khodse et al., 2008). Because carbohydrates are ubiquitous and abundant, they play an important role in biogeochemical cycles occurring in the marine water column and sediment–water interface. Thus, they may account for 10–85% of the dissolved organic carbon in seawater (Pakulski and Benner, 1994) and in sediments' pore waters (Arnosti and Holmer, 1999; Burdige et al., 2000). Also, about 3–16%, 2–13,

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3–20% of the particulate organic carbon are found in the suspended (D'souza and Bhosle, 2001) and sedimenting particles (D'souza et al., 2003; Panagiotopoulos and Sempéré, 2005) and in marine sediments (Burdige et al., 2000; Jensen et al., 2005), respectively. Moreover, carbohydrates serve as an important energy source for heterotrophic organisms (Decho, 1990) and are a potential precursor of refractory organic matter in sedimentary rocks (Sinninghe Damsté et al., 1998). In the marine system, total carbohydrates are present in monosaccharide, disaccharide, and polysaccharide forms (Borch and Kirchman, 1997; Skoog and Benner, 1997; Bhosle et al., 1998). Throughout the world, carbohydrates have received broad attention and are extensively studied by many investigators (Mecozzi et al., 2000; Unger et al., 2005; Wang et al., 2006; Khodse et al., 2007, 2008). A number of these studies focused on the relationship between carbohydrates and organic carbon. Moreover, the distribution of carbohydrates in relation to mineralogic and granulometric composition of surface sediments was taken into consideration (Hazdija et al., 1985). However, to our best knowledge, there is little information available about the distribution of total carbohydrates in sediments in relation to some inorganic factors. Therefore, it is essential to gain insights on this topic.

Several studies have been focused on the presence of organic and inorganic contaminants in the Mediterranean coast of Egypt. However, only rare studies focused on the distribution of total carbohydrates in relation to different inorganic factors along the Egyptian Mediterranean coast. Therefore, this study was under taken to investigate the distribution of total carbohydrates and some inorganic components (calcium, magnesium, carbonate and fluoride) in the surface sediments of the Egyptian Mediterranean Sea coast. The correlations between total carbohydrates and major inorganic factors of sediments were investigated.

2. Sediment quality of the studied area

The Egyptian Mediterranean Sea coast's sediments differ in their mineral composition (Fig. 1). Among them are off the Nile Delta, off Alexandria and the western sectors. Off the Nile Delta sector, the mud and sands of the inner and middle shelf contain very little biogenic carbonate. The mud and mud–sand mixture from the outer shelf is moderately calcareous, and the sands and some of the sand–mud mixture from the lower terraces are highly calcareous. However, the sediments of the western part of the Nile Shelf are mainly aragonite and calcite carbonate (Summerhayes et al., 1978). The mud fraction of the eastern part of the Nile Shelf deposits is dominantly terrigenous, composed of (1) detrital sands which are primarily quartz admixed with pyroxenes, amphiboles, epidote, garnet, zircon, tourmaline, rutile and apatite (Stanley et al., 1979); (2) detrital mud which is composed of 15% kaolinite, 8% illite, 72% montmorillonite and 5% chlorite (El-Sammak, 1987). El-Wakeel and El-Sayed (1978) stated that biogenic clastics are the major

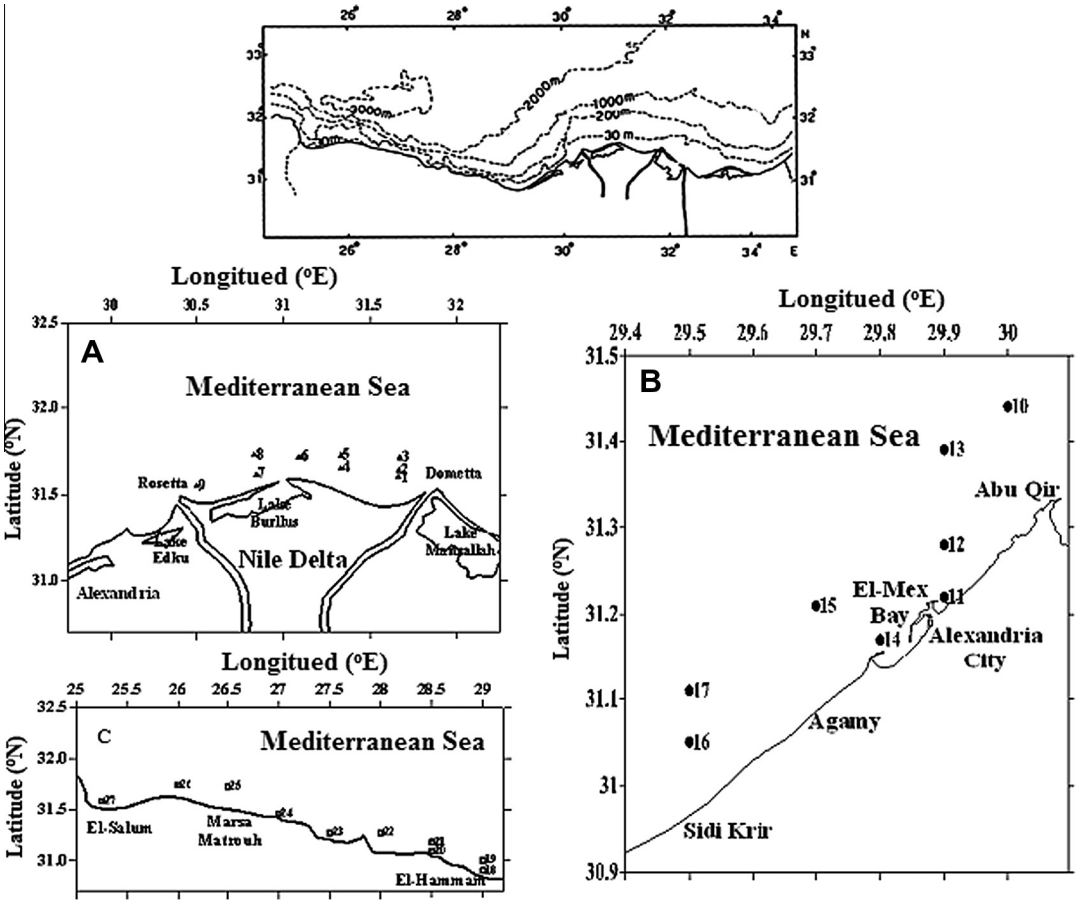

Figure 1 Sampling locations of marine sediments along the Mediterranean coast of Egypt.

source of carbonate in the Eastern Harbor sediments (off Alexandria sector), especially in the central part, as well as in the adjacent shelf. On the other hand, the western side sector of the Egyptian coast comprising the northern margin of the western desert is a typical carbonate province and it is mainly composed of calcite. Moreover, it is recognized by two major types of carbonate sediments including the skeletal parts of various calcareous organisms (molluscs, echinoids, bryozoa, foraminifera and coralline algae) and oolites; true oolites (Moussa, 1999). It is expected that the sediments of the three previously mentioned sectors differ in their total carbohydrates.

3. Experimental methods

3.1. Study area and sampling

Twenty-seven sediment samples were collected during the summer of 2008 from three sectors along the Mediterranean coast of Egypt, using a stainless steel Peterson grab sampler (20 × 13 cm). Sediment sampling locations were detected using GPS localization and representing different aquatic environments (Fig. 1 and Table 1). Marine sediments of the studied sectors have been subjected to various kinds of hazardous substances as a result of industrial development and different anthropogenic activities (Table 2). Sector A represents nine stations off the Nile Delta (stations 1–9, Fig. 1A). The Nile Delta is a fragile environment; it is subjected to erosion of its shores as a result of the ceasure of sediment supply resulting from the construction of the High Dam at Aswan. Before the construction of the first Aswan Dam, up to 100 billion m^3 of water was discharged annually from the Nile into the Mediterranean. After the construction of the High Dam, no fresh water reaches the sea and the shelf is covered by typical Mediterranean water with a salinity of 39‰. In addition, the transport of sediment to the Mediterranean shelf off the Nile Delta is diminished as a result of damming the river (Moussa, 1999; Rifaat, 2005). As shown in Fig. 1A, the three Nile Delta lakes Edku, Burllus and Manzallah are connected with the Mediterranean Sea through an open namely El-Boughaz at their northern regions. Lake Edku is subjected to huge inputs of terrigenous and anthropogenic nutrient discharge, sewage and agricultural runoff ($2.06 \times 109\ m^3\ y^{-1}$) via three main drains, Edku, El-Boseily and Barzik situated at its eastern margin. Lake Burllus receives mainly agriculture drainage water ($3.2 \times 109\ m^3\ y^{-1}$) from six drains at its southern region. Lake Manzallah receives annually about $6.7 \times 109\ m^3$ of raw sewage, agricultural and industrial wastewater (Saeed and Shaker, 2008). Sector B (stations 10–17, Fig. 1B) is off the Alexandria coast; whereas stations 10–14 are under the effect of different kinds of land disposal (El-Said and Youssef, 2009). Thus station 10 (Abu-Qir Bay) receives different kinds of water from

Table 1 Sample locations and grain size analysis of sediment samples collected from the Mediterranean coast of Egypt.

	Position	Mean size (Ø)*	Sediment type*
Sector A (off the Nile Delta)			
1	31° 06′ 40″N-31° 38′ 36″E	1.93	Silty sand
2	31° 06′ 40″N -31° 41′ 40″E	3.64	Silty sand
3	31° 06′ 03″N-31° 46′ 34″E	3.92	Silty sand
4	31° 20′ 04″N-31° 43′ 12″E	5.83	Sandy silt
5	31° 20′ 04″N-31° 47′ 11″E	2.86	Silt
6	30° 51′ 50″N-31° 42′ 54″E	4.46	Sandy clayey
7	30° 40′ 28″N-31° 43′ 00″E	4.36	Clayey silt
8	30° 39′ 52″N-31° 43′ 49″E	1.07	Sand
9	30° 28′ 35″N-31° 31′ 15″E	2.41	Sandy silt
Sector B off Alexandria			
10	30° 00′ 00″N-31° 26′ 39″E	6.08	Silt
11	29° 54′ 10″N-31° 12′ 33″E	2.10	Sand
12	29° 54′ 10″N-31° 17′ 09″E	1.24	Sand
13	29° 54′ 10″N-31° 22′ 58″E	0.53	Sand
14	29° 41′ 59″N-31° 12′ 33″E	0.03	Sand
15	29° 30′ 25″N-31° 02′ 26″E	0.35	Sandy mud
16	28° 59′ 57″N-30° 53′ 15″E	0.85	Muddy sand
17	29° 00′ 15″N-30° 59′ 59″E	0.20	Sand
Sector C West of Alexandria			
18	28° 45′ 20″N-31° 00′ 18″E	0.48	Muddy sand
19	28° 45′ 20″N-31° 04′ 17″E	0.70	Sandy mud
20	28° 30′ 43″N-31° 05′ 12″E	0.63	Sand
21	28° 30′ 24″N-31° 09′ 48″E	0.20	Sand
22	27° 59′ 57″N-31° 16′ 51″E	0.49	Sand
23	27° 30′ 24″N-31° 16′ 14″E	2.48	Muddy sand
24	26° 59′ 38″N-31° 27′ 16″E	1.20	Sand
25	26° 30′ 05″N-31° 42′ 54″E	0.99	Sand
26	25° 59′ 56″N-31° 40′ 26″E	0.98	Sand
27	25° 15′ 28″N-31° 41′ 03″E	0.96	Sand

* Abdel Ghani et al. (2013)

Table 2 Ranges of heavy metals (μg/g dry weight) in the studied regions.

Heavy metals	Sector A	Sector B (off Alexandria)			Sector C
	(off the Nile Delta)[a]	(Abu-Qir)[b]	(Eastern harbor)[c]	(El-Mex)[d]	(West of Alexandria)[e]
Fe	942.00–15703.00	3240.00–30690.00	–	–	846.43–1433.93
Mn	71.00–965.00	166.95–841.71	–	–	32.37–108.92
Cd	0.26–1.51	1.51–4.15	0.08–3.11	1.8–5.0	0.52–0.92
Cu	8.52–46.67	4.00–59.00	23.00–117.10	15.2–62.8	26.53–33.33
Ni	3.23–65.79	8.33–65.01	–	–	31.70–43.59
Pb	13.59–43.70	–	37.00–154.00	35.8–93.0	20.67–35.62
Zn	33.03–119.00	–	83.40–3168.70	79.1–130.3	26.27–112.73

[a] Draz et al. (2009).
[b] Youssef and Abbas (2005).
[c] Abdallah (2007).
[d] Masoud et al. (2007).
[e] Ahdy and Khaled (2009).

three sources: (1) considerable amounts of fresh water from the Rosetta branch of the River Nile, (2) brackish water from Lake Edku (~$3.3 \times 106\ m^3$ daily, Anon, 1984) through the El-Maadyia inlet and (3) drainage waste water from the El-Tabia pumping station (~$2 \times 106\ m^3$ daily, Said et al., 1995). Stations 11, 12 and 13 represent the Eastern Harbor. For a long time, the Eastern Harbor has been affected by sewage waste disposal through many outfalls. During February 2003, the sewage disposal was diverted to Lake Mariut. Station 14 (El-Mex Bay) receives huge volumes of drainage water via the El-Umum drain as well as mixed wastes from Lake Mariut (~$10 \times 106\ m^3$ daily, Youssef, 2001). However, station 15 is considered as a famous recreational beach. The western coast of Alexandria (sector C) was represented by ten stations (stations 18–27; Fig. 1C), where most of them are recreational beaches especially stations 23 and 24. Moreover, station 22 is far from any land based sources (Hamed and Emara, 2006). At each station, three replicates of sediment samples were collected at the surface layer (0–5 cm depth). The three replicate samples were composed and placed in clean closed Petri dishes. All samples were immediately frozen and transferred to the laboratory. In the laboratory, the samples were air dried. Each sample was homogenized, sieved using a 0.75 mm plastic sieve and finely powdered in an agate mortar for chemical analysis.

3.2. Grain size and chemical analyses

Grain size analysis was carried out using the conventional method (Folk, 1974) and as reported by Abdel Ghani et al. (2013). The proportions of sand, silt and clay were determined by a combined technique of dry sieving and pipette analysis. For the chemical analysis of calcium and magnesium, 0.2 g of sediment samples were completely digested using HNO_3, $HClO_4$ and HF acids (3:2:1). The residue was dissolved in 10 ml diluted HNO_3 and preserved in an acid-clean PVC bottles for analysis. For each digestion program, a blank was prepared using the same procedure. Sample solutions and reagent blanks were analyzed for calcium and magnesium using a Perkin Elmer 2830 flame Atomic Absorption Spectrophotometer. Total carbonate was determined by the titration technique (Black, 1965). One gram of each sediment sample was treated with an excess of 0.5 N HCl and the released amount of CO_2 was determined by back titration with previously standardized 0.25 N NaOH solution using phenolphthalein as the indicator. The obtained results were calculated as mg carbonate per gram sediment. Regarding fluoride, 0.5 g of fine powder of each sediment sample was mixed with 3.5 g anhydrous sodium carbonate in a platinum crucible (Jeffery, 1975). The mixture was fused in an electric muffle furnace at a temperature of about 900°C for 20 min, and then allowed to cool. 4.1 ml of concentrated HNO_3 acid was added to each fused sediment sample, and then stirred to release most of the CO_2 and diluted to 50 ml. However, these solutions were preserved in clean well stoppered polyethylene bottles until use for the determination of fluoride content in sediment samples. Fluoride ion concentration in the digested samples was determined by following the procedure of zirconium alizarin red S (Courtenary and Rex, 1951; Masoud et al., 2004). 1 ml of the sample solution was treated with 1.5 ml (0.004 M) of alizarin red S and 1 ml (0.004 M) of $ZrOCl_2$, and then diluted to 25 ml. The absorbance was measured after 2 h using a UV/visible single

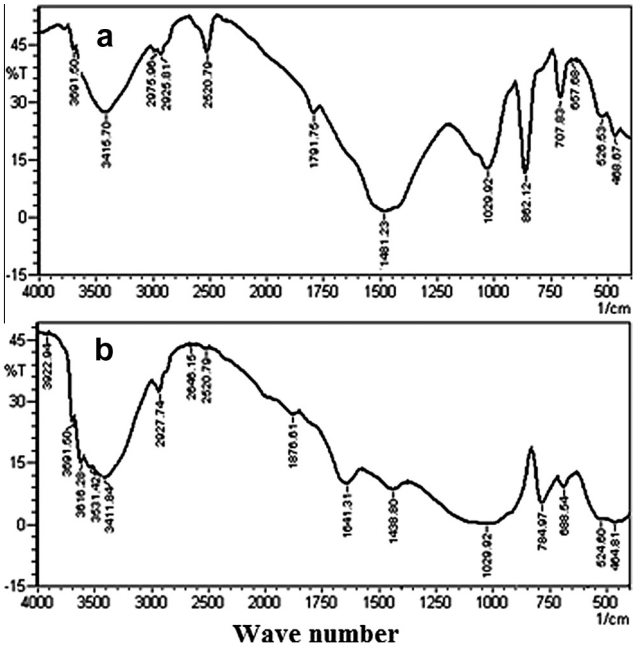

Figure 2 FTIR spectra of a sediment sample (a) before 1 M CH_3COOH-ultrasound treatment and (b) after 1 M CH_3COOH-ultrasound treatment.

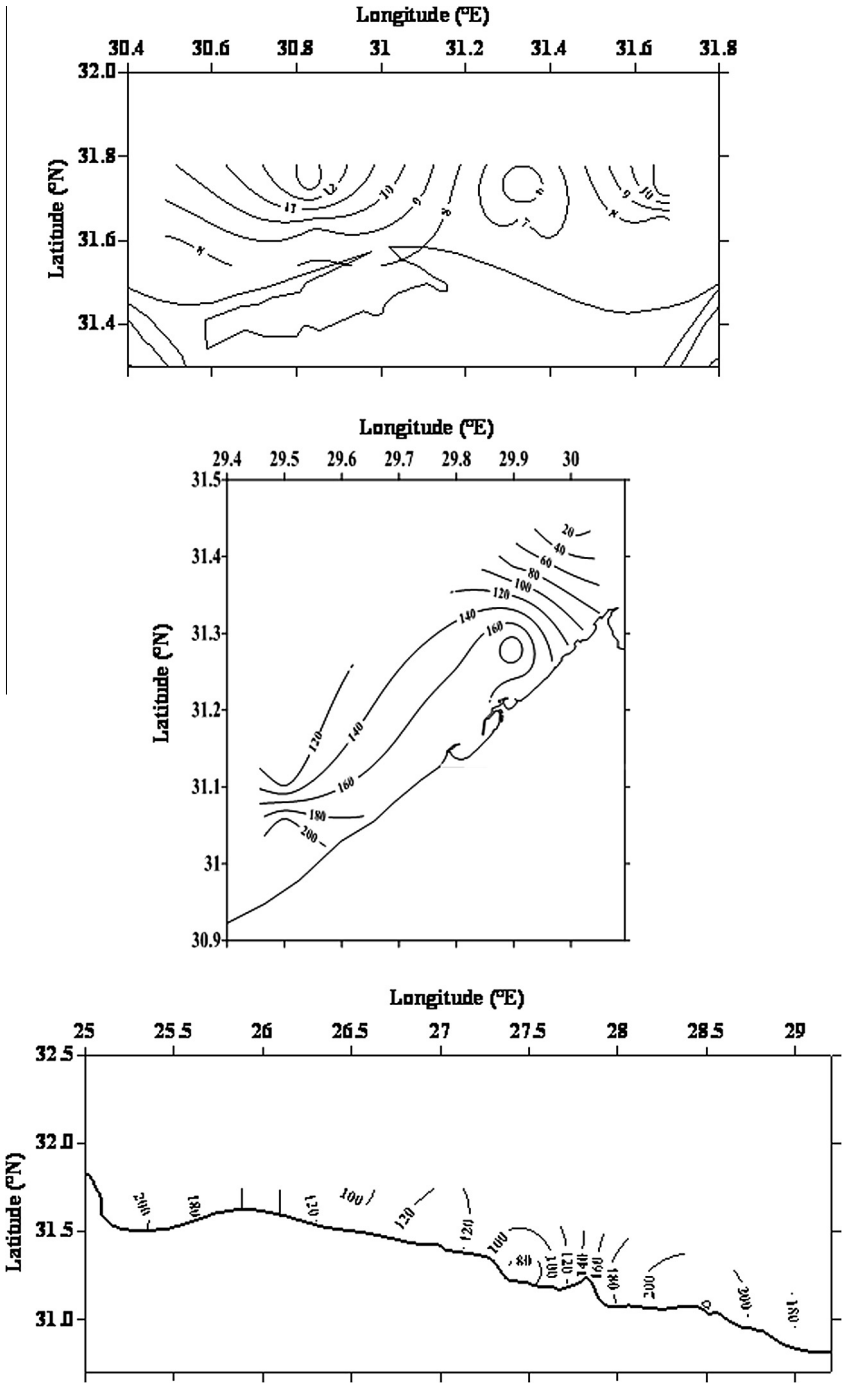

Figure 3 Distribution of total carbohydrates in marine sediments of the selected sectors along the Egyptian Mediterranean coast.

beam Spectronic 21 D Milton Roy spectrophotometer at $\lambda = 420$ nm. The concentration of the unknown sample (mg/l) was obtained using the calibration curve in which the standard NaF was of 10 μ F^-/ml and then the concentration was expressed as μg/g dry weight.

3.3. Extraction and hydrolysis of total carbohydrates (THCO)

The ultrasound-acetic acid method is used for the extraction and hydrolysis of total carbohydrates in the sediments. This method is based on an ultrasound treatment coupled to an acid treatment, followed by the colorimetric determination of carbohydrates according to the phenol–sulfuric acid method (Mecozzi et al., 2000; Dubois et al., 1956). In this procedure, the extraction and hydrolysis of carbohydrates are quantitative since the oxidative reactions which cause the underestimation of the (THCO) amount are minimized. In the present study, the ultrasound treatment was performed in an ultrasonic cleaning bath (CREST model; Model No.:2800 TAE, New York) containing distilled water and ethylene glycol as the antifouling agent. In a 100 ml glass container, 1 M CH_3COOH (50 ± 0.05 ml) was added to (1.0 ± 0.01 g) of dried marine sediment. All samples were sonicated at room temperature for 4 h. After sonication, the samples were centrifuged and

Table 3 Distribution of carbohydrates, calcium, magnesium, carbonate and fluoride in sediments along sector A (off the Nile Delta) off the Mediterranean coast of Egypt.

Station number	Carbohydrates (μg/g)	Calcium (mg/g)	Magnesium (mg/g)	Carbonate (mg/g)	Fluoride (μg/g)
1	7.89 (0.12)**	400.80 (2.20)**	60.77 (0.99)**	9.40 (0.29)**	1061.12 (11.15)**
2	7.06 (0.25)	200.40 (0.88)	121.55 (1.10)	9.40 (0.25)	896.06 (11.09)
3	11.66 (0.23)	196.47 (0.89)	59.58 (0.58)	9.40 (0.31)	618.28 (12.03)
4	7.06 (0.15)	100.20 (0.56)	121.55 (0.98)	8.89 (0.27)	1801.08 (12.99)
5	4.93 (0.22)	192.69 (0.99)	58.44 (0.41)	8.39 (0.24)	1318.24 (15.02)
6	9.20 (0.33)	300.60 (2.20)	121.55 (0.95)	29.60 (0.30)	1102.15 (13.11)
7	8.54 (0.19)	200.40 (1.06)		9.20 (0.28)	1528.57 (16.11)
8	13.47 (0.34)	200.40 (1.44)	121.55 (0.95)	9.20 (0.30)	600.04 (11.00)
9	7.23 (0.09)	283.58 (1.66)	114.67 (0.88)	70.00 (0.55)	2029.31 (13.06)
Mean	8.56	230.62	86.63	18.16	1217.20
SD	2.60***	85.89***	43.62***	20.59***	498.49***

** Standard deviation of the three replicates of each sample.
*** SD; Standard deviation of sector A.

the supernatant was used for colorimetric analysis. The colorimetric quantification of (THCO) was performed according to Mecozzi et al. (2000). Infrared measurements were performed using Fourier transform infrared (FTIR) spectrophotometer: FTIR-8400S Shimadzu–Japan. Samples were scanned from 500 to 4000 cm^{-1}. All the chemicals used throughout this study were of analytical grade reagents. Double-distilled water was used for all the treatments.

3.4. Statistical analysis

Using the Minitab 13.1 software program, a simple correlation analysis and the linear regression model with one predictor as well as stepwise regression were done to assess and estimate the distinction between parameters. Mapping of Fig. 3 was carried out using Surfer 8 (Golden software, USA).

4. Results and discussion

4.1. Extraction and hydrolysis of total carbohydrates (THCO) and FTIR measurements

The determination of total carbohydrates in solid samples is often a troublesome analytical procedure. Recently, an ultrasound-acetic acid method has been used for the simultaneous extraction and hydrolysis of (THCO) in marine sediments (Mecozzi et al., 2000). In the present study the extraction and hydrolysis of (THCO) in marine sediments were under taken by using an ultrasound and a non-oxidizing acid such as CH_3COOH. However, ultrasound can accelerate the rate of polysaccharide hydrolysis and an acid medium is necessary for the conversion of polysaccharides to monosaccharides (Mecozzi et al., 2000). FTIR spectra were measured to confirm the efficiency of the ultrasound-acetic acid method. However, the spectra of sediment samples were determined before and after sonication in acid medium. For example, Fig. 2 represents the FTIR spectra before and after 1 M CH_3COOH-ultrasound treatment of the sand sediment sample (mean grain size = 0.99 ϕ, Table 1) from station 25. FTIR before the sonication shows a wide and intense band of the OH stretching vibration of the polysaccharide group at 3415.70 cm^{-1} (Fig. 2a). The absorption bands in the 2900 cm^{-1} region are usually superimposed on the shoulder of the broad O–H stretching band (Qi et al., 2004). The band at 1029.92 cm^{-1}, can be attributed to C–O and C–C stretches (Mecozzi et al., 2002). The spectrum also shows signals at 2520.79 cm^{-1}, 1791.75 cm^{-1} and 862.12 cm^{-1} due to the presence of carbonate salts (Tatzber et al., 2007). The band at 1791.75 cm^{-1} may be assigned to the stretching vibrations of the carbonyl groups in alkyl and alkyl–aryl ester bonds such as those found in plant biopolyesters (Spaccini and Piccolo, 2008). In Fig. 2b, FTIR after sonication, demonstrates that the band at 1481.23 cm^{-1} decreases and appears at 1438.80 cm^{-1} while the bands at 862.12 cm^{-1} and 2520.79 cm^{-1} disappear after acid treatment. The band at 1029.92 cm^{-1} becomes broader after extraction. Moreover, the two peaks at 1641.31 cm^{-1} and 1481.23 cm^{-1} are due to the COO^- deprotonated carboxylic function (Marry et al., 2000; Boulet et al., 2007). Mecozzi et al. (2000) studied the FTIR spectra of starch, a standard polysaccharide, before and after treatment with 2 M CH_3COOH ultrasound. It was observed the presence of an absorption band at 1670 cm^{-1} was attributed to the C═O stretching after a 5 h treatment, however, the spectrum of untreated starch showed the absence of this band. In the present study, this band is found at 1641.31 cm^{-1} which confirms the presence of degradation products resulting from oxidative reactions of carbohydrates as stated by Mecozzi et al. (2000). From these data we can conclude that this method is successful for the extraction of carbohydrates from sediments. Indeed, this method is rapid since it requires only 5 h for the whole analysis (extraction, hydrolysis and colorimetric determination by the phenol–sulfuric acid method), and it has recoveries generally higher than 80% (Mecozzi et al., 2000).

4.2. Levels of (THCO), calcium, magnesium, carbonate and fluoride in sediments

The concentrations of total carbohydrate (THCO), calcium, magnesium, carbonate and fluoride in the sediments of the three investigated sectors along the Egyptian Mediterranean coast are presented in Tables 3–5. Table 3 shows that, in sediments of sector A (off the Nile Delta), the (THCO) concentration varies from 4.93 ± 0.22 μg/g to 13.47 ± 0.34 μg/g, with an average concentration of 8.56 ± 2.60 μg/g. The higher con-

Table 4 Distribution of carbohydrates, calcium, magnesium, carbonate and fluoride in sediments along sector B (off Alexandria) off the Mediterranean coast of Egypt.

Station number	Carbohydrates (μg/g)	Calcium (mg/g)	Magnesium (mg/g)	Carbonate (mg/g)	Fluoride (μg/g)
10	10.84 (0.31)**	589.41 (1.30)**	59.58 (0.44)**	19.00 (0.30)**	1693.55 (14.03)**
11	139.98 (1.09)	491.18 (1.08)	59.58 (0.50)	459.86 (1.99)	1897.53 (14.11)
12	197.15 (2.10)	481.73 (1.09)	58.44 (0.49)	499.25 (1.44)	1395.78 (12.08)
13	76.23 (0.99)	472.64 (1.99)	34.40 (0.25)	499.25 (1.09)	1827.96 (10.96)
14	150.49 (2.22)	196.47 (0.67)	71.50 (0.29)	614.39 (1.09)	2292.85 (15.16)
15	175.79 (1.44)	100.20 (0.54)	60.78 (0.55)	588.13 (1.10)	1532.26 (14.00)
16	215.22 (2.09)	196.47 (0.78)	178.75 (0.60)	622.47 (1.19)	2503.69 (12.99)
17	104.49 (1.08)	385.38 (2.02)	175.31 (0.90)	439.66 (0.99)	2635.46 (15.50)
Mean	133.77	364.19	87.29	467.75	1972.39
SD	67.63***	176.81***	56.35***	194.26**	455.92***

** Standard deviation of the three replicates of each sample.
*** SD; Standard deviation of sector B.

Table 5 Distribution of carbohydrates, calcium, magnesium, carbonate and fluoride in sediments along sector C (West of Alexandria) off the Mediterranean coast of Egypt.

Station number	Carbohydrates (μg/g)	Calcium (mg/g)	Magnesium (mg/g)	Carbonate (mg/g)	Fluoride (μg/g)
18	186.47 (1.55)**	200.40 (0.88)**	121.55 (0.91)**	620.45 (0.98)**	2424.63 (14.49)**
19	173.49 (1.13)	196.47 (0.67)	83.42 (0.62)	620.45 (1.15)	2609.11 (12.99)
20	222.61 (1.98)	400.80 (1.23)	182.33 (0.87)	470.97 (0.98)	1586.02 (11.98)
21	210.29 (1.88)	196.47 (0.47)	35.75 (0.22)	611.36 (1.08)	2016.13 (13.10)
22	193.04 (2.12)	378.11 (1.99)	57.33 (0.34)	479.05 (1.03)	1344.09 (11.56)
23	62.10 (0.48)	501.00 (2.60)	36.46 (0.31)	497.23 (0.82)	1809.35 (13.02)
24	141.29 (1.66)	192.69 (0.88)	93.50 (0.33)	601.26 (1.12)	1532.26 (11.06)
25	89.54 (0.34)	501.00 (2.30)	66.91 (0.65)	583.08 (1.03)	2455.54 (14.01)
26	151.15 (1.03)	385.38 (1.96)	58.44 (0.55)	589.14 (1.02)	1639.78 (11.21)
27	207.83 (1.44)	289.04 (1.05)	116.88 (0.87)	619.44 (1.10)	1775.21 (12.99)
Mean	163.78	324.14	85.26	569.24	1919.21
SD	53.28***	125.40***	45.31***	61.58***	438.54***

** Standard deviation of the three replicates of each sample.
*** SD; Standard deviation of sector C.

centration was found at station 8; however, the lower one was recorded at station 5. The concentration of calcium ranged between 100.20 ± 0.56 mg/g and 400.80 ± 2.20 mg/g, with a mean of 230.62 ± 85.89 mg/g. The highest concentration was detected at station 1 while the lowest level was recorded at station 4. The mean concentration of magnesium was 86.63 ± 43.62 mg/g whereas the highest Mg level (121.55 mg/g) was determined at stations 2, 4, 6, 7 and 8. Generally, based on the average values, the concentrations of Ca and Mg (230.62 ± 85.89 mg/g and 86.63 ± 43.62 mg/g, respectively) were higher than the base values (45.00 mg/g for Ca and 16.40 mg/g for Mg), reported by Martin and Meybeck (1979). Carbonate concentrations ranged between 8.39 ± 0.24 mg/g and 70.00 ± 0.55 mg/g (average concentration = 18.16 ± 20.59 mg/g), where the highest concentration was recorded at station 9, while the lowest one was detected at station 5. However, fluoride levels fluctuated between 600.04 ± 11.00 μg/g and 2029.31 ± 13.06 μg/g with an average of 1217.20 ± 498.49 μg/g.

In sediments of sector B (off Alexandria, Table 4), total carbohydrates exhibited a maximum concentration of 215.22 ± 2.09 μg/g. It ranged from 10.84 ± 0.31 μg/g at station 10 to 215.22 ± 2.09 μg/g at station 16. Calcium content exhibited elevated levels along all stations of this sector in general. The highest calcium content (589.41 ± 1.30 mg/g) was recorded at station 10 while the lowest one was detected (100.20 ± 0.54 mg/g) at station 15, with an average value of 364.19 ± 176.81 mg/g. Magnesium concentration ranged from 34.40 ± 0.25 mg/g to 178.75 ± 0.60 mg/g with an average value of 87.29 ± 56.35 mg/g, which is higher than the reported base value (Martin and Meybeck, 1979). The average concentration of carbonate was 467.75 ± 194.26 mg/g. However, station 16 had the highest CO_3 level (622.47 ± 1.19 mg/g) while station 10 gave the lowest value (19.00 ± 0.30 mg/g). Total fluoride concentrations ranged between 1395.78 ± 12.08 μg/g at station 12 and 2635.46 ± 15.50 μg/g at station 17 with an average of 1972.39 ± 455.92 μg/g. The results of the present study showed lower values compared with those reported by El-Said (2005) for the Egyptian Mediterranean coast.

Table 5 shows that, in the western part of the Alexandria (sector C), (THCO) content ranges from 62.10 ± 0.48 μg/g to 222.61 ± 1.98 μg/g. However, the maximum concentration was observed at station 20. Calcium had an average concentration of 324.14 ± 125.40 mg/g, whereas the highest Ca levels (501.00 ± 2.60 mg/g) and (501.00 ± 2.30 mg/g) were recorded at stations 23 and 25, respectively. Magnesium exhibited concentration ranges from 35.75 ± 0.22 mg/g to 182.33 ± 0.87 mg/g, with an average of 85.26 ± 45.31 mg/g. Carbonate

concentration varied from 470.97 ± 0.98 mg/g to 620.45 ± 1.15 mg/g. However, the highest concentrations were recorded at stations 18 and 19, while the lowest level was detected at station 20. On the other hand, the fluoride content fluctuated between 1344.09 ± 11.56 μg/g at station 22 and 2609.11 ± 12.99 μg/g at station 19, with a mean value of 1919.21 ± 438.54 μg/g.

Grain size distribution of sediments in shallow water environments plays an important role in providing information about the nature of the current or wave motion (Shepard, 1973). Table 1 summarizes the grain size analysis. It is observed that sediments of the investigated sectors differ in their grain size characteristics. In sector A, off the Nile Delta area, the mean grain size ranged from 1.07 ϕ (sand) to 5.83 ϕ (sandy silt). In sediments of sector B (off Alexandria), it varied from 0.03 ϕ to 6.08 ϕ (i.e. sand to silt). However, it ranged between 0.20 ϕ (sand) and 2.48 ϕ (muddy sand) in sediments of the western area of Alexandria (sector C) (Abdel Ghani et al., 2013).

4.3. Horizontal distribution of total carbohydrates (TCHO)

In the present study, Total carbohydrates (TCHO) varied with respect to the sampling sectors exhibiting a particular distribution trend. Table 3 and Fig. 3 show that sector A has the lowest values ranging from 4.93 ± 0.22 μg/g to 13.47 ± 0.34 μg/g. Generally, these concentrations increased westward to reach a value of 215.22 ± 2.09 μg/g at station 16 (sector B). This value decreased gradually westward and then increased to reach a maximum value of 222.61 ± 1.98 μg/g at station 20 (sector C). Actually, it was observed that the spatial distribution of TCHO is not affected to a considerable extent by land disposal. For example, the concentration of TCHO at station 22 was about eighteen times higher than that observed at station 10. Station 22 is far from any land based sources (Hamed and Emara, 2006). However, station 10 is under the effect of different kinds of land disposal (El-Said and Youssef, 2009). This indicates that there is another factor affecting the distribution of TCHO in the studied sediments. Based on the average values, TCHO concentrations for sector C sediments (163.78 ± 53.28 μg/g) were obviously higher than those measured for sectors A and B (8.56 ± 2.60 μg/g and 133.77 ± 67.63 μg/g, respectively). El-Saraf (1994) stated that the wide fluctuations in carbohydrate concentrations are usually related to the degree and the type of organic matter content which precipitates on the bottom sediments.

The levels of carbohydrates obtained in this study are lower than those determined for Khor Kalabsha; western Lake Nasser, Egypt [4.67–8.69 mg/g (El-Saraf, 1994)]. This indicates that marine surface sediments posses lower carbohydrate content than the lake sediments. Indeed, El-Saraf (1994) mentioned that marine surface sediments are low in organic content and carbohydrates, which are related to the presence of a high concentration of inorganic matter.

4.4. Statistical analysis

Sodium alginate as a polysaccharide has the ability to interact with the divalent metal ions such as Ca^{+2}, Sr^{+2}, and Ba^{+2} (Katchalsky et al., 1961). Thus in the presence of divalent calcium ions, calcium is ionically substituted at the carboxylic site located on the polymer backbone and a second alginate strand can also connect at the calcium ion, forming a link in which the Ca ion attaches two alginate strands together (Shilpa et al., 2003). Unexpectedly, in the present study, no correlation was observed between the carbohydrates and calcium. Indeed, the linear regression model between carbohydrates and calcium reveals that TCHO = 102.438 + 0.002 Calcium (R^2 = 0.0%, $p < 0.05$) and the points are scattered and do not give a fitted straight line referring to the absence of any relationship between carbohydrates and calcium. Similarly carbohydrates showed no correlation with magnesium where the linear regression equation is TCHO = 74.48 + 0.33 Magnesium (R^2 = 3.4%, $p < 0.05$). Shilpa et al. (2003) found that no interaction is observed between magnesium and sodium alginate. Conversely, carbohydrates had strong positive correlation with carbonate (r = 0.893, confidence limit = 100% and n = 27), and to a lesser degree with fluoride (r = 0.473, confidence limit = 95% and n = 27). Moreover, the fitted line plots especially between carbohydrates and carbonate are good and the regression equations are as follows: TCHO = 4.41 + 0.28 Carbonate (R^2 = 79.7%, $p < 0.05$) and TCHO = −15.82 + 69.94 Fluoride (R^2 = 22.4%, $p < 0.05$), respectively. Fluoride not only correlated with carbohydrates but also, it related with carbonate (r = 0.637, confidence limit = 100% and n = 27). However, these relations suggest that these inorganic factors are of a common origin. Moreover, the relation between carbonate and fluoride in sediments was documented (Lv et al., 2007; Abe et al., 2004). Results indicated that carbonate is a common factor between carbohydrates and fluoride. In spite of the linear regression model with one predictor signifying that the correlation between carbohydrates and magnesium is absent, stepwise regression equation shows that total carbohydrate concentration is a function of the concentrations of carbonate, magnesium and fluoride (TCHO = 15.31 + 0.32 Carbonate + 0.33 Magnesium − 0.03 Fluoride, R^2 = 84.40%, confidence limit = 89% and n = 27). However, it seems likely that carbonate is the dominant factor affecting the concentration of TCHO in the studied sediments. As shown in Table 5 the high levels of TCHO at sector C is accompanied with the high concentration of carbonate (569.24 ± 61.58 mg/g). Indeed, the sediments of the western side of the Egyptian coast (sector C) are carbonate sediments and are mainly consisting of calcareous organisms such as algae, molluscs, echinoids, protozoa and carbonate peteoids with amorphous silica (Moussa, 1999; Håkanson and Jansson, 1983). Carbohydrates can serve in the composition, the component storage in marine and terrestrial organisms as well as in the transport of organic matter from the surface to greater depths; however, they are preferentially utilized by in situ organisms (Ittekkot et al., 1982; Tanoue and Handa, 1987). According to Bohm (1973), polysaccharides are accompanied by carbonate skeleton sediments. Moreover, Bohm et al. (1980) studied the suitability of monosaccharides as markers for particle identification in carbonate sediments and revealed that the coral and algal aragonite contributing to these sediments can be distinguished on the basis of total sugar concentration and the respective xylose and fucose levels. This may account for the significant correlation between carbohydrates and carbonate. The present study demonstrates clearly the impact of inorganic carbon (carbonate) on the TCHO concentration; however, a number of previous studies were interested in studying the relation between TCHO and organic carbon regardless of the role of the inorganic carbon (Jensen et al., 2005; Wang et al., 2006; Khodse et al., 2007;

Paez-Osuna et al., 1998). Because carbohydrates make up a significant fraction of the organic matter present in soils and marine sediments and due to their interaction with metals (Linnik and Vasil'chuk, 1995), they play a fundamental role in the bioavailability of inorganic pollutants.

5. Conclusion

This study deals with the effect of some inorganic factors (Ca, Mg, F and CO_3) on the distribution of total carbohydrates in three sectors (A, B and C) along the Egyptian Mediterranean Sea coast. The recent, rapid ultrasound-acetic acid technique of Dubois was used for good extraction and analysis of total carbohydrates. Sector C, west of Alexandria, had the highest levels of total carbohydrates. However, the distribution of carbohydrates in the sediments was highly affected by carbonate. Additionally, statistical analysis showed significant correlations between total carbohydrates, carbonate and fluoride that may accompanied with their common origin. Results showed that the quantitative determination of total carbohydrates in marine sediments is extremely important for the characterization of ecological studies. Therefore, it is recommended that any future investigations on the distribution of total carbohydrates along the Egyptian Mediterranean coast should include several inorganic variable measurements as an aid for a better understanding of their relationships in marine sediments.

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