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Fluoride distribution and the effect of some ions along Alexandria coastal Mediterranean seawater of Egypt

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Abstract: The coastal seawater of Mediterranean of Alexandria receives large amount of discharged waters containing industrial wastes, sewage, and agricultural and domestic drainage. Fluoride and some parameters were (chemical and physical) determined. The data gave indication that the content and the amount of the discharged water largely affect the chemical composition of the coastal water. Stepwise regression analysis was highly significant and the model was very fruitful, where the observed and calculated values were mostly concordant. This may indicated that there was a relation between fluoride content in coastal seawater and its content in the discharged water.

Keywords: fluoride distibution; Alexandria costal Mediterranean; Egypt; physical and chemical parametrs; regression analysis

Introduction

Fluoride possesses biological effects on humans, animals and plants. It affects the bone structure, causes enzyme inhibition and reducing dental caries (Plato, 1979; Dijkman, 1985; Jan, 1991; Thibodeau, 1985). It possesses pronounced effect on the growth, metabolism and respiration of plants and crabs (Moore, 1971; Miller, 1974). In most open ocean seawaters, the F/Cl ratio approaches $6.7 \pm 0.1 \times 10^{-5}$. In some very localized bottom waters, the ratio may reach 9.0×10^{-5} (Riley, 1975). The reported speciation of fluoride in seawater is 46% MgF^{+}, 2% CaF^{+} and 51% F^{-} ion (Goldbers, 1974). High amounts of fluoride are toxic according to the Committee on Dietary allowance less than 4 mg F^{-} daily are harmless to man (NAS, 1980).

The aim of our investigation is to study the distribution of fluoride concentration in seawater at different stations in Alexandria coastal waters under variable conditions (different ions, pH, temperature, salinity etc.).

1 Experimental

Alexandria coastal water is subjected to different pollutants which are conveyed to sea from several outlets distributed along the shores of El-Mex Bay, Western Harbour Qayet Bay, Eastern Harbour and Abu Qir Bay.

Five perpendicular sectors to the Mediterranean shore belt area were selected to represent different parts of Alexandria coastal waters. They extend between Sidi Krir in the west to Abu Qir Bay in the east of Alexandria for a distance of about 35 km long and 10 km from the shore line with depths less than 60 m (Fig.1). All the samples were stored in 1-liter polyethylene bottles and were frozen until analysis.

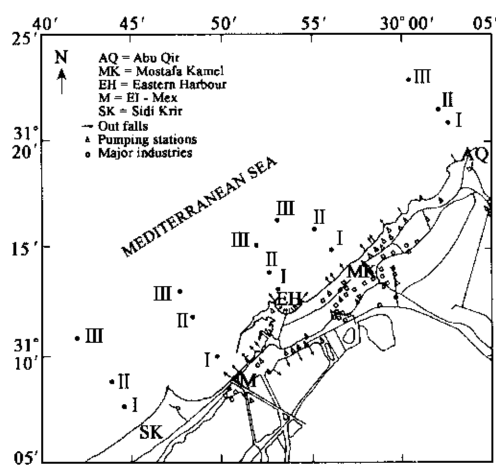

Fig.1 Map of the locations of sampling stations of Alexandria Coast

The samples were represented by five sectors, each of them is divided to three stations (Ⅰ, Ⅱ, Ⅲ) collected at different depths 0, 10, 20 and 50 m during December 1996. These sectors are: (1) Sidi Krir is located to the west of Alexandria. (2) El-Mex Bay is lying at the western side of Alexandria. It is an estuarine zone of agricultural drain called El-Umum its discharged rate is 6×10^6 m^3 day, in addition to untreated industrial wastes from chloro-alkali plant, cement factory, slaughterhouse and twelve tanneries beside the Alexandria iron and steel factory. (3) The Eastern Harbour of Alexandria is semicircular basin with an area of 2.53 km^2 and an average depth of 6 m. The harbour is basically used as the main fishing and hatching harbour of Alexandria. (4) Mostafa Kamel sector lies to the east of Alexandria and subjected to the effect of the current from west to the east. (5) Abu Qir sector is shallow and receives annually about 370×10^6 m^3 of sewage and industrial wastes discharged to the bay through El-Tapia pumping station. The industrial wastes include fertilizers, food processing, textile, paper, dyes and weaving industries. The brackish water of agricultural drainage discharged to the bay from Lake Edku. The bay receives also considerable amounts of fresh water discharged from Rosetta Nile branch.

Ca^{2+}, Mg^{2+}, SO_4^{2-}, pH, temperature, salinity and total hardness were determined following the usual methods of analysis(APHA, 1975).

The temperature of water and air was determined using a thermometer in the range of 0—200℃.

The salinity of seawater samples was calculated by measuring its electrical conductivity using an inductive salinometer(Beckman model RS 10).

The pH value was measured using a calibrated digital pH-meter(model Extech digital pH meter 607).

The F^- concentration was determined applying the following modified procedure(Courtenary, 1951). 1.5 ml 1 mol/L NaOH solution was added to the samples before the addition of the Zr-ARS reagent to avoid the interferences of some metals especially Ca and Mg. The samples were warmed and filtered after cooling. 5 ml of the filtered sample was treated with 1.5 ml(0.004 mol/L) ARS, 1 ml of standarized $ZrCl_4$ (0.004 mol/L) and then diluted to 25 ml by distilled water. The pH's of the samples were adjusted as that of the blank. The absorbance was measured at $\lambda = 420$ nm after two hours where Zr-ARS was used as a blank with a Shimadzu Double-Beam spectrophotometer UV-150-02.

The data of the different parameters were computed to calculate the correlation coefficient(r), using the following equation(Clarke, 1992).

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

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

2 Results and discussions

2.1 Temperature

The minimum and maximum air temperature values(17.2℃ and 23.5℃) were recorded at Sidi Krir and Eastern harbour sectors, respectively. The horizontal distribution patterns of water temperature showed that their maximum values at 0, 10 and 20 m depths were recorded at Eastern harbour and Mostafa Kamel sectors, respectively. The minimum and maximum water temperatures are 18.0℃ and 22.2℃ at El-Mex and Eastern harbour sectors, respectively. The water temperature values at 20 m depth were decreased gradually from the eastern to the western side.

The vertical distribution pattern of water along 50 m depth at station III gave minimum and maximum values of 18.7℃ and 22.2℃ at El-Mex and Eastern harbour sectors, respectively. Meanwhile, high temperature values were recorded mainly near the bottom of the studied area.

2.2 Salinity

The horizontal distribution patterns of salinity value of 0, 10 and 20 m depths were recorded(Fig.2). The surface showed a lowest salinity of 32.29‰ at Abu Qir sector with gradual increase in the salinity values from the eastern to the western side of offshore direction with a maximum value 40.21‰ at El-Mex sector . The horizontal distribution of 10 and 20 m depths gave a minimum value 37.06‰ at Sidi Krir sector. The maximum salinity value was 39.76‰ at Eastern harbour sector. However, the highest values were in the inshore area and gradually decreased in the offshore direction.

The vertical distribution pattern of salinity along 50 m depth at station III gave values of 37.06‰ and 40.48‰ at Sidi Krir and near the bottom of El-Mex sectors, respectively. Generally, the minimum and maximum salinity values determined along all the sectors were 32.29‰ and 40.48‰ recorded at Abu Qir and El-Mex sectors, respectively. The minimum value probably attributed to the dilution caused by the discharged water coming from El-Tapia pumping station, brackish water of Lake Edku and fresh water coming from Rosetta mouth. The maximum value may reflect the high potassium, magnesium and calcium contents. Chlorine and chemical factories affect the data of El-Mex sector. However, the domestic sewage is probably due to human and animal excretion (Cole, 1979).

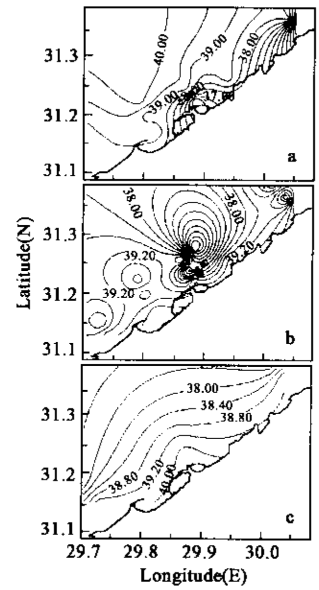

Fig. 2 Horizontal distribution patterns of salinity along Alexandria Coast in December 1996

a. surface; b. 10 m; c. 20 m

2.3 pH

The horizontal distribution patters of pH values showed two main zones(Fig.3). The first one in front of Eastern harbour sector is accompanied by increase in pH value. The second one in front of El-Mex sector is characterized by a decrease in pH values. A gradual increase in pH values from the eastern side to the western side was recorded along all the horizontal distribution patters. The minimum and maximum values of pH equal 7.98 and 8.42 at Abu Qir and El-Mex sectors, respectively.

The vertical distribution pattern of pH along 50 m depth at station III showed that the minimum pH value(8.01) recorded at Abu Qir sector, while the maximum value(8.42) at El-Mex sector. The weak alkalinity at El-Mex sector may be attributed to the photosynthesis of algae(Reid, 1967).

2.4 Calcium content and Ca/Cl relation

The horizontal distribution patterns of calcium content of surface and 10 m depth recorded an increase from the eastern to the western direction(Fig.4). The minimum and maximum calcium contents were 120.2 mg/kg and 633.3 mg/kg recorded at Abu Qir and Eastern harbour sectors, respectively. In case of 20 m depth, there was a gradual decrease in the offshore direction were the minimum and maximum calcium contents were 184.4 mg/kg and 649.3 mg/kg at Au Qir and Eastern harbour sectors, respectively.

The vertical distribution pattern of calcium content along 50 m depth at station III showed the minimum and the maximum calcium contents of 144.3 mg/kg and 649.3 mg/kg recorded at Mostafa Kamel and Eastern harbour sectors, respectively. The pattern showed an increase in the calcium content near the bottom from the eastern to the western direction.

The minimum calcium content of 120.2 mg/kg may be attributed to the dilution caused by the discharged water coming from El-Tapia pumping station, brackish water of Lake Edku and the fresh water from Rosetta mouth. Generally, the low calcium content recorded along all the studied area may be attributed to the precipitation of calcium in the structures of different forms e.g. carbonate, dolomite, aragonite, fluoroappatites and so on. The maximum calcium content(649.3 mg/kg) recorded at Eastern harbour sector, indicated the respiration of algae and bacterial activity that lead to the increase of $CaCO_3$ formation(Cole, 1979), beside the high potassium content probably contributed to the agricultural runoff from fertilized land specially El-Umum drain at El-Mex Bay. However, sodium and potassium salts increase the solubility of $CaCO_3$ even in the absence of CO_2 (Martin, 1970). The high calcium contents determined at Sidi Krir may be attributed to the deposited calcium salts(mainly $CaCO_3$) discharged the refining petroleum factories.

The minimum Ca/Cl value (0.006) recorded at Abu Qir sector may be due to the probable precipitation of $CaCO_3$, $CaMg(CO_3)_2$, $CaSO_4$, $Ca_5(PO_4)_3F$ and $Ca_3(PO_4)_2$ and so on. However, the maximum Ca/Cl value(0.030) recorded at Eastern harbour, reflected the high calcium content as discussed before.

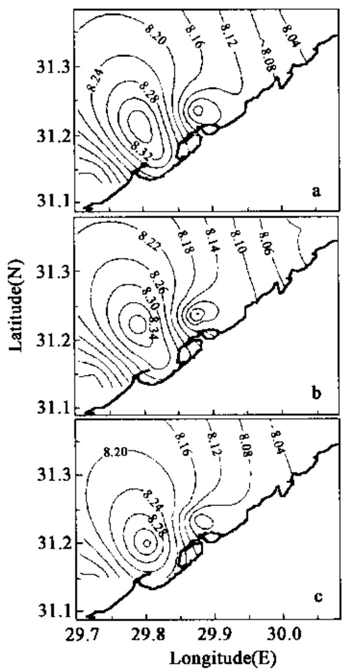

Fig.3 Horizontal distribution patterns of pH along Alexandria Coast in December 1996
a. surface; b. 10 m; c. 20 m

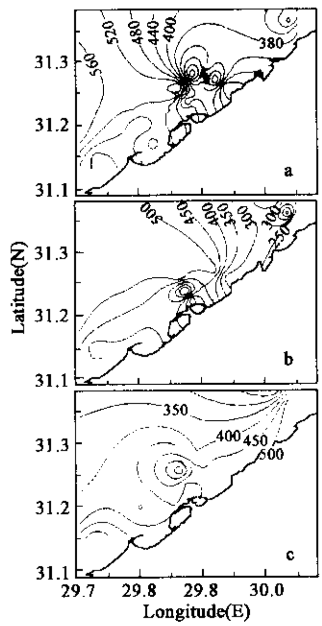

Fig.4 Horizontal distribution patterns of calcium content (mg/kg) along Alexandria Coast in December 1996
a. surface; b. 10 m; c. 20 m

2.5 Magnesium content and Mg/Cl relation

The horizontal distribution patters of magnesium content goes parallel to that of calcium(Fig.5). The minimum and maximum magnesium contents were 414.8 mg/kg and 2620.0 mg/kg at Abu Qir and Eastern harbour sectors, respectively.

The vertical distribution pattern of magnesium along 50 m depth at station III showed that the minimum and maximum magnesium contents were 512.4 mg/kg and 2410.7 mg/kg at Abu Qir and Eastern harbour sectors, respectively. There was a gradual increase in the magnesium content near the bottom from the eastern to the western direction of the studied area. The variation in the magnesium content along all the sectors may be due to the decrease of its content by precipitation, dilution of outlets, or by its increase according the external factors e.g. industrial discharged water of chemical and pharmaceutical factories, beside the bacterial activity(Cole, 1979).

The Mg/Cl assess the change on the chemical composition of coastal water seawater affected by the runoff of the discharged water. The minimum and maximum Mg/Cl values of 0.019 and 0.124 were detected at Abu Qir and Eastern harbour sectors, respectively. The lowest value of Mg/Cl is probably due to the dilution by discharged water coming from El-Tapia pumping station, brackish water of Lake Edku and fresh water of Rosetta mouth. The low Mg/Cl values may be due to the precipitation of $MgCO_3$, $MgSO_4$, hydroxylated magnesium silicate and $CaMg(CO_3)_2$ and so on. The maximum Mg/Cl reflected the high magnesium content.

2.6 Sulphate content and SO_4/Cl relation

The horizontal distribution patterns of the sulphate content at 0, 10 and 20 m depths showed that the sulphate content was gradually increased from the eastern side to the western side of the offshore area (Fig. 6). This may be attributed to the dilution caused by the outlets and the discharged water coming from El-Umum drain, El Tapia pumping station, brackish water of Lake Edku and the fresh water of Rosetta mouth. The minimum and maximum sulphate contents were 1615.3 mg/kg and 3546.7 mg/kg at Mostafa Kamel and El-Mex sectors, respectively. The data of 10 m and 20 m depths showed the same trend of its increase in the surface pattern, reflecting the external sulphate content obtained from industrial, agricultural and petroleum wastes. The minimum and maximum sulphate contents along 10 m and 20 m depths (1840.5 mg/kg and 3850.0 mg/kg) were detected at Mostafa Kamel and Sidi Krir sectors, respectively.

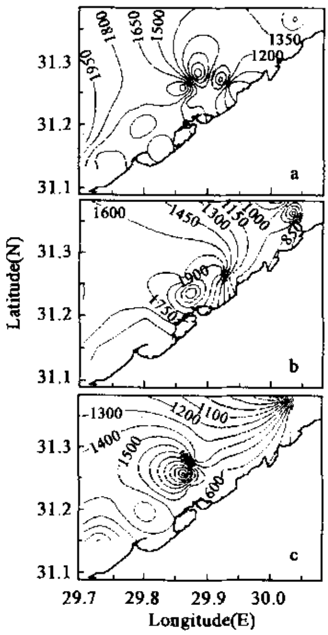

Fig.5 Horizontal distribution patterns of magneslium (mg/kg) along Alexandria Coast in December 1996
a. surface; b. 10 m; c. 20 m

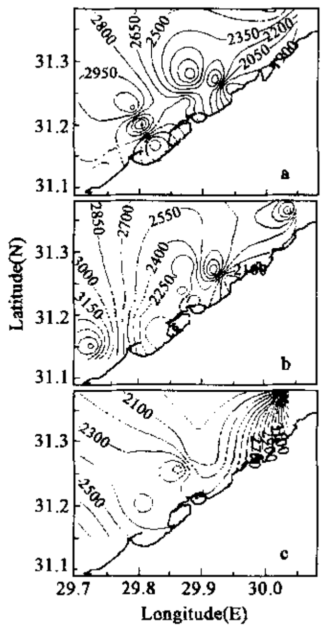

Fig.6 Horizontal distribution patterns of sulphate content (mg/kg) along Alexandria Coast in December 1996
a. surface; b. 10 m; c. 20 m

The vertical distribution pattern of sulphate along 50 m depth at station Ⅲ showed that the maximum sulphate contents were recorded near the bottom of Sidi Krir and El-Mex sectors, reflecting that the high sulphate content accompanied to refining petroleum factories and other factories (e.g. paper, coal, agricultural fertilizers, etc.). The minimum and maximum sulphate contents (1602.1 mg/kg and 4344.5 mg/kg) were recorded at Mostafa Kamel and Sidi Krir sectors, respectively. Sulphate content suffers a large variation along all the water columns of all the studied sectors. The low sulphate contents may reflect the dilution caused by the outlets, El-Tapia pumping station, brackish water of Lake Edku and fresh water coming from Rosetta mouth. The formation of $CaSO_4 \cdot 2H_2O$ (gypsum) and $MgSO_4 \cdot 7H_2O$ (epsomite; Cole, 1979) can be taken as an extra arguments. This may be related to the reduction of sulphate to sulphide by anaerobic bacteria with the evolution of H_2S (Culkin, 1965). The precipitations of metal sulphides especially pyrite (FeS_2) may be accompanied to its low content (Cole, 1979). The presence of nitrosonaphthol and azo compounds by Esmadye, Kafr El-Dawar, Egypt, may be one of the factors that lower the sulphate content. However, these compounds have the ability to reduce sulphate in the presence of some transition metals forming some precipitated compounds. The high sulphate content recorded along the water columns of the studied area may be accompanied to sulphur oxidizing microbes' (Cole, 1979).

This may be related to the discharged waters containing untreated wastes of the fertilizers (superphosphate may contain up to 20% of $CaSO_4$) (Beauchamp, 1953) and paper manufacturing refining petroleum factories and aluminum and copper smelting. The use of copper sulphate as a fungicide in controlling the alga blooms in Nile Delta Lakes (Nady, 1996) causes high sulphate content.

The SO_4/Cl can be regarded as a constant value of 0.1400 (S‰ = 35.000, and Cl‰ = 19.374) in surface and deep waters of ocean (Morris, 1966). The minimum and maximum SO_4/Cl values were 0.035 and 0.200 recorded at Mostafa Kamel and Sidi Krir sectors, respectively. The minimum values of SO_4/Cl may be related to the dilution factor of the discharged water, the decomposition of organic matter, and the precipitation of sulphate ion as $CaSO_4$, $MgSO_4 \cdot 7H_2O$ (Cole, 1979). The maximum SO_4/Cl is attributed to the El-Umum drain, which contains large sulphate content according to its agricultural and industrial wastes. Refining petroleum's wastes, also, play an important role in increasing SO_4/Cl especially in Sidi Krir sector.

2.7 Fluoride content and F/Cl relation

The horizontal distribution patterns of fluoride content at 0, 10, and 20 m depths were in harmony with pH's, reflecting that there is a great relation between pH and fluoride content (Fig.7), the data for fluoride at surface, 10 and 20 m depths decreased from the eastern to the western side of the offshore of the studied area. The high fluoride contents were recorded at the inshore area reflecting that the effect of the fluoride of the discharged water on the chemical composition of the coastal water of the studied area. However, the discharged water may contain CaF_2, fluoroapatite that occur as natural impurity in ores to produce phosphoric acid (Hamza, 1986). Also, hydrofluosilicic acid (H_2SiF_6) and sodium silicoflouride (Na_2SiF_6) and most fluoride are byproducts of phosphoric acid manufacture. It is the main gradient of phosphate fertilizer (Pontius, 1990). Fluoride is also produced during the manufacturing of toothpaste, where SnF_2 and sodium monofluorophosphate are used. Fluoride pollution from aluminum smeltert are in the form of gaseous HF, and in particulate forms as Al_2O_3 with adsorbed HF, $NaAlF_4$, $Na_5Al_3F_{14}$ (chiolite), Na_3AlF_6 (cryolite), AlF_3, NaF, KF and CaF_2 (Arnesen, 1998a; 1998b; Gurdeep, 1999; Harbo, 1974). Fluoride can be introduced into the seawater from the waste water contains textile, fertilizer rayon, paper, and pulp aluminum smelters, chemical and pharmaceutical industries (Zingad, 1988). The minimum and maximum fluoride contents (1.36×10^{-3} g/kg and 3.10×10^{-3} g/kg) were recorded at Mostafa Kamel, eastern harbour and El-Mex sectors, respectively.

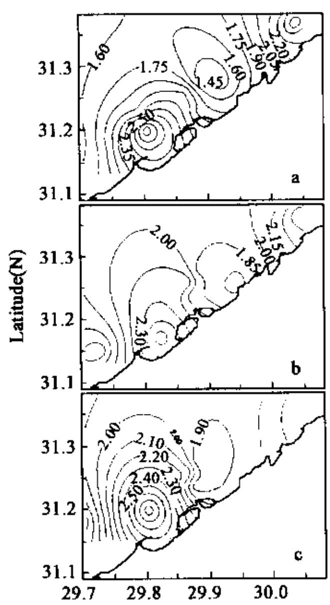

Fig.7 Horizontal distribution petterns of fluoride content (mg/kg) along Alexandria Coast in December 1996
a. surface; b. 10 m; c. 20 m

The vertical distribution pattern of fluoride along 50 m depth at station Ⅲ gave a minimum and maximum fluoride contents of 1.39×10^{-3} g/kg and 2.44×10^{-3} g/kg recorded at Sidi Krir and Eastern harbour sectors, respectively (Fig.8). The highest values of fluoride contents were recorded at Abu Qir and El-Mex sectors, of mean values 2.35×10^{-3} g/kg and 2.56×10^{-3} g/kg. These two mean values of fluoride are approximately twice higher than that recorded for open seawater (Krumgatz, 1990). This may reflect the high fluoride content in the discharged waters that contain untreated wastes of fertilizers, textiles, dyes, papers, weaving, chemicals, pharmaceutical industries, aluminum smelters beside the sewage and agricultural wastes. The high fluoride content recorded at deep waters may reflect the dissolution of minerals at water sediment interface (Kullenberg, 1973). The low fluoride content values along all the sectors may de due to its precipitation as CaF_2 (*Ksp* equals 3.95×10^{-11}) (Martin, 1970) and $Ca_5(PO_4)_3F$. However, calcium phosphate minerals and calcium phosphate hydroxyapatite undergo conversion to other minerals (fluroapatite and francolite [$Ca_5(PO_4, CO_3)_3$]) (Martin, 1970). Fluoride may precipitate as MgF^+ (Brewer, 1970). It appears, therefore, that fluoride in the studied area is lost to the sediments probably in association with magnesium ion or with the formation of appatites or both (Brewer, 1970).

The F/Cl can be taken as a key to record the pollution phenomena and the dilution by river system (Harbo, 1974). The minimum and maximum F/Cl values were 6.3×10^{-5} and 14.4×10^{-5} recorded at Eeastern harbour and El-Mex sectors, respectively. The low F/Cl may be due to the removal of fluoride by precipitation or the high chlorinity or both. The high F/Cl values may reflect the dilution of fluoride from an external source (agricultural, industrial or sewage sources), the dissolution of minerals at water sediment interface (Kullenberg, 1973), and the low chlorinity or both.

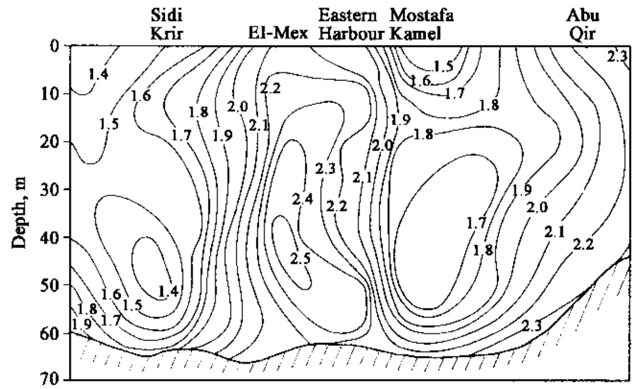

Fig.8 Vertical distribution pattern of fluoride content (mg/kg) along 50 m depth of Alexandria Coast at station Ⅲ in December 1996

2.8 Ion chlorinity relationship in seawater

The relation between chlorinity and the content of each of the different ions (mg/kg) report that all the major conservative constituents ions of open seawater are of constant values of chlorinity ratio, this is lost in the systems under discussion (Morris, 1966). Their concentrations were different along the same chlorinity in all stations and at different columns. These results reflect that the studied shores are expected to obtain large quantities of pollutants that may change the chemical composition of coastal water.

2.9 Data analysis of seawater of Alexandria coastal water

A stepwise regression model between the fluoride content as a dependent parameter and some important physico-chemical as independent parameters (F/Cl, S‰, Cl‰, Mg/Cl and Mg^{2+}) is highly significant ($r = 0.999$, $P < 0.05$, $n = 44$). The regression model was given as follows:

$$[F^-] = -0.0384 + 1.023\ F/Cl + 1.36\ S‰ + 0.038\ Cl‰ - 0.312\ Mg/Cl + 0.311\ [Mg^{2+}].$$

The data of the observed and the calculated fluoride content (by stepwise regression equation) are diagrammed in Fig.9. It seems that, the model is fruitful, where the observed and calculated values were very close to each other. Accordingly, the type of water probably affects the fluoride content whether it is of seawater or diluted by the discharged water. The good relation between fluoride and Mg^{2+} reflects the presence of MgF^+ ion pair, however, about 50% of fluoride is presented as MgF^+ (Kullenberg, 1973).

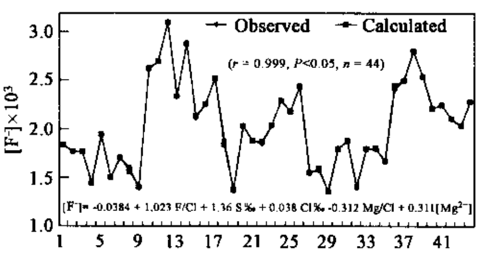

Fig.9 Distribution of the fluoride content (g/kg) at different stations along Alexandria Coast in December 1996

High positive significant correlation coefficient values (r) obtained from the correlation matrix of all Alexandria coastal water samples ($n = 44$, $P < 0.05$). Good relation between fluoride content and F/Cl ($r = 0.9783$) was obtained. This may reflect that the domestic sewage contains high fluoride content (Choubisa, 1996) and also the discharged water may contain high amounts of fluoride content. Positive correlation between pH and F^- ($r = 0.3455$), was obtained reflecting the precipitation of F^- as MgF^+ ion pair or apatite by its association with large amount of phosphate(Kullenberg, 1973) .

In Sidi Krir sector, the correlation between F^- and SO_4^{2-} was of opposite trend($r = -0.7305$, $P < 0.05$, $n = 9$), probably due to the possible existence Ca^{2+} or Mg^{2+} with different stabilities. The presence of some refining petroleum companies probably adds excess quantities of reported sulphato compounds (Goldberg, 1974).

3 Conclusions

Fluoride and some parameters (physical and chemical) were determined along Alexandria coastal Mediterranean sea water of Egypt. Stepwise regression analysis was highly significant and the model was very fruitful. Temperature, salinity, pH, ratios of Ca/Cl, Mg/Cl, SO_4/Cl, F/Cl were determined and explained. The chemical composition is changeable due to the discharged waters containing industrial wastes, sewage and agricultural and domestic drainage.

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