The Effect of Fluoride and Other Ions on Algae and Fish of Coastal Water of Mediterranean Sea, Egypt

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Abstract: Sea grass, marine algae and fish samples were collected from the Egyptian coast of Mediterranean Sea during September 2000 and March 2001. The contents of fluoride and some interfering ions (calcium, magnesium, sulphate, phosphorus and some heavy metals) ions and their concentration factors were determined in the dried samples. Fluoride contents in macrophytes, algae, muscle of fish samples were ranged between 29.79 and 34.30 mg g^{-1}, 19.17 and 53.70 mg g^{-1} and 1.875 and 3.379 μg g^{-1}, respectively. Calcium contents for sea grass, algae and fish samples were varied between 21.82 and 45.30, 45.63 and 325.37 and 18.04 and 93.00 mg g^{-1}, respectively. Magnesium contents were fluctuated between 3.62 and 28.96, 1.21 and 15.70 and 45.58 and 107.84 mg g^{-1}, respectively. Sulphate contents ranged between 69.78 and 140.00 and 17.22 and 117.22, 54.68 and 185.19 mg g^{-1}, respectively. Phosphorus contents were varied from 0.24 to 0.74, 0.198 to 1.854 and 3.205 to 5.477 mg g^{-1}, respectively. Fluoride analysis indicated that there is no risk for human consumption of the muscles of fish samples collected from the Egyptian coast of Mediterranean Sea. The data were exposed to some statistical analyses to study the effect of fluoride and the interfering ions on the behavior of sea grass, marine algae and fish species.

Key words: Effect of fluoride, interfering ions, sea grass, marine algae, environmental chemistry

INTRODUCTION

Fluoride is present in several tropical plants as mono-fluorinated carbon compounds. The toxic principle of *Dichapetalum cymosum* (a poisonous South African plant "*gifblaar*") is fluoroacetate, which has been isolated from two Australian plants, *Acacia georginae* and *Gastrolobium grandiflorum*. Long-chain fluoro carboxylic acids have also been identified in few other Dichapetalum species[1]. The highest fluoride concentration caused 25-30 % growth rate inhibition of a diatom, a dinoflagellate and a haptophyt, other diatoms and species from other classes of algae were virtually unaffected. It is hypothesized that the unexpected lack of toxicity from fluoride ion may be due to the formation of innocuous complexes with one or more ions of seawater. The ecological inference is drawn that fluoride pollution may be readily tolerated by some marine phytoplankton under nutrient-sufficient conditions[2].
Fluoride complexation attenuated aluminum toxicity to Juvenile Salmon (*Salmo salar*) and the accumulation of it in gill tissues. Total red and white blood cell dropped consistently as fluoride in the water was increased from 5 to 300 ppm in adult *Rana pipiens* showing its toxicity[3].
Ninety-six-hours LC$_{50}$s for fresh water fish range from 51 mg L^{-1} fluoride (rainbow trout, *Oncorhynchus mykiss*) to 460 mg L^{-1} (three spine stickleback, *Gasterosteus aculeatus*). All of acute toxicity tests on marine fish gave results greater than 100 mg L^{-1}. Inorganic fluoride toxicity to fresh water fish appears to be negatively correlated with water hardness (CaCO$_3$) and positively correlated with temperature. The symptoms of acute fluoride intoxication include lethargy, violent and erratic movement and death[4].
Behavioral experiments on adult Pacific Salmon (*Oncorhynchus* sp.) in Soft Water Rivers indicated the changes in water chemistry resulting from an increase in the fluoride concentration to 0.5 mg. These can adversely affect migration and migrating salmon and are extremely sensitive to changes in water chemistry of their river of origin[4].
While 1-2 mg F/day are recommended for caries prevention, the daily consumption of 20-80 mg fluoride in humans led to calcification of muscles and ligaments. After several years of intake, symptoms of osteosclerosis such as superaclification and thereby reduction of bone marrow followed, leading to decreased production of erythrocytes[5].
The aim of the present study is to study the distribution and the effect of fluoride on some bottom marine algae and fish samples collected from the Egyptian coast of Mediterranean Sea.

MATERIALS AND METHODS

Locations and collection of samples: Fix perpendicular stations to the Mediterranean shore belt were selected to represent different parts of Egyptian

coast, Fig. 1. They extend between Sidi Barrani in the west to Damietta in the east of the Egyptian coast for a distance of about 500 Km long and 3 Km from the shore line. Random bottom fauna samples were collected using trawl net of research vessel El Yarmook from Damietta, Abu Qir, El Alamein, Ras El Hikmah, Marsa Matruh and Sidi Barrani at depths of about, (24-91), (30-50), (37-41), (55-67) , (43-67) and (42-66) m, respectively. However, the algal and fish samples were selected for analysis. These stations are given as follows:

Damietta: It is in the eastern side of Nile Delta region. It receives large amounts of drainage water (agricultural, sewage and industrial effluents) coming from both Damietta and Lake El Manzalah.

Abu Qir: It is in front of Abu Qir bay that receives large amounts of three types of waters; Rosetta mouth of the river Nile, Lake Edku via Boughaz El Maadiya and Tapia pumping station. These waters enter the coastal area causing change in its chemical composition and contain high components of discharged water from industrial wastes (fertilizer industry, textile manufacturing, paper industry, chemical and soap, salt factories and food processing), fresh water, domestic, fertilizers and agricultural wastes.

El Alamein, Ras El Hikmah, Marsa Matruh and Sidi Barrani: These are located in the western side of Alexandria.

Samples classification: The algal and fish samples were identified to their possible species and genus, Tables 1 and 2).

Samples preservation: They were washed by tap water followed by distilled water and then stored in polyethylene bags. They were frozen under –20°C and dried in an oven at 70°C to a constant weight then crushed to a fine powder.

Samples preparation: They were exposed to many types of digestions according to its purpose of analysis.
* A mixture of nitric, hydrochloric and hydrofluoric acids in Teflon cubs digested 0.5 gm of the dried fine powdered samples of algae. The digested solutions were used for the analyses of heavy metals, phosphorus, sulfur, calcium and magnesium contents.
* 1.0 gm of the dried fine powdered fish samples were digested using a concentrated nitric acid in Teflon cubs at room temperature and used for fluoride, sulphur, phosphorus, calcium magnesium and heavy metals analyses.
* 0.1 gm of the fine powdered algal samples was digested using a concentrated perchloric acid in Teflon cubs at room temperature and used for the

fluoride analysis. Table 3, represents a comparative study for the analysis of fluoride content in different digestive media containing the same weight of NaF. It seems that HNO_3 and $HClO_4$ acids are the suitable media for fluoride analysis. The low fluoride content obtained from the digestion of NaF with HNO_3-H_2O_2 and its fusion with sodium bismuthate and sodium hydrogen sulphate, may be attributed to the liberation of volatile HF or probably due to the oxidation of the alizarin reagent.

Calcium and magnesium concentrations were determined by EDTA titration in presence of murexide and Eriochrome black T indicator[6].

Sulphate concentration was estimated by turbidimetric method[6], using Perkin Elmer Lambda/UV/visible single beam spectrophotometer at λ=420 nm.

Fluoride ion concentration was determined following the procedure of zirconium alizarin red S[7]. Phosphorus content was evaluated based on the reaction with an acidified molybdate reagent to yield phosphomolybdate complex, which then reduced to a coloured blue compound[8].

Heavy metals contents in the samples were determined using Perkin-Elmer 2380, atomic absorption spectrophotometer.

The data of the different parameters are used to calculate the correlation coefficient (r), using the following equation[9].

$$r = \frac{\sum xy - \frac{\sum x \sum y}{n}}{\sqrt{\left[\sum x^2 - \frac{(\sum x)^2}{n}\right]\left[(\sum y^2) - \frac{(\sum y)^2}{n}\right]}}$$

Where: x, y are two different parameters.
n: is the number of samples.

RESULTS AND DISCUSSION

Calcium: Calcium content in *Posidonia oceanica* (Sea grass) is ranged between 21.82 and 45.30 mg g^{-1} in Abu Qir and El Alamein, respectively, Table 3. This is probably due to precipitation of carbonates on the leaves during photosynthesis process[10]. The results are in harmony with the macrophytes of Lake Edku. However, the calcium content was ranged between 18.1 and 34.7 mg g^{-1} for *Ceratophyllum demersum* and *Eiphyteson C. demersum,* respectively[11], higher than in Lake Mezzola (Northern Italy)[12]. Calcium concentration in the algal species (green, red and brown) is varied between 45.63 and 325.37 mg g^{-1} for *Asparagoposis* sp. (red algae) and *Amphiroa* sp. (red algae) collected from El Alamein and Ras El Hikmah, respectively, Table 3. The change in this content in the present work may refer to the different requirements of algal species[10]. Calcium concentration factor is varied between 78.04 and 1608.1 mg g^{-1} between *Posidonia*

oceanica and *Amphiroa* sp. from El Alamein during September 2000 and March 2001, , Table 4, respectively. Calcium seems to be variable along all the algal species possibly due to the specific character for each species of algae[10]. The determined data, Table 3, reflect that *Penicillus capitatus* (green algae) and *Amphiroa* sp. (red algae) are calcareous algae of high calcium content. However, the red algae are aragonitic but contain some magnesium calcite[14]. The present investigation gives higher values in the algal species of the western studied area (El Alamein, Ras El Hikmah and Sidi Barrani) than in the eastern ones (Abu Qir), Table 3. This may refer to the higher existence in sediments and column water. *Codium bursa* and *Sargassum* sp. contain higher contents than *Codium tomentosum* and *Sargassum hornschuchii* collected from Alexandria coast[13]. This may confirm the higher accumulation in the western region of the coastal water of Mediterranean Sea Egypt.

Fish species live on the bottom of the sea are of lower calcium content, than the pelagic, Fig. 2 and ranged between 18.04 and 93.00 mg g^{-1} for *Bothus podas* and *Hippocampus hippocampus* collected from El Alamein and Damietta during 2001, respectively. *Bothus podas, Arisoma balearicum* and *Synodus saurus* show contents of 18.04, 39.21 and 39.36 mg g^{-1} at El Alamein, Marsa Matruh and Sidi Barrani, respectively. However, the mean calcium contents of seawater of El Alamein and Marsa Matruh sectors are of lower values than that of Damietta and Sidi Barrani. The whole body of *Hippocampus hippocampus* caught from Damietta sector shows the highest calcium content (93.00 mg g^{-1}) due to the presence of phosphate apatites in bone structure[15]. The high content in *Boops boops, Lepidotrigla cavillone* and *Stephanolepis diaspros* is not only affected by its value in both sediment and water but also by feeding[16]. However, fish can absorb calcium and magnesium directly from water and food[17]. The calcium concentration factor is ranged between 93.13 and 257.95 for *Bothus podas* and *Lepidotrigla cavillone* collected from El Alamein and Sidi Barrani, respectively. *Hippocampus hippocampus* shows the highest concentration factor (282.50).

Magnesium: Magnesium content and concentration factor for *Posidonia oceanica* (sea grass) are ranged between 3.62 and 28.96 mg g^{-1} and 4.65 and 31.11 in Abu Qir and El Alamein, respectively, Tables 3 and 4. The high magnesium accumulation in El Alamein is probably due to its content in water and sediment and the different chlorophyll value in varies species[11]. The magnesium concentration in macrophytes from Lake Mezzola was 2.372, 3.413 and 3.083 mg g^{-1} for *Potamogeton crispus, Callitriche stagnatis and Ranunculus* sp., respectively[12], lower than the present work. Magnesium content is varied from 1.21 to 15.70 mg g^{-1} for *Penicillus capitatus* and *Codium bursa* from Sidi Barrani and Abu Qir, respectively, Table 3.
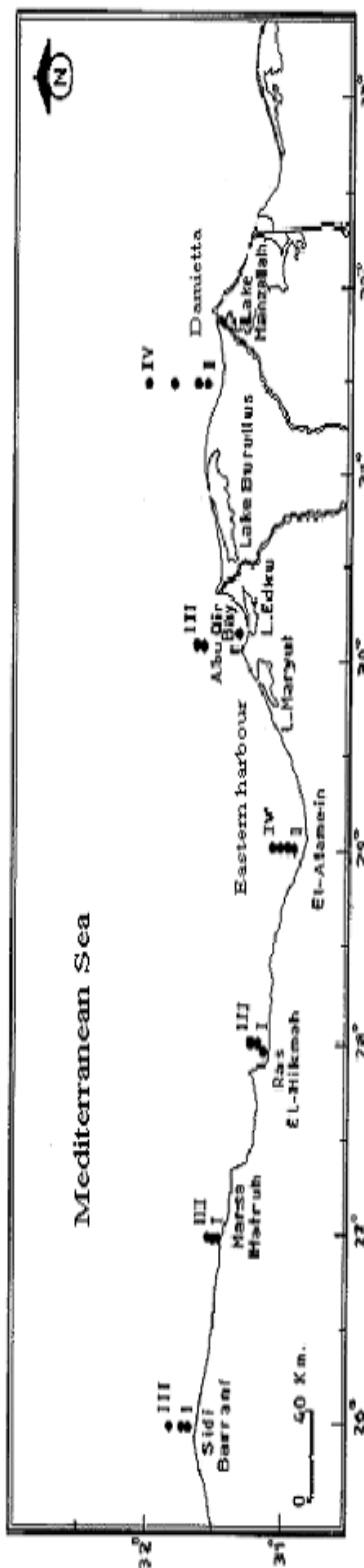

Fig. 1: Sampling locations of the Egyptian coast of Mediterranean Sea during 2000-2001

Its concentration factor is fluctuated between 1.8 and 23.71 for *Codium bursa* and *Sargassum* sp. from Sidi Barrani, respectively. *Codium bursa* (green algae) and
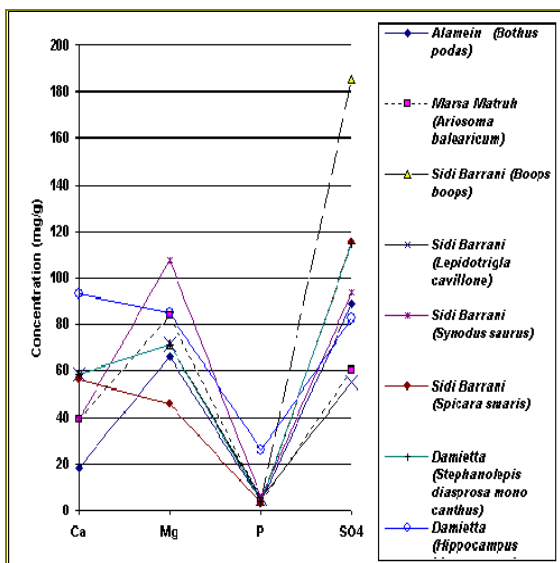
Fig. 2: Distribution of some parameters content (mg/g) in different fish samples collected from the Egyptian coast of Mediterranean Sea during March 2001
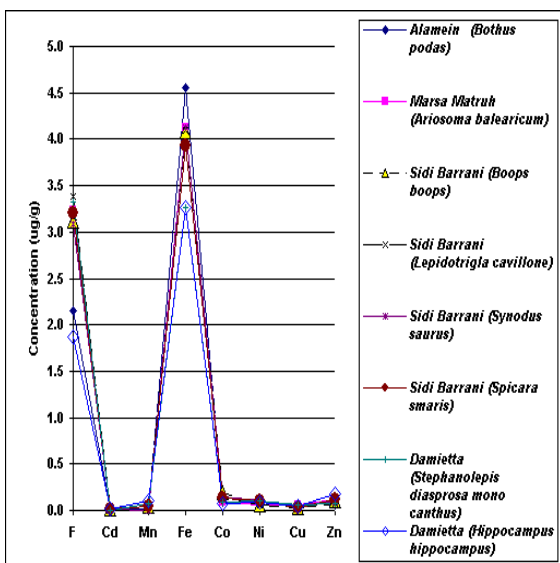

Fig. 3: Distribution of some parameters content (μ/g) in different fish samples collected from the Egyptian coast of Mediterranean Sea during March 2001

sargassum sp. (brown algae) showed higher magnesium contents, probably accompanied with the periodic fluctuations in the ambient environment and with the changes in the organisms, metabolism[14]. The present study indicates that the algal magnesium content is of lower values than for the beaches of Alexandria[13], may be attributed to the changes in environment and the difference in the organisms metabolism[14].

The magnesium content, Fig. 2 and concentration factor of *Spicara smaris* and *Synodus saurus* are ranged between 45.58 and 107.84 mg g^{-1} and 68.97 and 163.17

Table 1: Classification of the Sea grass and algae (Phylum: Thallophyta) collected from the coast of Mediterranean Sea during. September 2000 and March 2001

Macrophyta and algae	Species	Location	Date of collection
Sea grass	Posidonia oceanica	El Alamein	2000
		Abu Qir	2001
		El Alamein	2001
	Penicillus capitatus	El Alamein	
		El Alamein	2000
		Abu Qir	2001
		Marsa Matruh	2001
		Sidi Barrani	2001
			2001
Chlorophyta (Green algae)	Codium bursa	Abu Qir	
		El Alamein	2001
		Ras El	2001
	Ulva lactuca	Hikmah	2001
		Marsa Matruh	2001
		Sidi Barrani	2001
		Sidi Barrani	2001
Rhodophyta (Red algae)	Amphiroa *sp.*	El Alamein	2001
		Abu Qir	2001
		Ras El	2001
	Asparagoposis sp.	Hikmah	2001
		Sidi Barrani	
		El Alamein	2000
Phaeophyta (Brown algae)	**Sargassum sp.**	**El Alamein**	2000
		Ras El	2001
		Hikmah	2001
		Marsa Matruh	2001
		Sidi Barrani	

at Sidi Barrani sector, respectively, may be related to the type of feeding of the two species[19]. Generally, the present study shows that the fish which live on the bottom of the sea water contain higher magnesium content than the pelagic ones. However, *Spricara smaris* contains lower magnesium content than *Synodus saurus*. Its content in the whole body belongs to *Hippocampus* species is of 84.92 mg g^{-1}, Fig. 2. Magnesium contents in the present study are of higher values than that recorded[16]. This may be attributed to the analysis of the dry weight samples and the high magnesium content in the marine fish samples.

Sulphate: Sulphate content and its concentration factors are ranged between 69.78 and 140.00 mg g^{-1} and 23.2 and 174.5 in *Posidonia oceanica* collected from El Alamein and Abu Qir, respectively, Tables 3 and 4. Sulphate concentration is ranged between 17.22 and 117.22 mg g^{-1} in *Penicillus capitatus* and *Sargassum* sp. from Marsa Matruh and Ras El Hikmah, respectively, Table 3. Most algae can supply their sulphur reqiuement by reducing sulphate, or other sources of sulphur such as: methionine, cysteine, homocysteine, sulpholipid and sulphite[10]. Sulphur is considered as an important component, while a large part of it in most algae is incorporated into protein, sulpholipids, sulphite, sulphonium compounds, sulphate, sulphuric acid, …etc[10]. Many studies on algae indicated a special requirement for sulphur in cell

Table 2: The family of fish species collected from the coastal water of the Mediterranean Sea of Egypt during March 2001 and their type of feeding

Family	Fish species	Existence[36]	Feeding[36]
Bothidae	*Bothus podas*	Live on the bottom	Small mollusca and crustaceans
Congridae	*Ariosoma balearicum*	Live on the bottom	Fish and crustaceans
Sparidae	*Boops boops*	Live in schools either in wide waters or close to the bottom (pelagic)	Small crustaceans, mollusca, seaweeds, algae and sponges
Triglidae	*Lepidotrigla cavillone*	Live on the bottom (bottom dwelling fishes)	Shrimp, swimming crabs, small crustaceans and small squids
Synodontidae	*Synodus saurus*	Live on the bottom	Fish and crustaceans
Centracanthidae	*Spicara smaris*	Live between the surface and bottom (pelagic)	Crustaceans, algae, copepods and small benthic invertebrate
Monacanthidae	*Stephanolepis diaspros mono canthus*	Live over rocky bottom (10-100 m)	Mollusca and crustaceans
Syngnathidae	*Hippocampus hippocampus*	Live in shallow inshore water among algae	Phytoplankton

Table 3: Comparative studies for the analysis of fluoride content of NaF in the presence of different digestive media

Digestive Media	Fusion			Acidic media					
	$NaHSO_4$	$NaBiO_3$	Na_2CO_3	HNO_3 room Temp.	HNO_3 Warming	$HNO_3 + H_2O_2$	$HNO_3 + HClO_4$	$NaOH + HClO_4$	$HClO_4$
F % (F_{exp}/F_{calc})	14.63	27.31	90.33	99.22	99.22	64.40	96.89	95.80	96.9

Table (3): Distribution of some parameters (mg/g dry wt) in some sea grass and algal species collected from the coastal water of Mediterranean Sea during September 2000 and March 2001.

species	Sector	Ca	Mg	SO_4	P	F	Cd	Mn	Fe	Co	Ni	Cu	Zn
Sea grass *Posidonia Oceanica*	El Alamein (2000)	45.30	28.96	73.90	0.240	33.78	0.002	0.022	0.237	0.006	0.011	0.014	0.029
	Abu Qir (2001)	21.82	3.62	140.00	0.740	29.79	0.001	0.100	0.453	0.004	0.012	0.035	0.163
	El Alamein (2001)	38.69	17.70	69.78	0.520	34.30	0.003	0.051	0.100	0.004	0.016	0.022	0.064
Green Algae: *Penicillus capitatus*	El Alamein (2000)	253.40	1.21	52.26	0.708	53.70	0.009	0.006	0.366	0.029	0.040	0.009	0.028
	El Alamein (2001)	215.78	9.25	69.78	0.857	47.86	0.009	0.022	0.212	0.028	0.037	0.010	0.031
	Abu Qir (2001)	236.38	14.39	55.16	0.773	19.17	0.006	0.028	0.489	0.030	0.036	0.011	0.070
	Ras El Hikmah (2001)	263.90	3.62	43.33	0.488	24.79	0.007	0.031	0.560	0.030	0.044	0.020	0.038
	Marsa Matruh (2001)	285.70	2.42	17.22	0.807	25.42	0.008	0.031	0.560	0.033	0.044	0.011	0.038
	Sidi Barrani (2001)	299.14	10.71	60.53	0.716	30.14	0.008	0.025	0.400	0.033	0.041	0.011	0.053
Codium bursa	Abu Qir (2001)	117.05	15.70	94.44	0.700	25.21	0.005	0.049	1.513	0.019	0.040	0.018	0.054
	El Alamein (2001)	49.60	13.29	77.78	0.198	26.88	0.001	0.011	0.169	0.004	0.008	0.009	0.029
	Ras El Hikmah (2001)	71.42	12.08	104.44	0.241	35.00	0.000	0.014	0.299	0.007	0.016	0.011	0.034
	Marsa Matruh (2001)	81.34	12.08	64.44	0.481	32.81	0.001	0.043	0.683	0.022	0.012	0.014	0.034
	Sidi Barrani (2001)	22.22	1.21	70.00	0.389	27.90	0.005	0.031	1.112	0.022	0.032	0.013	0.027
Ulva lactuca	Sidi Barrani (2001)	84.17	13.39	343.95	1.012	23.13	0.002	0.036	0.375	0.006	0.019	0.021	0.087
Red Algae: *Amphiroa sp.*	El Alamein (2000)	263.28	7.25	43.64	0.324	26.72	0.009	0.019	0.145	0.034	0.042	0.011	0.018
	Abu Qir (2001)	303.60	3.62	38.89	1.854	28.33	0.007	0.023	0.215	0.033	0.044	0.020	0.038
	El Alamein (2001)	311.48	8.46	25.56	0.297	30.42	0.006	0.020	0.207	0.037	0.044	0.011	0.015
	Ras El Hikmah (2001)	325.37	12.08	62.78	0.488	32.92	0.009	0.026	0.123	0.033	0.044	0.013	0.023
	Sidi Barrani (2001)	299.58	3.62	30.56	0.446		0.008	0.017				0.011	0.022
Asparagopsis sp.	El Alamein (2000)	45.63	10.87	54.44	0.156	27.68	0.000	0.031	0.154	0.004	0.012	0.011	0.038
Brown Algae: *Sargassum sp.*	El Alamein (2000)	59.36	13.23	93.04	0.289	30.14	0.003	0.031	0.123	0.007	0.012	0.011	0.050
	Ras El Hikmah (2001)	85.31	3.62	117.22	0.311	30.42	0.001	0.040	0.439	0.004	0.016	0.012	0.128
	Marsa Matruh (2001)	101.18	8.46	82.22	0.694	26.88	0.004	0.040	0.600	0.015	0.020	0.027	0.098
	Sidi Barrani (2001)	89.10	15.67	63.76	0.629		0.002	0.049	0.706	0.007	0.012	0.053	0.861

division[10]. Its concentration factor is ranged between 13.7 and 307.8 for *Amphiroa* sp. and *Sargassum* sp. from El Alamein and Ras El Hikmah, respectively, Table 4. Generally, the present data indicated that *Penicillus capitatus* and *Amphiroa* sp. contain lower sulphate content than the present species, Table 3.

The sulphate content, Fig. 2 and concentration factor in the muscle of the fish samples are ranged between 54.68 and 185.19 mg g^{-1} and 125.90 and 426.41 in *Lepidotrigla cavillone* and *Boops boops* species collected from Sidi Barrani sector and affected by the feeding of each species and their existence[16]. However, *Boops boops* (pelagic) shows the highest value of 185.19 mg g^{-1} and *Lepidotrigla cavillone* (lives near the bottom) is of low content (54.68 mg g^{-1}).

Phosphorus: Phosphorus content in *Posidonia oceanica* is ranged between 0.24 and 0.74 mg g^{-1} in El Alamine and Abu Qir, respectively, Table 3. The high content in Abu Qir sector may be accompanied with its concentration in sediment and water column and the discharged water coming from El Umum drain and Rosetta branch. Its concentration in the algal species is varied from 0.198 and 1.854 mg g^{-1} for *Codium bursa* and *Amphiroa* sp. in El Alamein and Abu Qir, respectively, Table 3. The algal species in Abu Qir are of high phosphorus contents, Table 3 and may be attributed to the metabolic reactions[10], environmental conditions[10] and seasonal variation[10].

Nearly half of the phosphorus in fish is located in bone and scales[19]. Fish are often long lived and thus can serve as reservoirs of nutrients[19]. Phosphorus contents in the muscles of fish samples are ranged between 3.205 and 5.477 mg g^{-1} for *Spicara smaris* and *Synodus saurus* collected from Sidi Barrani sector, respectively, Fig. 2. The phosphorus content of the

whole body of *Hippocampus hippocampus* collected from Damietta is of 25.546 mg g^{-1} to reflect its high content in the bone skeleton[19]. The phosphorus contents of the whole body of *Cottus bairdi* and *Lota lota* were 26.8 ± 2.4 and 19.1 ± 2.4 mg g^{-1} collected from Bark Bay, Wisconsin, respectively[19]. However, the content is not only dependent on trophic level, location and length but also depends on both growth rate indices and fineness[19].

Fluoride: Its concentration is varied from 29.79 to 34.30 mg g^{-1} for *Posidonia oceanica* collected from Abu Qir and El Alamein, respectively, Table 3 and Fluoride concentration factor is varied from 6081.6 to 9129.7 during March 2001 and September 2000, respectively. In algal species it is flactuated between 19.17 and 53.70 mg g^{-1} in *Penicillus capitatus* from Abu Qir and El Alamein, respectively, Table 3 and its concentration factor is ranged between 4065.0 and 12935.1 in *Ulva lactuca* and *Penicillus capitatus* from Sidi Barrani and El Alamein in Spring 2001, respectively, Table 4. However, its accumulation not only shows variable contents along all the studied species but also in the same species collected from different sectors. Furthermore, the seasonal variation appears to contribute in the fluctuation. Fluoride has possible beneficial effect on algal development[20]. Previous studies reported that the respiration rate was affected by fluoride accumulation and either inhibition or stimulation may depend on its concentration and other factors such as the species and age of plant and the time of exposure[4].

The fluoride content in the muscle of the fish species is ranged between 1.875 and 3.379 μg g^{-1} in *Hippocampus hippocampus* and *Lepidotrigla cavillone* in Damietta and Sidi Barrani sectors, respectively, Fig. 3. However, the fluoride content is probably attributed to the constituents of the food of nutrition[21]. The concentration factor is ranged between 0.38 and 0.87 for *Bothus podas* and *Ariosoma balearcium* in El Alamein and Marsa Matruh, respectively. However, *Ariosoma balearicum* is feeding on fish and crustaceans (of high fluoride content). The maximum fluoride content in seawater column, may cause its accumulation in the muscle of fish species. The fluoride content in the wet weight of the muscle tissue of *Gadus morrhua* and *Gadus aeglifinus* was 1.7 and 1.8 mg Kg^{-1} caught in the North Sea[21]. However, the increased fluoride content in the muscle tissue of the species fed on crustaceans, algae, molluscs, small fish,…etc, is due to the nutritional availability of fluoride[21]. Its content in the fish flesh is lower than the permissible limit in USA (100 mg Kg^{-1}), probably due to its accumulation to skin, scales, bone skeleton, gills, ..etc[21,22] and its distribution between seawater and sediment[23].

Heavy metals: Iron concentration in *Posidonia oceanica* (macrophyta) is ranged from 0.100 to 0.453

mg g^{-1} from El Alamein and Abu Qir, respectively, Table 3, may be accompanied with its content in sediment and water column. However, rooted aquatic plants can absorb metals through both their leaves and roots via the surrounding water and sediment interstitial water, respectively[24]. In the present study, *Posidonia oceanic* from Abu Qir shows the highest iron content, may be attributed to its existence in sediment and water column[12]. Iron content in *Posidonia oceanica* agrees with the reported data in Edku, Mariut Lakes and Alexandria beaches[11,25]. Its concentration in algal species is 0.123, 0.123 and 1.513 mg g^{-1} for *Amphiroa* sp. *Sargassum* sp. and *Codium bursa* from Sidi Barrani, El Alamein and Abu Qir, respectively, Table 3. Green and brown algae are of higher content than red algae, Table 3, to reflect the different requirements of the various species[26] and the environmental change[26]. Iron content in green algae seems to be higher than the recorded data except *Ulva lactuca* which contains lower value than the determined in Suez Canal[16], probably due to the environmental change[27]. However, the variation of the metal content in algae from site to site is depended on the physicochemical factors such as: temperature, pH, salinity, wave exposure, light, etc[16].

Iron concentration is ranged between 3.26 and 4.55 μg g^{-1} in *Hippocampus hippocampus* and *Bothus podas* species collected from Damietta and El Alamein, respectively, Fig. 3. The iron contents in the fish samples collected from El Alamein, Marsa Matruh and Sidi Barrani record relatively higher value than that for Damietta samples, probably due to its content in their feeding[16]. The iron content of the muscle of *Boops boops* taken from Shanshoulla working in Alexandria coastal water was ranged from 5.633 ± 2.424 and 41.519 ± 76.486 μg g^{-1} in August and March, respectively. The high content determined in all organs was in spawning month, March[27]. However, the fish muscles are of lower values than reported[27].

The manganese concentration of *Posidonia oceanica* is varied between 0.022 and 0.100 mg g^{-1} for El Alamein and Abu Qir, respectively, Table 3. The high content may be accompanied with its existence in sediment and water[26]. Its content in algal species is ranged between 0.011 and 0.049 mg g^{-1}, respectively, Table 3. *Codium bursa* is of variable contents along the different sectors, Table 3. Brown algae show higher concentrations than green and red, Table 3. Manganese content in the present algal species agrees with the reported data[25,28].

The manganese content of the muscles of the fish samples is ranged between 0.000 and 0.069 μg g^{-1} in *Synodus saurus* and *Stephanolepis diaspros* in Sidi Barrani and Damietta sectors, respectively, Fig. 3. The relative high manganese content in the fish species may reflect its existence in food and sediment. Its relative maximum content in *Hippocampus hippocampus* species (0.109 μg g^{-1}) may be accompanied with the

analysis of the whole body. Generally, the determined manganese content in the muscle of the fish samples is lower than the reported data[29]. However, it was reported that[35] its content was 4.87 ± 0.30, 7.68 ± 1.15 and 6.65 ± 0.36 µg g^{-1} for the muscle of *Chactadon jayakeri*, *Rastrelliger kanagurta* and *Pomadysis maculatum* collected from the Arabian Sea, respectively[35].

Cobalt content in *Posidonia oceanica* is ranged between 0.004 and 0.006 mg g^{-1} from Abu Qir and El Alamein, respectively, Table 3, however, sea grass is lower than in *Potamogeton crispus* (0.007 ± 0.010 mg g^{-1}) collected from Lake Mezzola[12]. Its content in the algal species is fluctuated between 0.004 and 0.037 mg g^{-1}, Table 3. *Penicillus capitatus* and *Amphiroa* sp. show higher cobalt content than the other species, Table 3, probably due to the change of requirement of each species[10]. Its content in *Ulva lactuca* is relatively similar to that determined in Suez Canal[16].

The deduced content in the muscle of fish samples is ranged between 0.074 and 0.187 µg g^{-1} determined in *Hippocampus hippocampus* and *Boops boops*, in Damietta and Sidi Barrani , respectively, Fig. 3. The relative high content of *Boops boops* (0.187 mg g^{-1}), is probably due to is a pelagic fish feeding on algae and invertebrates[18]. The total content of trace metals is higher in plankton and invertebrates[27]. The cobalt content in the muscle of *Mugil seheli* and *Solea solea* collected from Suez Canal was 0.205 ± 0.02 and 0.116 ± 0.04 µg g^{-1} wet wt, respectively[27]. The mean cobalt content in the muscles of *Sparus auratus* and *Scaiena aqiulla* ranged from 0.005 to 0.170 and 0.02 to 0.07 mg Kg^{-1}, respectively[27].

Nickel content in *Posidonia oceanica* is varied from 0.011 to 0.016 mg g^{-1} from El Alamein, Table 3. Its concentration in the algal species is ranged between 0.008 and 0.044 mg g^{-1}, Table 3. *Codium bursa* collected from Abu Qir shows the highest content (0.040 mg g^{-1}), probably due to its existence in sediment and water column[16], Table 3. The high contents in both *Penicillus capitatus* and *Amphiroa* sp. are probably attributed to the requirement of each species[10].

The nickel content in the fish samples is ranged between 0.052-0.103 µg g^{-1}, Fig. 3, lower than the reported[29], probably due to the change in the water properties, time of collection and feeding[27]. It was reported that[29] its content in the muscle of some marine fish samples collected from Arabian Sea was 12.12 ± 1.59, 18.28 ± 3.67 and 12.09 ± 1.18 µg g^{-1} wet wt for *Chactadon jayakeri*, *Rasterlliger kanagurta* and *Pomadysis maculatum*, respectively[29]. Its content in the muscle of *Mugil seheli* collected from Suez Canal (Port Tawfik) was 1.098 ± 0.58 µg g^{-1} wet wt, respectively[16].

The copper content in *Posidonia oceanica* is varied between 0.014 and 0.035 mg g^{-1} from El Alamein and Abu Qir, respectively, Table 3 and of higher value (0.035 mg g^{-1}) than of the macrophytes collected from Edku, Maruit lakes and Alexandria beaches[11,25], probably accompanied with the environmental conditions[16]. The concentration in the algal species (seaweeds) is fluctuated between 0.004 and 0.053 mg g^{-1}, respectively, Table 3. Furthermore, *Sargassum* sp. (brown algae) and *Amphiroa* sp.(red algae) seem to be affected by the ambient medium[16], Table 3.

The copper contents in the fish samples are ranged between 0.034 and 0.053 µg g^{-1}, Fig. 3. Generally, its content is lower than reported[27,29,30]. However, many factors affect its existence in the muscle of fish for example: spawning season, feeding rate , its content in water and in sediment[27]. It was reported that[16] its content in *Mugil seheli* collected from Suez Canal was 1.185 ± 0.38 µg g^{-1} wet wt[16].

The zinc content in *Posidonia oceanica* is ranged between 0.029 and 0.163 mg g^{-1} from El Alamein and Abu Qir, respectively, Table 3. Its content in algal species is fluctuated from 0.015 to 0.861 mg g^{-1} for *Amphiroa* sp. and *Sargassum* sp. from El Alamein and Sidi Barrani, respectively, Table 3. The present data proved that its content in both green and brown algae is higher than in red. In general, machrophyte and seaweeds collected from Abu Qir sector show high zinc contents, Table 3, possibly due to the environmental conditions and growth stages[16,13].

It is ranged between 0.055 and 0.113 µg g^{-1}*Bothus podas* and *spicara smaris* along El Alamein and Sidi Barrani, respectively, Fig. 3. It involves many physiological mechanisms such as: growth, vision, sexual, maturity, spawning and organic functions. The increase in its content was toxic for sensitive species[27]. The present results are of lower contents than reported[27,29,30]. Its content in the muscle of *Boops boops* and *Sadrinellaa aurita* collected from Mediterranean Sea was 10.00 ± 4.43 and 12.15 µg g^{-1} [27]. It was recorded that[16] the zinc content in the muscle of fish of *Mugil seheli* and *Tilapia aurata* was 7.96 ± 2.02 and 9.91 ± 3.05 µg g^{-1} wet wt, respectively. Its content in the muscle of some fish samples collected from the Arabian Sea were: 4.99 ± 0.36, 19.83 ± 2.00 and 7.22 ± 0.51 µg g^{-1} wet wt in *Chactadon jayakeri*, *Rastrelliger kanagurta* and *Pomadysis maculatum*, respectively[29].

Cadmium content in *Posidonia oceanica* is ranged between 0.001 and 0.003 mg g^{-1} from Abu Qir and El Alamein, respectively, Table 3. Its content in algal species is varied from 0.000 to 0.009 mg g^{-1}, respectively, Table 3. *Penicillus capitatus* and *Amphiroa* sp. show high cadmium contents, possibly accompanied with the physiological variations of each species[31]. However, in both calcareous algal species Cd^{2+} may substitute Ca^{2+} in the crystal lattice of $CaCO_3$, according to their similarity in ionic radius[32].

Table 4: Concentration factor for some ions in sea grass and algae species collected from the coastal water of Mediterranean Sea during September 2000 and March 2001

Species	Sector	Ca	Mg	SO₄	F
Sea grass	El Alamein (2000)	78.04	16.88	23.2	9129.7
Posidonia Oceanica	Abu Qir (2001)	94.05	4.65	174.5	6634.7
	El Alamein (2001)	199.74	31.11	169.6	6081.6
Green Algae	El Alamein (2001)	371.70	5.39	21.9	12935.1
Penicillus capitatus	Abu Qir (2001)	1018..9	18.50	147.6	4269.5
	Ras El Hikmah (2001)	1301.9	6.12	113.8	6340.2
	Marsa Matruh (2001)	1562.1	4.59	47.4	6851.8
	Sidi Barrani (2001)	1317.2	16.21	139.4	5297.0
Codium bursa	Abu Qir (2001)	504.5	20.18	252.7	5614.7
	El Alamein (2001)	256.1	23.36	189.0	4765.9
	Ras El Hikmah (2001)	352.3	20.41	274.3	8951.4
	Marsa Matruh (2001)	444.7	22.75	177.3	8843.7
	Sidi Barrani (2001)	978.4	1.80	161.2	4903.3
Ulva lactuca	Sidi Barrani (2001)	370.63	20.26	791.9	4065.0
Red Algae:	El Alamein (2000)	453.5	4.23	13.7	7221.6
Amphiroa sp.	Abu Qir (2001)	1308.6	4.64	104.1	5614.7
	El Alamein (2001)	1608.1	14.68	62.1	5023.1
	Ras El Hikmah (2001)	1605.2	20.41	164.9	7780.1
	Sidi Barrani (2001)	1319.2	5.48	70.4	5785.6
Brown Algae:	Ras El Hikmah (2001)	420.9	6.12	307.8	7780.1
Sargassum *sp.*	Marsa Matruh (2001)	553.2	15.44	226.3	5897.6
	Sidi Barrani (2001)	392.3	23.71	146.8	4724.1

So, each algal species seems to have certain chemical composition. Some algae appear to uptake certain elements rather than others, according to many factors such as: ambient environment, the availability of metals to be accumulated, physiological variations among species[33], growth stages, time of collection, temperature, ..etc[16].

Cadmium content in the muscle is ranged from 0.005 to 0.016 $\mu g\ g^{-1}$, Fig. 3. The relative high content in the fish samples reflects its existence in seawater, feeding and sediment[27]. The cadmium concentration in the muscle of *Mugil seheli* and *Tilapia aurata* was fluctuated between 0.33 ± 0.01 and 0.22 ± 0.03 $\mu g\ g^{-1}$ wet wt along Suez Canal, respectively[27]. It was recorded that[27] its content in the muscle of *Boops boops* gathered from Mediterranean Sea was ranged between 0.92 ± 0.66 and 1.38 ± 0.13 $\mu g\ g^{-1}$, respectively[27]. It was reported that the cadmium content in the flesh of varies marine fish gathered from the Arabian Sea was 0.35 ± 0.09, 0.36 ± 0.10 and 0.26 ± 0.03 $\mu g\ g^{-1}$ wet wt for *Chactadon jayakeri*, *Rastrelliger kanugurta* and *Pomadysis maculatum*, respectively[29]. The present study revealed lower levels of cadmium particularly in the different fish species compared with those of Health Standard Levels (0.5 mg Kg^{-1}), established by U.S. National Academy of Science. The recommendation of National Health and Medical Research Council in Australia (NHMRC), stated that the concentrations of cadmium and lead in edible parts of fish should not exceed 2.0 mg Kg^{-1}.

In contrast to NHMRC levels, the Western Australian Food and Drug Regulations gave concentrations of 5.5 and 40 mg Kg^{-1} for Cd and Zn, respectively[29]. Generally, the present data demonstrate that there is no risk for the human consumption of the fish samples collected from the Egyptian coast of Mediterranean Sea.

The order of the determined constituents in algal species is as follows:

Sea grass: SO₄> Ca> F> Mg> P> Fe> Zn> Mn> Cu> Ni> Co> Cd

Green algae: Ca> SO₄> F> Mg> P> Fe> Zn> Ni≥ Mn> Co> Cu> Cd

Red algae: Ca> SO₄> F> Mg> P> Fe> Ni> Co> Zn> Mn> Cu> Cd

Brown algae: SO₄> Ca> F> Mg> P> Fe> Zn> Mn> Ni> Cu> Co> Cd

Sea grass Ca> SO₄> F> Mg> P> Fe> Zn> Mn> Ni> Co> Cu> Cd

and algae:

It seems that both *Posidonia oceanica* (macrophyte) and brown algae contain high sulphate content, while green and red algae show maximum calcium concentration.

The order of the parameters contents in the collected fish species is given as follows: SO₄>Mg>Ca>P> F>Fe>Co>Zn>Ni>Mn≥Cu>Cd.

It was stated that[16] the heavy metal contents in the muscle of fish samples collected from Red Sea were in order : Fe> Zn> Mn> Pb> Cu>Ni> Cr>Co> Cd.

Statistical analysis:
a) Correlation matrix: The correlation matrices for all the parameters (Ca, Mg, SO_4, P, F, Cd, Mn, Fe, Co, Ni, Cu and Zn), indicate that:

Algae: ($n=25$, $p<0.05$): High significant negative correlations for calcium among magnesium ($r=-0.4937$, $p< 0.012$), sulphate ($r=-0.4622$, $p< 0.020$) and manganese contents ($r=-0.4604$, $p<0.021$), respectively, are probably attributed to the inhibition of $CaCO_3$ formation by magnesium ions. However, magnesium can substitute for calcium in calcite[28]. It seems that the decrease in sulphur and manganese contents is accompanied with large calcium existence in the algal species.

High positive significant correlations for calcium among cadmium ($r=0.8929$, $p<0.000$), cobalt ($r=0.9792$, $p<0.000$) and nickel ($r=0.9420$, $p<0.000$), may reflect the substitution of calcium ion by both cadmium and nickel into the crystal lattice of $CaCO_3$ minerals[32]. The increase in calcium content probably increase the formation of compounds containing cobalt[10].

The high positive significant relations for cadmium among both cobalt ($r=0.9304$, $p<0.000$) and nickel ($r=0.9155$, $p<0.000$) contents, possibly show the great effect of cadmium on the formation of both elements in algal species[10].

A positive correlation between manganese and copper ($r=0.6096$, $p<0.001$), indicating that the accumulation of copper content leads to the stimulation in both photosynthesis and growth of the algal species[10].

A positive high significant relation between cobalt and nickel contents ($r=0.9632$, $p<0.000$), may show that the stimulation of cobalt components is accompanied with the increase in nickel content[10].

Zinc and copper contents show a high significant positive correlation ($r=0.8228$, $p<0.000$), where, Cu^{2+} may substitute Zn^{2+} in the growth mechanisms of the algal species[32].

Fish: ($n=8$): The correlation matrix for Ca, Mg, SO_4, P, F and length values indicates a positive significant relation between calcium and phosphorus contents in the muscle of the fish samples ($r=0.7512$, $p< 0.032$). However, the inhibition of phosphate metabolism is accompanied with a decrease in the intestinal absorption of calcium[34].

The correlation matrix for F and the studied heavy metal contents shows a positive significant relation between Mn and Zn ($r=0.8452$, $p< 0.008$). However, manganese or zinc binds the acceptor substrate to the enzyme during the carboxylate transfer[34]. A negative significant correlation between Ni and Cd ($r=-0.8957$, $p< 0.003$) is assigned reflecting that the decrease in the nickel content is accompanied with an increase in cadmium accumulation.

b) Stepwise regression analysis:
1)Algae: ($n=25$)
$$F=33.08-0.26\ Cu \tag{1}$$
$R=0.263422$, $R^2=0.069391$, $p< 0.2033$
$$Cd=-0.003 + 1.40\ Co + 0.22\ F + 0.08\ Cu-0.42\ Ca + 0.09\ SO_4 \tag{2}$$
$R=0.959857$, $R^2=0.921326$, $p< 0.0000$
$$Co=0.55\ Ca + 0.22\ Cd + 0.24\ Ni-0.06\ SO_4-0.04\ F + 0.04\ Mg \tag{3}$$
$R=0.992246$, $R^2=0.984552$, $p< 0.0000$
$$Cu=0.01 + 0.68\ Zn + 0.32\ Mn + 0.19\ P-0.12\ F \tag{4}$$
$R=0.916399$, $R^2=0.839787$, $p< 0.0000$

All these equations lead to conclude that algal calcification process is affected by the chemical composition of sediment and water column in each sector. Protein, chlorophyll and cobalt components contents are probably accompanied with the specific uptake of each species, ambient environment, availability of the uptake of elements from sediment, temperature, time of collection, ..etc. Cadmium plays an important role in many physiological processes and substitutes Ca^{2+} in the crystal lattice of $CaCO_3$ formation. Furthermore, Cu^{2+} can substitute also for Zn^{2+} in essential growth mechanisms[29]. Significant correlations indicate that cadmium content may affect the formation of protein and cobalt components, growth mechanisms and photosynthesis processes.

Fluoride shows high accumulation in both seaweeds and sea grass. Although, the correlation matrix analysis doesn't give any significant relation between fluoride and any determined parameters contents at $p<0.05$, stepwise regression leads to a weak relation between it and copper, [equation (2)]. Also, fluoride shows significant relations among Cd, Co and Cu contents, equations (3, 5 and 7), reflecting its effect on the physiological processes in both marine machrophytes and algal species[3]. This conclusion may indicate the probability of the transportation of this ion to fish, molluscs, crustaceans, echinoderms and other aquatic species by feeding process. However, algae form the base of many aquatic food chains[10].

Fish: ($n=8$):
* When using this analysis for fluoride as a dependent parameter and the others as independent ones (Ca, Mg, SO_4 and length), an insignificant relation is obtained. The result indicates that fluoride content in the muscle of the fish is not affected by the value of previous parameters.
* The stepwise regression analysis for F and heavy metal contents (Fe, Mn, Co, Ni, Zn, Cu and Cd) are shown in these equations:
$$Co=0.23 + 0.31\ F-0.92\ Cu-1.2\ Mn + 0.72\ Zn \tag{1}$$
$R=0.956127$. $R^2=0.914180$, $p < 0.0596$
$$Ni=0.17-0.19\ F-0.89\ Cd \tag{2}$$
$R=0.915935$, $R^2=0.838937$, $p < 0.0104$

The stepwise regression and correlation matrix analyses, indicate that fluoride content in the muscle of fish samples is not accompanied with either the major components (Ca, Mg, SO_4 and P) or the minors concentrations (heavy metal). Equations 1 and 2, show

that fluoride plays as an important role in metabolism, growth, reproduction and other biological processes[3]. However, Co and Ni are essential elements for the physiological mechanisms in marine organisms[35].

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