

Incorporation of fluoride and boron into surface sediments along the Egyptian Mediterranean coast

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Abstract

Egyptian Mediterranean Sea coast is subjected to different drainage waters following from distributed outlets including, Tapia pumping station, El-Umum Drain, etc. These drainage waters contain industrial, agricultural, sewage and domestic wastes. The study was directed to estimate the incorporation of fluoride and boron in the surface sediments along the Egyptian Mediterranean Sea coast, where they are byproducts of some industrial and fertilizers products. Surface sediments showed relatively similar fluoride and boron average contents of 1.38 ± 0.46 - 1.99 ± 0.47 and 0.84 ± 0.30 - 0.74 ± 0.26 mg/g along eastern and western sides of the Egyptian shoreline, respectively. Also, phosphorus, sulfate, chloride parameters were determined to represent the land sources composition. The sediments were characterized by grain size analysis, calcium, magnesium, total carbonate, total silicate and aluminum contents. The average contents of Ca, Mg, Al, TCO_3 and TSiO_4 along the eastern and the western sides of the studied shore line were of 300.75 ± 147.68 and 301.80 ± 130.78 , 74.90 ± 35.80 and 97.49 ± 53.21 , 8.04 ± 4.93 and 2.37 ± 1.83 , 91.7 ± 67.52 and 223.7 ± 15.59 , 158.3 ± 67.52 and 26.3 ± 15.59 mg/g, respectively. Correlation matrix and multiple regression analyses were applied to estimate the relations among all the studied parameters. The statistical analyses reflect the combination of fluoride and boron in presence of magnesium sediments' component. In contrast, fluoride seems to be freely loosed from the clay sediments. Also, there is an adsorption competition between chloride and fluoride in all surface sediments. The human health risk assessment for both fluoride and boron in surface sediment was evaluated. The dermal and ingestion magnitude of the sediments didn't exceed 1 for both child and adult. The Egyptian Mediterranean Sea coast doesn't pose a health risk in relation to human activities.

Keywords: Fluoride, Boron, Surface sediments, Statistical analysis, Risk assessment, Mediterranean coast, Egypt.

1. Introduction

Fluoride and boron compounds are naturally occurring and rarely exist in the elemental forms (WHO, 1984 and 2002; Moore, 1991; ATSDR, 2003). Fluoride is the 13th abundant element in the earth's crust of about 0.09% (WHO, 1984 and 2002). Fluoride is released into the environment naturally through the weathering of minerals, in emissions from volcanoes and in marine aerosols (ATSDR, 2003; Symonds *et al.*, 1988). Also, it is released via exhaust fumes, process waters and waste from various industrial processes, including steel manufacture, primary aluminum, copper and nickel production, phosphate fertilizer production and use, glass, brick and ceramic manufacturing, and glue and adhesive production (WHO, 2002). Additionally, the decaying plants and marine organism material can incorporate it in the sediment (WHO, 2002; Camargo, 2003; Dobbs, 1974, Ares *et al.*, 1983; Rajagopal and Tabin, 1991; Camargo, 1996; Sarma and Rao, 1997; Datta *et al.*, 2000; Cape *et al.*, 2003 and El-Said, 2010). Fluoride can be considered as a serious pollutant since its concentration in many aquatic

ecosystems is significantly increasing as a consequence of man's activities (Camargo, 1996; Roy *et al.*, 2000; Draz *et al.*, 2009). To the best of our knowledge, there are few data available on the fluoride concentrations in the Egyptian aquatic environment (El-Said, 2005; El-Said and Sallam, 2008; El-Sarraf *et al.*, 2001 and 2003; Masoud *et al.*, 2005, 2006 and 2008; El-Sikaily and El-Said, 2010; El-Said and Draz, 2010). Fluoride has its adverse effect on human being (Mohapatra *et al.*, 2009) and its long term exposure leads to skeletal fluorosis, lesions of the endocrine glands, thyroid and liver ((Mohapatra *et al.*, 2009; Tor *et al.*, 2009). Also, it may interfere with the functioning of the brain, pineal gland, kidney, and reproductive system (ATSDR, 2003). Earth's crust contains about <10 ppm boron, but boron-rich areas are of concentrations as high as 100 ppm (Woods, 1994; Culver *et al.*, 2001; EPA, 2008). Boron is classified as moderate to high toxic element in the aquatic environment. Its presence in marine sediments is accompanied with natural and/or anthropogenic sources. The elemental boron is naturally released through weathering, volcanism, and other geothermal processes (Moore, 1991). It includes the drainage from

coal mines and mining industry and the fly ash. It is a minor constituent in fertilizers and pesticides as well as detergents (Voutsas *et al.*, 2009). Human activities such as: agriculture, waste and wood burning, power generation using coal and oil, glass product manufacture, use of borates/perborates in the home and industry, borate (mining processing, leaching of treated wood, and sewage/sludge disposal) can release boron to the environment (EPA, 2008; Voutsas *et al.*, 2009). Its short term exposure may cause irritant effects on the upper respiratory tract, nasopharynx, and eyes as well as it can cause irritability, seizures and gastrointestinal disturbances. Also, it causes the inflammation, congestion, oedema, exfoliative dermatitis, exfoliation of the mucosa, and findings of cloudy swelling and granular degeneration of renal tubular cells (Nielsen and Penland, 1999 and EGVM, 2003).

The aim of this work points to the determination of fluoride and boron concentrations in surface sediments and to assess the quality of these sediments using the human health risk assessment calculations. Recalling that, these areas are subjected to different sources of land-runoff.

2. Materials and methods

2.1. Sampling

Twenty eight surface sediment samples were collected from the Egyptian Mediterranean coast during summer, 2008 (Figure 1 and Table 1). The sampling stations include areas near the industrial and domestic effluent discharge points, agricultural areas and places of recreational activities. The studied area can be divided to eastern and western sides according to the sediment type, human activities, and type of drainage waters (Table 1). Eastern side is subjected to drainage waters contaminated with petroleum, domestic sewage and fertilizers, pesticides, agricultural and hazardous industrial wastes (El-Nemr, 2008). Also, this side is vital for fishing and marine activities. The western side is affected by land disposal, domestic sewage and petroleum wastes from the human activities along the recreational places containing recreation beaches. Sediment sampling location was detected using GPS localization. At each station, three replicates of sediment samples were collected at the surface layer (0-5cm depth) using a stainless steel Peterson grab sampler (20 x 13 cm). The three replicate samples were composed and placed in self-sealed acid pre-cleaned plastic bags. All samples were immediately stored in an ice-cooled box and transferred to the laboratory. In the laboratory, the samples were air dried, and then the quartered samples were divided into two portions for the different analyses. The first portion was used for grain size analysis and chloride determination. While, the second one was finely powdered in an agate mortar and preserved in clean PVC bottles until used in digestion for chemical analysis.

2.2. Grain size analysis

The first portion was used for grain size analysis using dry sieving for sand and by pipette technique for silt and clay fractions (Krumbein and Pettijohn, 1938), and then the data were treated following Folk (1980).

2.3. Digestion of sediment samples

2.3.1. Digestion for Ca, Mg, Al, P, SO₄ and B

For Ca, Mg, Al, P, SO₄ and B analysis, the second finely powdered portion of sediment samples were digested by adding a mixture of HNO₃, HClO₄ and HF acids (3: 2: 1) onto 0.2 g of each powdered sample in a closed Teflon vessels at 70°C. The residue was dissolved in a known volume of deionized water and preserved in acid clean PVC bottles for analysis. Triplicate digestion was carried out for each sample and blank determinations were done using the same procedure.

2.3.2. Digestion of sediment samples for fluoride

The digestion process was made by mixing 0.5 g finely powdered (second portion) of each sediment sample with 3.5 g anhydrous sodium carbonate in a platinum crucible. The mixture was fused in an electric muffle furnace at a temperature of about 900 °C for twenty minutes, and then allowed to cool. 4.1 ml of concentrated HNO₃ acid was added, and then stirred to release most of CO₂. The solution was diluted to 50 ml. These samples were preserved in clean well stoppered polyethylene bottles until it was used for the determination of fluoride content in sediment samples (Jeffery, 1975).

2.4. Chemical analysis

2.4.1. Total carbonate and total silicate concentrations

Total carbonate (TCO₃) was estimated as described by Molnia (1974). About 0.5 g of dry finely powdered sediment (second portion) was weighed in a clean dry beaker to which 25 ml 3 N hydrochloric acid was added and heated to 50-60°C, left to react, after complete reaction, filtered through glass filter paper, washed several times with distilled water, then dried in an oven at 40 °C. Finally, the filter paper was reweighed until it reached a constant weight. The difference in weight is the weight of carbonate and residue is the non-carbonate fraction (total silicate).

2.4.2. Ca, Mg and Al concentrations

These were determined in the digested samples (mg/g dry weight) using Perkin Elmer 2830 flame Atomic Absorption Spectrophotometer.

Table 1: Characteristics of the surface sediments of the Egyptian Mediterranean Sea coast.

Location number	Longitude (E)	Latitude (N)	Grain size	Total carbonate (mg/g)	Total silicate (mg/g)	Calcium (mg/g)*	Magnesium (mg/g)*	Aluminium (mg/g)
Eastern side								
1	33.836	31.256	Silty Clay	47.30	202.7	200.40	60.78	12.38
2	32.5	31.302	Clayey Silt	54.00	196.0	200.40	60.78	12.08
3	31.663	31.602	Sand	98.00	152.0	400.80	60.77	0.30
4	31.666	31.64	Sandy Silt	57.90	192.1	200.40	121.55	11.93
5	31.671	31.715	Silt	38.80	211.2	196.47	59.58	11.42
6	31.332	31.653	Clayey Silt	87.80	162.2	100.20	121.55	11.64
7	31.333	31.727	Silt	44.40	205.6	192.69	58.44	11.34
8	31.091	31.72	Silty Sand	44.90	205.1	300.60	121.55	9.86
9	30.845	31.617	Silty Sand	31.30	218.7	200.40	10.34	10.75
	30.832	31.73	Sandy Clayey Silt	88.00	162.0	200.40	121.55	9.04
10								
11	30.501	31.55	Silty Clay	58.20	191.8	283.58	114.67	0.52
12	30.01	31.438	Silty Sand	76.00	174.0	589.41	59.58	0.59
13	29.914	31.263	Sand	231.00	19.0	491.18	59.58	3.63
14	29.91	31.272	Sand	216.50	33.5	481.73	58.44	12.60
15	29.937	31.344	Silty Sand	201.20	48.8	472.64	34.40	2.52
			Range	31.3 - 231.0	19.0 - 218.7	100.20 - 589.41	10.34 - 121.55	0.30 - 12.6
			Average	91.69	158.3	300.75	74.90	8.04
			S.D.	67.52	67.52	147.68	35.80	4.93
Western side								
16	29.677	31.117	Sand	232.40	17.6	100.20	60.78	2.15
17	29.504	31.072	Sand	234.90	15.1	196.47	178.75	0.15
18	29.503	31.105	Silty Sand	204.50	45.5	385.38	175.31	4.08
19	29.02	30.956	Sand	237.30	12.7	200.40	121.55	3.56
20	29.013	30.989	sand	227.70	22.3	196.47	83.42	6.52
21	28.5	31.086	Sand	231.40	18.6	400.80	182.33	0.22
22	28.507	31.136	Sand	226.10	23.9	196.47	35.75	1.19
23	28.0001	31.275	Sand	229.50	20.5	378.11	57.33	1.85
24	27.45	31.234	Silty Sand	186.10	63.9	501.00	36.46	3.71
		31						
25	27	.456333	Sand	232.30	17.7	192.69	93.50	1.56
		31						
26	26 30.5	43.12	Silty Sand	202.80	47.2	501.00	66.91	0.52
	25.99166	31						
27	6	.73533	Silty Sand	230.20	19.8	385.38	58.44	1.85
28	25.25	31.583	Sand	232.60	17.4	289.04	116.88	3.48
			Range	186.1 - 237.3	12.7 - 63.9	100.20 - 501.00	35.75 - 182.33	0.15 - 6.52
			Average	223.68	26.3	301.80	97.49	2.37
			S.D.	15.59	15.59	130.78	53.21	1.83
* unpublished data								

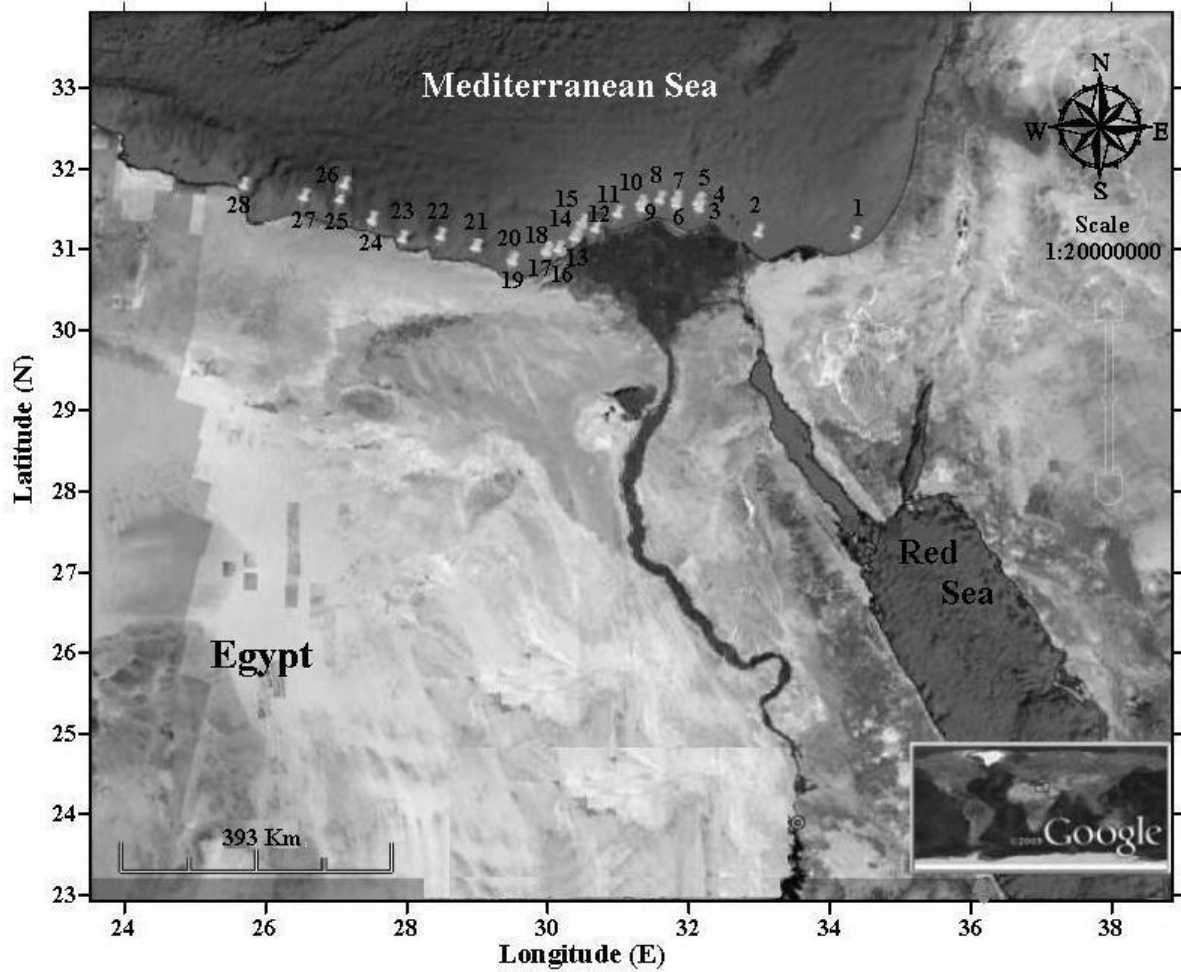


Figure 1. The surface sediment sampling location along the Egyptian Mediterranean coast.

2.4.3. P concentration

The phosphorus concentration ($\mu\text{g/g}$ dry weight) in the digested samples was determined based on the reaction with an acidified molybdate reagent to yield phosphomolybdate complex, which then reduced to a coloured blue compound (Strickland and Parson, 1965).

2.4.4. Cl content

It was determined in the first portion (mg/g dry weight) following Mohr's method (Manual of Methods of Foods, 2005; APHA-AWWA-WPCF, 1999).

2.4.5. SO_4 concentration

It was determined in the digested sediment samples by the turbidimetric method (APHA-AWWA-WPCF, 1999).

2.4.6. F concentration

Fluoride ion concentration in the digested samples (mg/g) was determined following the procedure of zirconium alizarin red S (Courtenary and Rex, 1951; Masoud *et al.*, 2004).

2.4.6. B concentration

B concentration was determined using the curcumin colorimetric technique (APHA-AWWA-WPCF, 1999).

2.5. Quality assurance

The accuracy and precision of the results were checked by analyzing standard reference material, International Atomic Energy Agency, Analytical Quality Control Services (IAEA-433; marine sediments). Analysis of the reference material showed a good accuracy for the elements with recovery ranges between 95.85% and 96.69%, where all used reagents were of analytical grade.

2.6. Statistical analyses

Correlation matrices and multiple regression analyses were performed using Statistica computer software version 5. These analyses were applied with significance level of 0.05 to determine the relation among all the determined parameters in the different sediment samples.

3. Results and Discussions

3.1. Sediment characteristics

The grain size analysis shows that the eastern side of the Egyptian Mediterranean coast is mainly

composed of silt mixed with clay or/and sand (Table 1). Meanwhile, the western side is dominantly composed of sand mixed with silt in some locations (18, 24 and 26-27). Total carbonate, calcium and magnesium concentrations reflect the dominant calcite and magnesium calcite composition in locations 14-28 along the eastern and western sides (Table 1). The eastern and western sides show average TCO_3 , Ca and Mg of 91.69 ± 67.52 , 300.75 ± 147.68 and 74.90 ± 35.80 mg/g and 223.68 ± 15.59 , 301.80 ± 130.78 and 97.49 ± 53.21 mg/g, respectively. On the other hand, the high total silicate ($218.7 - 152.0$ mg/g) recorded in the eastern side (locations 1-12) refers to the dominate presence of clay and/or sand components. The high aluminum concentration in some sediment locations (1-2, 4-10) reflects the presence of the clay component. However, clay minerals are mainly composed of aluminum, silicon and oxygen elements (Mackenzie, 1999). Whereas, the high aluminum contents in locations 14 (12.60 mg/g), in eastern side and 16, 18-20, 23 and 27, along the western side may accompany with the existence of calcareous organisms such as algae, molluscs, echinoids, Protozoa and carbonate peteoids with amorphous silica (Degens, 1976; Moussa, 1999; Frihy *et al.*, 1994). The data are related to previous results dealing with the geochemical composition of the Egyptian Mediterranean coast (Moussa, 1999; Frihy *et al.*, 1994; Rifaat, 2005; El-Nemr, 2008).

3.2. The concentration of P, Cl, SO_4 , F and B

These are discharged annually into seawater through land sources including, Nile River and discharged waters from the outlets and atmospheric precipitation on the surface of seawater (Okumura *et al.*, 1983).

3.2.1. P concentration

It varies along all the locations with averages 6.67 ± 7.54 and 17.16 ± 23.16 $\mu\text{g/g}$ in the eastern and western sides, respectively (Table 2). The maximum phosphorus content (31.53 $\mu\text{g/g}$) in location 11 along the eastern side reflects to the huge amount of discharged water containing agricultural, industrial and sewage as well as domestic wastes (Rifaat, 2005; Tarek, 2005; Said and Fattah, 2006; Khalil *et al.*, 2007; El-Nemr, 2008). Meanwhile, the high concentrations recorded in locations 18, 19 and 22 (32.14, 55.71 and 43.69 $\mu\text{g/g}$) relate to the discharge waters containing the wastes of SUMED oil terminal, beside the industrial wastes from; Alexandria company for Iron and Steel, Misir Company for Chemicals, Mobil Oil Company, Al-Amriyah Oil Company, and the breaker water (El Wakeel *et al.*, 2006). The highest recorded phosphorus content (64.28 $\mu\text{g/g}$) in location 28 may relate to the land sources. The lower average phosphorus concentrations in the eastern side sediments

may reflect the activity of Fe(III)-reducing bacteria that catalyze the reduction of $\text{Fe}(\text{OH})_3(\text{s})$, binding with inorganic phosphorus, to Fe(II) and the release of phosphorus into seawater (Lake *et al.*, 2007). Microbes may also cause P release via cleavage of polyphosphate molecules. During P rich, oxic conditions, bacteria can store excess P as polyphosphate. During times of anoxic stress, it is proposed that bacteria hydrolyze polyphosphates providing a source of P flux from the sediments (Lake *et al.*, 2007).

3.2.2. Cl concentration

Chloride concentration varies along the studied area and gives average concentrations of 6.71 ± 5.63 and 10.97 ± 5.60 mg/g for eastern and western sides, respectively (Table 2). This variability may accompany with different factors, including; salinity, sediment type, temperature, pH, dilution by land sources waters

and the exchangeable of ions at sediment seawater interface (Ferrell *et al.*, 1971 and Pucci *et al.*, 1997).

3.2.3. SO_4 concentration

It shows relative similar average concentrations in the sediment samples of eastern (3.84 ± 1.92 mg/g) and western sides (3.00 ± 1.51 mg/g) (Table 2). This similarity may refer to the activity of the sulphate-reducing microbes that transfer sulphate to sulphur and hydrogen sulphide and precipitate CaCO_3 at the same time (McGowan and Martin, 2007). Youssef and El-Said (2010) detected complete sulphate depletion in some locations in Abu-Qir Bay due to the microbial activity that turn the sediments to the blackish color and release hydrogen sulphide gas in anoxic conditions as well as organic matter decomposition.

Table 2. The concentration of some components in the surface sediments of the Egyptian Mediterranean Sea coast.

Location number	Phosphorus ($\mu\text{g/g}$)	Chloride (mg/g)	Sulphate(mg/g)	Fluoride (mg/g)	Boron (mg/g)	
Eastern side	1	11.14	2.43	1.74	1.69	0.62
	2	3.44	4.58	4.63	1.24	0.71
	3	2.99	11.12	2.31	1.06	0.84
	4	2.94	4.87	3.76	0.90	0.82
	5	3.55	3.38	4.05	0.62	0.75
	6	2.90	5.99	2.31	1.80	0.75
	7	10.71	2.59	6.37	1.32	0.75
	8	3.55	7.08	4.63	1.10	0.92
	9	3.25	3.54	6.66	1.53	0.75
	10	3.00	5.56	3.47	0.60	1.78
	11	31.53	19.46	1.16	2.03	1.10
	12	4.00	2.88	6.08	1.69	0.73
	13	3.23	19.46	1.16	1.90	0.44
	14	3.29	4.87	6.37	1.40	0.74
	15	10.51	2.78	2.89	1.83	0.87
Range	2.90 - 31.53	2.43 - 19.46	1.16 - 6.66	0.60 - 2.03	0.44 - 1.78	
Average	6.67	6.71	3.84	1.38	0.84	
S.D.	7.54	5.63	1.92	0.46	0.30	
Western side	16	3.90	8.65	2.60	1.53	0.63
	17	4.01	19.46	1.74	2.50	1.21
	18	32.14	3.24	2.31	2.64	0.74
	19	55.71	7.78	2.03	2.42	0.56
	20	2.00	7.78	6.94	2.61	0.61
	21	2.02	19.46	1.45	1.59	1.04
	22	43.69	9.73	2.03	2.02	0.65
	23	2.35	9.73	4.05	1.34	0.50
	24	2.89	6.49	2.03	1.81	0.85
	25	3.02	19.46	3.47	1.53	0.35
	26	3.54	5.56	3.76	2.46	0.79
	27	3.56	9.73	4.34	1.64	0.59
	28	64.28	15.57	2.31	1.78	1.14
Range	2.00 - 64.28	3.24 - 19.46	1.45 - 6.94	1.34 - 2.64	0.35 - 1.21	
Average	17.16	10.97	3.00	1.99	0.74	
S.D.	23.16	5.60	1.51	0.47	0.26	

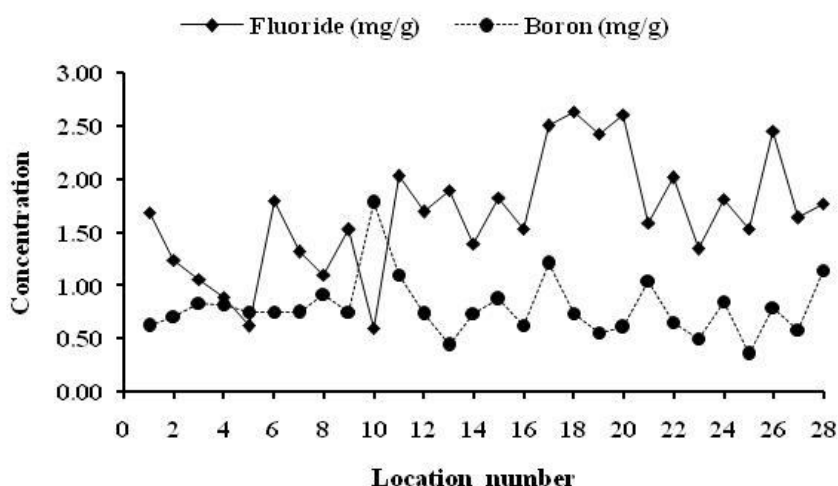


Figure 2. Distribution of fluoride and boron concentrations (mg/g) in the surface sediments of the Egyptian Mediterranean Sea coast.

3.2.4. F concentration

As sulphate, fluoride gives relative average concentrations in the sediments of both eastern (1.38 ± 0.46 mg/g) and western sides (1.99 ± 0.47 mg/g) of the coastal line with concentration ranges of 0.60 - 2.03 and 1.34 - 2.64 mg/g, respectively (Table 2 and Figure 2). The present study of the Egyptian Mediterranean coast shows lower contents of fluoride than those of the previous studies. However, the fluoride concentrations of 6.97 ± 1.07 mg/g and 2.1-3.7 mg/g were detected in Egyptian Mediterranean Sea coast and Tanzania sediments, respectively (El-Said, 2010; Kilham and Hecky, 1973). The present results are relatively similar to the oceanic sediments content of 0.45 - 1.10 mg/g (Carpenter, 1969). Also, they are approximately similar to the fluoride contents of 1.33 mg/g in Arabian Sea (Schenau *et al.*, 2000). The concentration variability of fluoride along the surface sediments deals with several factors including, sediment type (Klein, 2006), pH, temperature value (Reimers *et al.*, 1996), ion exchange between surface sediments and water interface, precipitation as calcium fluoride, fluorapatite and francolite minerals (Schenau *et al.*, 2000), salting out of NaCl (Abe *et al.*, 2004) and adsorption on surface sediments (Reddy *et al.*, 2010).

3.2.5. B concentration

Similar relative average concentrations are recorded for boron along the eastern (0.84 ± 0.30 mg/g) and (0.74 ± 0.26 mg/g) western sides (Table 2 and Figure 2). Generally, boron concentration in the present study shows higher content than that reported for marine sediments (0.5 mg/g (Eisler, 1990). This probably

attributes to the discharge, of the Nile River and land sources waters that falling into the coastal water. These waters contain industrial, agricultural, domestic and sewage wastes (Khalil *et al.*, 2007; El Wakeel *et al.*, 2006; El-Nemr, 2008). Also, the present data revealed to the elevation of boron levels along the coastal sediments. However, the detected boron contents in sediments of El-Max and Abu Qir Bays during 2007 were with lower averages of 0.18 ± 0.48 and 0.19 ± 0.51 mg/g, respectively (Faragallah *et al.*, 2010). Since, B can be anthropogenic and has environmental impact (Pennisi *et al.*, 2006), as it is used for many products, such as glass, ceramics, leather, fertilizers, cosmetics, detergents, etc.

3.3. Statistical analyses

Correlation matrices for eastern and western sides of the Egyptian Mediterranean Sea show high significant correlation coefficients of different signs (Ca & TCO_3 , Ca & TSiO_4 , Ca & Al and TCO_3 & TSiO_4) (Table 3). The high r values confirm the different mineral composition of sediments along the two studied coastal sides. However, the eastern side sediments are mainly composed of silt and clay minerals. While, the western side sediments are of carbonate type (calcite and Mg-calcite). Meanwhile, the moderate positive correlation coefficient ($r = 0.5818$, $p = 0.037$) between chloride and total carbonate in the western side refers to the adsorption of chloride by the carbonate sediment type (Okumura *et al.*, 1983 and Desbarats, 2009). The moderate correlations among chloride, aluminum, sulphate, and silicate ($r = -0.554$, $p = 0.032$, $r = -0.630$, $p = 0.012$ and $r = -0.582$, $p = 0.037$, respectively) may relate to unfavorable adsorption of both chloride and sulphate onto the clay

mineral sediments (Hamdi and Srasra, 2007; Meenakshi *et al.*, 2008).

The multiple regression analyses for the eastern and western side sediment components estimate the possible existence of fluoapatite, calcium carbonate and sparingly soluble fluoride magnesium complex (WHO, 2002). Boron may coprecipitates with magnesium compounds in the eastern and western sides' sediments (Deyhle *et al.*, 2001). Also, boron is entirely attributed to the carbonate fraction and can adsorb into clay minerals (Sohlenius *et al.*, 1996). It seems that chloride content compete the adsorption of sulphate in the clay minerals in the eastern side; meanwhile, it prefers to adsorb rather than fluoride onto the carbonate minerals of the eastern side. Also, phosphate adsorption is preferable than sulphate in the carbonate sediments of western side (Islam and Patel, 2007). However, the estimated phosphorus removal by carbonate sedimentation in seawater was about 28% (Okumura *et al.*, 1983).

3.4. Human Hazard risk assessment for fluoride and boron

Human Hazard risk assessment for fluoride and boron are estimated using the calculations made by Albering *et al.* (1999) (equations 1-4). However, the ingestion of contaminated sediment, dermal contact with contaminated sediment and lifetime daily exposure of fluoride and boron are estimated for both child and adult in the studied locations (Tables 5-7). Ingestion of contaminated sediment (ICS) (mg kg⁻¹day⁻¹) =

$$\left(\frac{CS \times IRS \times EF \times AF}{BW} \right) \quad (1)$$

Dermal contact with contaminated sediment (DCCS) (mg kg⁻¹day⁻¹) =

$$\left(\frac{CS \times SAS \times AD \times ASS \times Mf \times EDS \times EF \times AF}{BW} \right) \quad (2)$$

Calculated lifetime daily exposure (CLTDE) (mg kg⁻¹ day⁻¹): =

$$[(6 \times TEL_{child}) \div 70] + [(64 \times TEL_{adult}) \div 7] \quad (3)$$

Hazard index= CLTDE ÷ tolerable daily intake (TDI) (4)

Where, CS = concentration of heavy metals contaminant in sediment (mg kg⁻¹ dw), IRS = Ingestion rate of sediment (0.001 and 0.00035 kg dw / day for child and adult respectively), EF = exposure frequency (30 for both child and adult), AF = absorption factor (1 for both child and adult), SAS = Dermal surface area for sediment exposure (0.17 and 0.28 m² for child and adult respectively), AD = Dermal adherence rate for sediment (0.51 and 3.75 mg cm⁻² for child and adult respectively), ASS = Dermal absorption rate (0.01 and 0.005 liter/hr for child and adult respectively), Mf = Matrix factor (0.15 for both child and adult), EDS= Exposure duration to sediment (8 hr day⁻¹ for both child and adult), BW = Body weight (15 and 70 kg for child and adult respectively) and TEL = total exposure levels. The hazard index refers to the ratio between calculated daily exposure and tolerable daily intake [TDI] (Equation 4). Where, TDI refers to reference dose of a substance that can be taken in daily without identifiable risk at lifetime exposure. The documented TDI for both fluoride and boron are of 0.143 and 0.137 mg kg⁻¹ day⁻¹ (FSANZs, 2008; EGVM, 2003). Hazard index is evaluated by comparing the calculated lifetime daily exposure (CLTDE, Table 7) with the tolerable daily intake (TDI) values. These comparisons indicate the safety of the ingestion and the dermal contact with the Egyptian Mediterranean coastal sediments; however, the hazard index values are still below 1.

Table 3. Significant correlation coefficients (r) and their probabilities (p) for the correlation matrices between the different sediment components in the eastern and the western sides' sediments.

Two components	Eastern side		Western side	
	r	p	r	p
Ca & TCO ₃	0.674	0.006	-0.717	0.006
Ca & TSiO ₄	-0.674	0.006	0.717	0.006
Ca & Al	-0.667	0.007		
TCO ₃ & TSiO ₄	-1.000	0.000	-1.000	0.000
TCO ₃ & Cl			0.582	0.037
Cl & Al	-0.554	0.032		
Cl & SO ₄	-0.630	0.012		
Cl & SiO ₄			-0.582	0.037

Table 4: Multiple regression equations for eastern and western sides' sediments.

Dependent component	Eastern side Equation	R ²	Western side Equation	R ²
P	$P = -27.47 + 0.81 F + 0.46 B + 0.33 \text{TSiO}_4$	0.71756985	$P = -126.44 - 0.78 \text{SO}_4 + 0.55 \text{Al} + 0.54 \text{TCO}_3 - 0.36 \text{Cl}$	0.75325004
F	$F = 1.53 + 0.61 P - 0.48 B + 0.35 \text{TCO}_3$	0.79627583	$F = 2.03 - 0.64 \text{Cl} + 0.64 \text{Mg}$	0.68397036
B	$B = 1.04 + 0.32 \text{Mg} - 0.56 F + 0.39 P$	0.68214824	$B = 0.72 + 0.41 \text{Mg} - 0.33 \text{SO}_4$	0.61501653
Cl	$\text{Cl} = 15.63 - 0.49 \text{SO}_4 - 0.37 \text{Al}$	0.71661545	$\text{Cl} = 17.30 - 0.42 \text{SiO}_4 + 0.32 B - 0.46 F + 0.32 \text{Mg}$	0.8165322
Al	$\text{Al} = 19.18 - 1.05 \text{Ca} + 0.55 \text{SO}_4 - 0.52 \text{TSiO}_4$	0.86524518	$\text{Al} = 0.76 - 0.30 \text{Cl} + 0.57 \text{SO}_4 + 0.43 P$	0.73561058
SO ₄	$\text{SO}_4 = 5.28 - 0.63 \text{Cl}$	0.63005543	$\text{SO}_4 = -21.52 + 0.64 \text{Al} - 0.61 P + 0.95 \text{TCO}_3 - 0.59 \text{Mg} + 0.50 F + 0.56 \text{Ca}$	0.93100252
Ca	$\text{Ca} = 165.57 + 0.67 \text{TCO}_3$	0.67405707	$\text{Ca} = 176.31 + 0.76 \text{TSiO}_4 - 0.25 \text{Al}$	0.75960118
Mg	$\text{Mg} = 38.89 + 0.50 B - 0.44 \text{SO}_4 + 0.30 \text{Al}$	0.66062789	$\text{Mg} = -89.02 + 0.28 B - \text{TSiO}_4 + 0.50 F + 0.43 \text{Cl}$	0.73835251

Table 5. The ingestion contaminated sediment values (ICS) of fluoride and boron for child and adult in eastern and western sides' sediments.

Location number	ICS(Fluoride) _(Child)	ICS(Fluoride) _(Adult)	ICS(Boron) _(Child)	ICS(Boron) _(Adult)
1	3.37339E-03	2.53004E-04	1.23571E-03	9.26786E-05
2	2.48139E-03	1.86104E-04	1.42500E-03	1.06875E-04
3	2.12224E-03	1.59168E-04	1.67143E-03	1.25357E-04
4	1.79211E-03	1.34409E-04	1.64286E-03	1.23214E-04
5	1.23656E-03	9.27419E-05	1.50714E-03	1.13036E-04
6	3.60215E-03	2.70161E-04	1.50714E-03	1.13036E-04
7	2.63648E-03	1.97736E-04	1.49286E-03	1.11964E-04
8	2.20430E-03	1.65323E-04	1.83929E-03	1.37946E-04
9	3.05714E-03	2.29285E-04	1.50000E-03	1.12500E-04
10	1.20008E-03	9.00058E-05	3.55714E-03	2.66786E-04
11	4.05861E-03	3.04396E-04	2.20714E-03	1.65536E-04
12	3.38710E-03	2.54032E-04	1.46429E-03	1.09821E-04
13	3.79507E-03	2.84630E-04	8.78571E-04	6.58929E-05
14	2.79156E-03	2.09367E-04	1.47143E-03	1.10357E-04
15	3.65591E-03	2.74194E-04	1.73929E-03	1.30446E-04
16	3.06452E-03	2.29839E-04	1.25357E-03	9.40179E-05
17	5.00738E-03	3.75553E-04	2.41429E-03	1.81071E-04
18	5.27093E-03	3.95319E-04	1.48214E-03	1.11161E-04
19	4.84925E-03	3.63694E-04	1.11607E-03	8.37054E-05
20	5.21822E-03	3.91366E-04	1.21429E-03	9.10714E-05
21	3.17204E-03	2.37903E-04	2.08929E-03	1.56696E-04
22	4.03226E-03	3.02419E-04	1.30357E-03	9.77679E-05
23	2.68817E-03	2.01613E-04	1.00357E-03	7.52679E-05
24	3.61869E-03	2.71402E-04	1.70000E-03	1.27500E-04
25	3.06452E-03	2.29839E-04	7.07143E-04	5.30357E-05
26	4.91108E-03	3.68331E-04	1.58214E-03	1.18661E-04
27	3.27957E-03	2.45968E-04	1.17500E-03	8.81250E-05
28	3.55042E-03	2.66281E-04	2.28571E-03	1.71429E-04
Minimum	1.20008E-03	9.00058E-05	7.07143E-04	5.30357E-05
Maximum	5.27093E-03	3.95319E-04	3.55714E-03	2.66786E-04
Average	3.32575E-03	2.49432E-04	1.58807E-03	1.19106E-04
S.D.	1.09995E-03	8.24965E-05	5.56356E-04	4.17267E-05

Table 6. Dermal contact with contaminated sediment values (DCCS) of fluoride and boron for child and adult in eastern and western sides' sediments.

Location number	DCCS(Fluoride) _(Child)	DCCS(Fluoride) _(Adult)	DCCS(Boron) _(child)	DCCS(Boron) _(Adult)
1	3.50968E-03	4.55408E-03	1.28564E-03	1.66821E-03
2	2.58164E-03	3.34988E-03	1.48257E-03	1.92375E-03
3	2.20798E-03	2.86503E-03	1.73895E-03	2.25643E-03
4	1.86452E-03	2.41935E-03	1.70923E-03	2.21786E-03
5	1.28652E-03	1.66935E-03	1.56803E-03	2.03464E-03
6	3.74768E-03	4.86290E-03	1.56803E-03	2.03464E-03
7	2.74299E-03	3.55924E-03	1.55317E-03	2.01536E-03
8	2.29335E-03	2.97581E-03	1.91359E-03	2.48304E-03
9	3.18065E-03	4.12713E-03	1.56060E-03	2.02500E-03
10	1.24856E-03	1.62010E-03	3.70085E-03	4.80214E-03
11	4.22258E-03	5.47913E-03	2.29631E-03	2.97964E-03
12	3.52394E-03	4.57258E-03	1.52344E-03	1.97679E-03
13	3.94839E-03	5.12334E-03	9.14066E-04	1.18607E-03
14	2.90434E-03	3.76861E-03	1.53087E-03	1.98643E-03
15	3.80361E-03	4.93548E-03	1.80955E-03	2.34804E-03
16	3.18832E-03	4.13710E-03	1.30422E-03	1.69232E-03
17	5.20968E-03	6.75996E-03	2.51182E-03	3.25929E-03
18	5.48387E-03	7.11575E-03	1.54202E-03	2.00089E-03
19	5.04516E-03	6.54649E-03	1.16116E-03	1.50670E-03
20	5.42903E-03	7.04459E-03	1.26334E-03	1.63929E-03
21	3.30019E-03	4.28226E-03	2.17369E-03	2.82054E-03
22	4.19516E-03	5.44355E-03	1.35624E-03	1.75982E-03
23	2.79677E-03	3.62903E-03	1.04412E-03	1.35482E-03
24	3.76489E-03	4.88524E-03	1.76868E-03	2.29500E-03
25	3.18832E-03	4.13710E-03	7.35711E-04	9.54643E-04
26	5.10949E-03	6.62996E-03	1.64606E-03	2.13589E-03
27	3.41206E-03	4.42742E-03	1.22247E-03	1.58625E-03
28	3.69385E-03	4.79306E-03	2.37806E-03	3.08571E-03
Minimum	1.24856E-03	1.62010E-03	7.35711E-04	9.54643E-04
Maximum	5.48387E-03	7.11575E-03	3.70085E-03	4.80214E-03
Average	3.46012E-03	4.48977E-03	1.65223E-03	2.14390E-03
S.D.	1.14439E-03	1.48494E-03	5.78833E-04	7.51081E-04

Table 7. Calculated Lifetime daily exposure (CLTDE) for fluoride and boron in eastern and western sides' sediments.

Location number	CLTDE(Fluoride)	CLTDE(Boron)
1	4.45405E-02	1.63157E-02
2	3.27629E-02	1.88149E-02
3	2.80209E-02	2.20686E-02
4	2.36621E-02	2.16914E-02
5	1.63269E-02	1.98995E-02
6	4.75609E-02	1.98995E-02
7	3.48106E-02	1.97109E-02
8	2.91044E-02	2.42849E-02
9	4.03648E-02	1.98052E-02
10	1.58452E-02	4.69666E-02
11	5.35877E-02	2.91419E-02
12	4.47214E-02	1.93336E-02
13	5.01080E-02	1.16002E-02
14	3.68583E-02	1.94280E-02
15	4.82707E-02	2.29646E-02
16	4.04622E-02	1.65515E-02
17	6.61147E-02	3.18769E-02
18	6.95945E-02	1.95694E-02
19	6.40269E-02	1.47360E-02
20	6.88985E-02	1.60328E-02
21	4.18820E-02	2.75858E-02
22	5.32398E-02	1.72117E-02
23	3.54932E-02	1.32506E-02
24	4.77793E-02	2.24459E-02
25	4.04622E-02	9.33673E-03
26	6.48433E-02	2.08898E-02
27	4.33017E-02	1.55141E-02
28	4.68778E-02	3.01793E-02
Minimum	1.58452E-02	9.33673E-03
Maximum	6.95945E-02	4.69666E-02
Average	4.39115E-02	2.09681E-02
S.D.	1.47993E-02	7.42788E-03

4. Conclusion

The study points to the determination and the assessment of the human health risk of two toxic components, fluoride and boron in the surface sediments of the Egyptian Mediterranean Sea coast from twenty eight locations. Recalling that this area is subjected to different falling types of discharged waters that contain industrial, agricultural, domestic and sewage untreated wastes. Different sediment components (TCO_3 , TSiO_4 , Ca, Mg, Al, P, Cl, SO_4 , F and B) were determined. The sediment locations were divided into eastern and western sides according to the mineral composition of them. The results for TCO_3 , TSiO_4 , Ca, Mg and Al components in sediment samples confirm the mainly clay and silt composition for eastern side and dominate existence of carbonate minerals in the western side. The other determined components (Cl, SO_4 , F and B) were selected to estimate the land source's position and composition. The data obtained for both phosphorus and chloride concentrations reveal to the presence of different land sources, including, El-Tapia pumping station, El-Umm Drain and some outlets along the shoreline that fall huge discharged waters in the eastern side. Meanwhile, the other western side is subjected to oil pollution, industrial companies and places of recreational activities. The average concentrations for sulphate, fluoride and boron were relatively similar in the sediments of the eastern and western coastal sides. Fluoride in the sediments showed lower concentrations than that was previously recorded. This may accompanied with many factors including, sediment type, salinity, temperature, pH, ion exchange between the sediment and water interface and the adsorption capacity. In contrast, boron gave relatively higher concentrations in the sediments of both studied coastal sides than that recorded for marine sediment. This may refer to the anthropogenic activities and land sources composition. Correlation matrices and multiple regression analyses showed the possible formation of fluorapatites, CaCO_3 , sparingly soluble magnesium fluoride complex beside the presence of calcite, Mg-calcite, silt and clay minerals in the collected sediments. The assessment of the human health risk for both fluoride and boron components of child and adult gave values lesser than unit. So, there isn't any human health impact from the ingestion and dermal contact of these sediments in studied area along the human's lifetime. It is seriously recommended to treat the discharged waters before discarding into the coastal zone to overcome their adverse impacts on this marine environment in the future.

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إندماج الفلوريد والبورون في الرواسب السطحية على طول ساحل البحر الأبيض المتوسط المصري

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يتعرض ساحل البحر الأبيض المتوسط المصري لأنواع مختلفة من مياه الصرف الآتية من مخارج موزعة عليه مثل : محطة ضخ الطابية و مصرف العموم و غيرها و تحتوى هذه المياه على مخلفات صناعية و زراعية و صرف صحى و نفايات منزلية ، لذلك و جهت هذه الدراسة إلى تقدير إندماج كلا من الفلوريد و البورون في الرواسب السطحية على طول الساحل المصري المطل على البحر الأبيض المتوسط ، حيث أنهما ينتجان عرضياً من بعض المنتجات الصناعية و الأسمدة و لقد أظهرت الرواسب السطحية نسب متقاربة لمتوسط محتويات كلا من الفلوريد و البورون بقيم 0.46 ± 1.38 - 0.47 ± 1.99 و 0.30 ± 0.84 - 0.26 ± 0.74 مليجرام/جرام على طول الجانبى الشرقى و الغربى من خط الشاطئ المصرى على التوالي ، و لقد تم أيضاً تعيين كلا من عوامل الفوسفور و الكبريتات و الكلوريد لتمثيل تركيب المصادر الأرضية ، بينما تم التعرف على مواصفات الرسوبيات من خلال التحليل الحجمى للحبيبات و محتويات كلا من الكالسيوم و الماغنيسيوم و الكربونات الكلية و السليكات الكلية و الألومينيوم ، و تبين أن متوسط محتويات الكالسيوم و الماغنيسيوم و الألومينيوم و الكربونات الكلية و السليكات الكلية على طول الجانبى الشرقى و الغربى لخط الشاطئ المدروس كانت كما يلى: 147.68 ± 300.75 ، 130.78 ± 301.80 ، و 35.80 ± 74.90 و 53.21 ± 97.49 ، 4.93 ± 8.04 و 1.83 ± 2.37 ، 67.52 ± 91.7 و 15.59 ± 223.7 و 158.3 ± 67.52 و 15.59 ± 26.3 مليجرام/جرام على التوالي، و أوضح تطبيق مصفوفة الارتباط و التحليل المتعدد المضاعف مدى العلاقة المتواجدة بين كل العوامل المدروسة ، و لقد عكست التحاليل الإحصائية تجمع الفلوريد و البورون فى الرواسب المحتوية على مكون الماغنيسيوم و على النقيض من ذلك، تبين أن الفلوريد ينطلق بحرية من الرواسب الطينية و أيضاً ظهر التنافس الإدمصاصى بين الكلوريد و الفلوريد فى كل الرواسب السطحية ، و لقد تم تقييم خطر كلا من الفلوريد و البورون على صحة الإنسان و تبين أن مقدار التأثير الجلدى و الإبتلاع للرواسب للطفل و البالغ لم يتجاوز 1 و بذلك يتبين أن النشاط البشرى لا يشكل خطر على ساحل البحر الأبيض المتوسط المصري.