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FULL LENGTH ARTICLE

The effect of fluoride on the distribution of some minerals in the surface water of an Egyptian lagoon at the Mediterranean Sea

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Abstract The seasonal fluoride distribution in surface waters along Lake Edku and in the supplying land drains, as well as its effect on the formation of carbonated and fluoridated minerals were investigated. The data revealed that fluoride's content was affected by the chlorinity value of two feeding sources of water in Lake Edku, which were the seawater from El-Maadiya inlet and drainage water from land drains. Fluoride in surface water showed average contents of 0.62–1.59, 0.44–1.53, 0.13–1.07 and 0.23–1.17 mg/l in winter, spring, summer and autumn, respectively, with an annual average concentration of 0.8 ± 0.1 mg/l. The annual average of the saturation index (SI) of carbonated (calcite, aragonite and dolomite) and fluorapatite minerals along Lake Edku had values that exceeded the unity and referred to the over saturation of the lake water in respect to these minerals. In contrast, the average annual SI of fluorite and sellaïte gave values lower than unity. That indicated the under saturation in respect to these two minerals. The high saturation index values for fluorapatite may be related to the low solubility of calcite in apatite supernatants in alkaline conditions. Interestingly, the formation of the fluorapatite mineral leaves a small concentration of it, and that protects Lake Edku's ecosystem from the destructive impact of fluoride pollution.

Introduction

Fluorine is presented in aquatic ecosystems as fluoride (F^-). However, in volcanic emissions, marine aerosols and weathering of minerals some of its natural sources [Fluorite (CaF_2), cryolite (Na_3AlF_6) and fluorapatite ($Ca_5(PO_4)_3F$)] are present (Camargo, 2003). The concentration of fluoride in uncontaminated freshwater's ecosystems ranges from 0.01 to 0.3 mg/l (Camargo, 2003; Rosso et al., 2011). Fluoride is found in seawater in the forms of MgF^+ (46%), CaF^+ (2%) and F^- (51%) with a concentration of 1.3 mg/l (Liteplo et al., 2002). Fluoride can exceed its ranges that exist in aquatic systems when found in regions that contain geothermal and volcanic activities (Tekle-Haimanot et al., 2006). Its extremity is used in the production of some industrial products such as, fertilizers, graphite, semiconductors, and alumina electrolysis (El-Said

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and Draz, 2010). High levels of fluoride in freshwater ecosystems are harmful for aquatic organisms, animals and particularly humans (El-Said and Sallam, 2008; Naim et al., 2012). Freshwater animals are more affected by fluoride toxicity than both algae and macrophytes are (Camargo, 2003). Its high levels affect many physiological processes that lead to growth inhibition, change in enzymatic metabolism, bone abnormalities as well as delay in the hatching of fertilized eggs (CCME, 2002; Camargo, 2003; Moren et al., 2007; Shi et al., 2008). National Organic Standards (NOS) stated an environmental safety rule in March 2000 allowing the use of pesticides that contain fluoride (Masoud and El-Said, 2011). In contrast, US Department of Agriculture (USDA) opposed this rule and ended it in December 2000 because of the persistence and the inability of fluoride to degrade, causing it to accumulate in soil, organisms as well as in humans (Ellen and Connett, 2001).

Fluorite CaF_2 and sellaïte MgF_2 are considered as other natural fluoride minerals that can form in waters (Nezli et al., 2009). The high abundance of fluoride in sedimentary rocks and the presence of phosphorus could possibly lead to the formation of fluorapatite (Masoud and El-Said 2011). Fluorite and fluorapatite are considered the main fluoride minerals that exist in the phosphatic basins of rocks. Fluoride can combine with calcium carbonate minerals (aragonite or calcite) to form fluorapatite compounds (Okumur et al., 1983; El-Said et al., 2010; El-Said and Draz, 2010). The coprecipitation of fluoride ion with calcium carbonate is affected by many factors such as the crystal structure of calcium carbonate, the presence of certain cations (Mg, Cu, Zn, etc.) and some organic compounds (citrate, malate, lactate, etc.) as well as the process of carbonates' precipitation.

The dissolution of the minerals in water systems is controlled by the type of mineral and the properties of the solution which include the pH, ionic strength, temperature, type and concentration of other chemical species present in the solution (Clifford et al., 2006). Dissolved minerals can perform chemical processes such as complexation, hydrolysis, adsorption and precipitation. The equilibria of these reactions are complex and play an important role in expecting the possible formed species and the process of their performance (flotation, flocculation, etc.) in aqueous systems (Amankonah et al., 1985).

This work focuses on the evaluation of fluoride concentration and its effect on the formation of some mineral species in the water of Lake Edku.

Materials and methods

Area of study

Lake Edku extends between latitudes 31°10′ and 31°18′N and longitudes 30°80′ and 30°22′E with an area of ≈126 km^2 (Soliman, 2005; Fig. 1). El-Maadiya inlet connects Lake Edku to Abu-Qir Bay at its north western region. The lake is mostly vegetated especially with *Potamogeton* and *Eichormia crassipes* that cause difficulties in navigation (El-Sarraf et al., 2001). It is a shallow lake with depths of 0.4–1.5 m and average of 1 m (El-Said et al., 2014). The transparency of the lake water changes from clear to very turbid, and the areas of anoxic water are characterized by the hydrogen sulfide odor (Badr and Hussein, 2010). The lake is affected by 142×10^6 m^3 drainage effluents from Kom Belag and Bersik at its eastern and southern regions, respectively (Moneer et al., 2012). The first drain, Bersik, in the southern part is influenced by agricultural drainage water (Shakweer, 2006). Meanwhile, the second one Kom Belag is in the eastern side and is affected by agricultural, domestic, and industrial wastes discharged from other drains (Bosily, Edku and Khiery) along with the wastes of more than 300 fish farms (Youssef, 2003).

Sampling and chemical parameters' determinations

The investigated area was described by fourteen sampling sites located in the lagoon (Lake Edku) and outside in the sources of drains (Edku, Khiery and Berzik; Fig. 1). Location 1 represented the center of El-Maadiya region, while locations 2–4 and 11 are influenced by the Abu-Qir seawater coming from El-Maadiya channel. Sites 5–10, in the center of the lagoon, receive the drainage waters from the southern and eastern drains. Locations 12–14 described the characters of drainage waters of the main drains outside the lake. Seasonally, the surface lake water samples were gathered from studied stations in Lake Edku during January–November 2010 using a motor

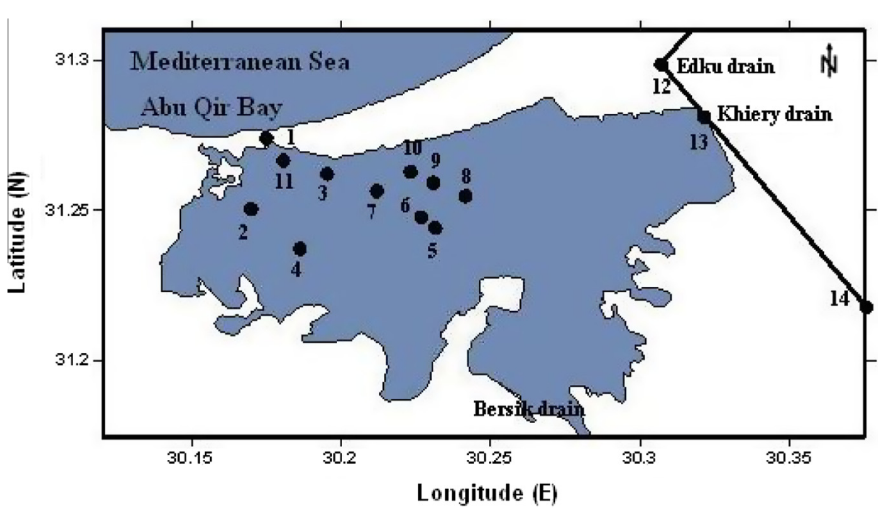

Figure 1 Sampling location in Lake Edku.

boat equipped with necessary tools. In each season, the water samples were preserved in clean poly ethylene bottles and were immediately protected in an ice box during their transportation to the lab. In the lab, the samples were kept frozen at −20 °C till measurements.

Fluoride ion concentration was analyzed using the colorimetric procedure of zirconium alizarin red S (Courtenary and Rex, 1951; Masoud et al., 2004). Calcium and magnesium were determined by EDTA titration (APHA–AWWA–WPCF, 1999). Phosphorus content was evaluated by the colorimetric method (Strickland and Parson, 1965). Total alkalinity was measured using a potentiometric titration with an open cell system (Dickson et al., 2007). Total alkalinity (TA) was measured using the open cell potentiometric titration system (Dickson et al., 2007). TA calibration was carried out using certified reference material CRM batch 15 made by Dickson. The pH was measured on a total scale by a pH meter (Jenway 3505; accuracy pH ±0.02) using tris- buffer. Carbonate and bicarbonate concentration (CO_3, HCO_3) were calculated by applying the software package CO_2SYS to inorganic carbon system parameters.

Water chlorinity (Cl) values were calculated based on the use of salinity values as follows (Strickland and Parsons, 1965):

$$\text{Salinity} = 0.03 + (1.8050 \times \text{Cl}) \quad (1)$$

The saturation index (SI) for each mineral species was calculated as the product of the ion activity of the component (IAP) divided by its equilibrium solubility constant (K_{sp}) at 25 °C as shown in Eqs. (2) and (3) (Chidambaram et al., 2011). However, the K_{sp} values of calcite, aragonite, dolomite, fluorite, sellaïte and fluorapatite were 3.36×10^{-9}, 6.0×10^{-9}, 1×10^{-11}, 3.45×10^{-11}, 5.16×10^{-11} and 1×10^{-60}, respectively (Faculty of Chemical Technology in Split, 2003). SI < 1 represented the water under saturation with a specified mineral, while, SI > 1 referred to the water of over saturation with the presented mineral:

$$\text{SI} = \log\left(\frac{\text{IAP}}{K_{sp}}\right) \quad (2)$$

For example the saturation index calculation for fluorite can be applied by the following Eq. (3):

$$\text{SI}_{\text{fluorite}} = \log\left(\frac{[\text{Ca}^{+2}][\text{F}^{-}]^2}{3.45 \times 10^{-11}}\right) \quad (3)$$

Statistical analyses

The statistical analyses of the correlation matrix and multiple regression equations for the data were performed by Statistica version 5.0. Statistical analyses were conducted for the seasonal levels of pH, fluoride concentration in the lake water and saturation indices of minerals (calcite, aragonite, dolomite, fluorite, sellaïte and fluorapatite) at a significant level of $\alpha = 0.05$.

Results and discussion

The seasonal variation of different determined parameters

The seasonal variation of pH shows its gradual decrease from the inlet of seawater (El-Maadiya) to the middle of the lake (stations 1–7 and 11). Lower values are recorded in stations 8–9 (in front of the stream of the discharged water coming from the Khiery Drain into the entire lake). Low pH values are determined in the drainage waters (Edku Drain, Khiery Drain and Bersik Drain) in stations 12–14. pH levels in Lake Edku are on the alkaline side during winter, spring, summer and autumn (7.2–8.8, 7.1–8.6, 7.8–8.8 and 7.2–8.3, respectively, with annual range of 7.4–8.5; Table 1). These values differ from those determined during 1996 (6.82–9.44; El-Sarraf et al., 2001; El-Said, 2005). The seasonal values of pH are significantly correlated with the saturation index of both calcite ($r = 0.744$; $p = 0.000$) and aragonite ($r = 0.7435$; $p = 0.000$) along the lake area. Accordingly, the variability in pH along stations at different seasons is found to be related to many factors including, photosynthetic activity, carbonate concentration, carbon dioxide level, and oxygen content as well as the discharged water components (Chernet et al., 2001).

The chlorinity of Lake Edku is affected by sources of water drainage that are dumped into the lake (Edku, Khiery and Bersik land drains) as well as marine water from El-Maadiya inlet section. Among all the investigated stations of the lake, El-Maadiya (Station 1) is the only station that gives the highest chlorinity levels. The seasonal ranges of chlorinity during winter, spring, summer and autumn are 4.0–4.6, 0.4–16.6, 0.3–1.3 and 0.8–4.2 g/kg respectively and with annual average of 2.4 ± 1.4 g/kg (Table 1). In general, higher values are determined at the stations inside the lake area (stations 2–11), while the lower ones are determined in the drainage sources outside the lake (stations 12–14). The present chlorinity values relatively differ from those reported in 1996 (0.28–18.15 g/kg; El-Said, 2005). This may be attributed to the increase in the amount of discharged land waters into the lake.

The distribution of carbonate content in the surface water of Lake Edku reflects the effect of drainage water on the studied area. However, its low values are recorded in the drains and the stations that are affected by the discharged waters (Table 1). The carbonate content of the draining water ranges between 1.0 mg/l at station 12 (Edku Drain) and 3.3 mg/l at station 13 (Khiery Drain) during winter and summer, respectively. Obviously, the high carbonate contents are determined in the stations which are affected by the flow of sea water into the lake (stations 1–7). The seasonal average range of carbonate contents and the annual average levels are 1.7–46.8 and 12.3 ± 10.2 mg/l respectively (Table 1). The harmony distribution of both carbonate and pH values along the investigated area is related to the quality and flux of the feeding water (Shaltout, 2008).

The levels of phosphorus along the lake area show average seasonal variations 0.03–0.15 of average annual value 0.09 ± 0.04 mg/l (Table 1). Generally its high levels in the lake water are distributed in the drains (stations 12 and 13) and the locations in front of the discharge water sources (stations 7–10) due to the presence of agricultural wastes (El-Said et al., 2014). The change in the phosphorus contents may also be attributed to the biological activities of organisms such as phytoplanktons, bacteria and aquatic animals (El-Said, 2013).

Stations 1, 2 and 11 at the entrance of the lake revealed the high average contents of calcium and magnesium (190.4, 128.3 and 154.3 and 413.3, 263.8 and 295.4 mg/l, in stations 1, 2, and 11 respectively; Table 1) caused by the mixing of the entering seawater with lake water. The rest of the stations, inside and outside the lake, record low average seasonal levels for calcium and magnesium that range from 55.1 to 85.2 and 107.6 to

Table 1 Range and average of seasonal and annual variation of the determined parameters and saturation index (SI) values of the minerals in Lake Edku during 2010.

Station	Cl‰ (g/kg)	pH	CO_3 (mg/l)	P (mg/l)	Ca (mg/l)	Mg (mg/l)	F (mg/l)	Calcite	Aragonite	Dolomite	Fluorite	Sellaite	Fluorapatite
1	3.1[a]	7.7–8.7[b]	16.3[a]	0.07[a]	190.4[a]	413.3[a]	1.0[a]	2.1[a]	1.9[a]	4.6[a]	−0.9[a]	−0.3[a]	33.8[a]
2	1.9	7.8–8.6	19.6	0.07	128.3	263.8	0.9	2.7	2.4	5.2	−0.8	−0.6	40
3	2.1	8.4–8.7	20.4	0.05	85.2	157.4	0.7	2.6	2.4	5.1	−1	−0.9	40.1
4	1.9	8.0–8.7	23.9	0.07	68.1	141.0	0.8	2.6	2.3	5.1	−1.5	−1.3	39.3
5	1.7	7.6–8.8	21.1	0.03	78.2	144.6	0.5	2.5	2.2	5	−1.1	−0.9	39.5
6	1.8	7.8–8.8	15.1	0.08	81.2	124.6	0.8	2.4	2.2	4.9	−1.2	−1	39.4
7	2.0	8.0–8.7	20.3	0.11	72.1	126.4	0.7	2.5	2.3	5.1	−1.2	−1	38.9
8	1.6	7.1–8.1	6.5	0.14	74.1	121.6	0.9	1.9	1.6	4.4	−1	−0.8	39
9	1.7	7.4–8.0	4.6	0.15	61.1	108.8	0.7	1.8	1.5	4.3	−1.5	−1.3	40.7
10	5.4	7.2–8.2	8.2	0.12	67.1	134.3	0.7	2	1.7	4.5	−1.3	−1.1	39.7
11	1.5	7.2–7.9	9.1	0.06	154.3	295.4	0.7	2.4	2.2	5	−0.9	−0.6	39.7
12	5.4	7.2–7.9	1.7	0.11	77.2	150.1	0.8	1.8	1.6	4.3	−1.1	−0.9	46.8
13	1.5	7.2–7.9	2.4	0.13	69.1	123.4	0.8	1.6	1.4	4.1	−1.1	−0.9	62.5
14	1.6	7.3–7.8	2.4	0.08	55.1	107.6	0.8	1.5	1.2	4	−1.1	−0.9	61.2
Range	1.5–5.4	7.4–8.5	1.0–46.8	0.03–0.15	55.1–190.4	107.6–413.3	0.5–1.0	1.5–2.7	1.2–2.4	4.0–5.2	1.5 to −0.8	−1.3 to −0.3	33.8–62.5
Average ± S.D.[c]	2.4 ± 1.4		12.3 ± 10.2	0.09 ± 0.04	90.1 ± 39.4	172.3 ± 89.0	0.8 ± 0.1	2.2 ± 0.4	1.9 ± 0.4	4.7 ± 0.4	−1.1 ± 0.2	−0.9 ± 0.3	42.9 ± 8.5

[a] Seasonal average of parameter.
[b] Range of seasonal variation of parameter.
[c] Average annual variation of parameter.

157.4 mg/l respectively. The values of calcium and magnesium along Lake Edku are obviously lower than those reported for open seawater (411.9 and 1294.0 mg/l, respectively; El-Sarraf et al., 2003) with average annual contents of 90.1 ± 39.4 and 172.3 ± 89.0 mg/l respectively. The variation in calcium and magnesium could have possibly been related to the formation and dissolution of minerals, pH value, CO_2 level, phototropic species, presence of potassium and sodium salts that increase $CaCO_3$ solubility, as well as the reaction of phosphate ion with Ca^{+2} to form calcium phosphate (Reid, 1966; El-Said, 2013). The lake area is also affected by the dilution of the drains' discharged waters especially at the eastern and southern regions (El-Sarraf et al., 2001; Abdel Ghani et al., 2013; El-Said et al., 2014). Interestingly, the concentrations of calcium and magnesium are lower than those reported in 1996–1997 (123–104 and 306–208 mg/l respectively; El-Sarraf et al., 2001) and relatively similar to those recorded during 2009–2010 by Abdel Halim et al. (2013).

The seasonal horizontal contour maps of fluoride contents are in harmony with those for the chlorinity contents. This indicates the great effect of the supplied water types (sea and drainage waters) on the fluoride distribution in the lake region. However, the supplied seawater from El-Maadiya region induces stations 1–4 to show higher fluoride contents than those inside the lake basin (Fig. 2). Meanwhile, the amounts of untreated discharged waters at stations 12–14 explain their fluoride levels. Fluoride enters the lake from El-Maadiya inlet during winter, spring and autumn by the action of the wind and water currents. The annual average record of fluoride content at station 1 is 1.03 ± 0.65 mg/l which is relatively similar to its level in seawater (1.3 mg/l; El-Sarraf et al., 2003). During winter and spring seasons, fluoride content shows two gradual decreases in the extremely northwestern and eastern sides of the lake, which are affected by the entrance of the sea and drainage waters. Lower levels however, are determined in the middle of the lake region. The opposite trend is observed in summer and autumn. The lower fluoride levels in the lake may have been accompanied with several factors including, the uptake of organisms (Camargo, 2003; El-Said and Sallam, 2008; El-Sikaily and El-Said, 2010; El-Said and El-Sikaily, 2012; Hansen et al., 2012), adsorption onto bottom sediment (El-Said et al., 2010; El-Said and Draz, 2010; Youssef et al., 2014), precipitation in the form of sparingly soluble magnesium complex and formation of its minerals (fluorite, fluorapatite, francolite, etc.; Martin, 1970; El-Said et al., 2010). Its seasonal levels in winter, spring, summer and autumn are 0.62–1.59, 0.44–1.53, 0.13–1.07 and 0.23–1.17 mg/l, respectively, with an average annual concentration of 0.8 ± 0.1 mg/l (Table 1).

Saturation index of carbonated minerals

The average saturation index (SI) of calcite, aragonite and dolomite minerals along Lake Edku has values >1, with annual average levels of 2.2 ± 0.4, 1.9 ± 0.4 and 4.7 ± 0.4, respectively (Table 1). Accordingly, the SI values refer to the over saturation of the lake area in respect to these minerals and their incapability to dissolve. Moreover, the saturation index of calcite, aragonite and dolomite gives similar horizontal distributions. Their values however, decrease from the western side to the eastern side of the lake

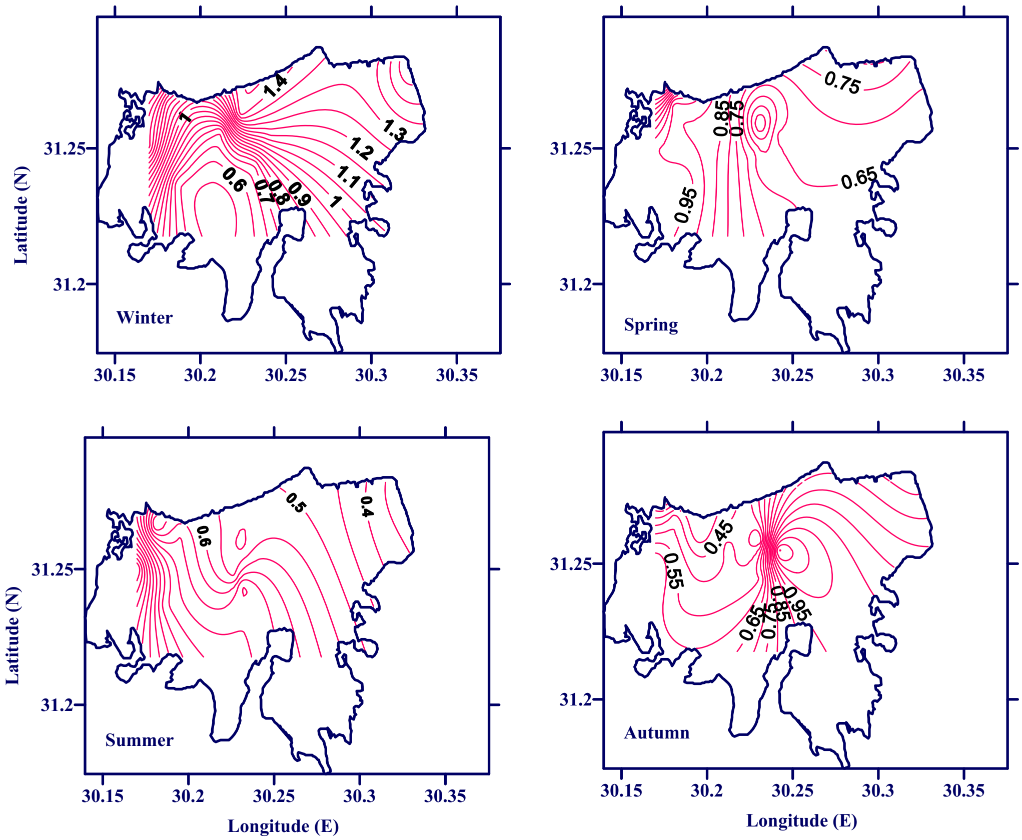

Figure 2 The contour maps of the seasonal fluoride variability (mg/l) in Lake Edku.

region (Fig. 3). This indicates the effect of seawater on the production of these minerals. Lake Edku however contains brackish water. The carbonate precipitation increases proportionally with the alkalinity of water however, reflects the character of the common ion, which is calcium (Nezli et al., 2009). It was also stated that calcite is less soluble in apatite supernatant solutions (Amankonah et al., 1985). The similar distributions of carbonated minerals are confirmed by the high significant correlations of calcite & aragonite ($r = 0.827$; $p = 0.000$), calcite & dolomite ($r = 0.827$; $p = 0.000$), aragonite & dolomite ($r = 1.000$; $p = 0.000$) and calcite & pH ($r = 0.664$; $p = 0.000$).

Saturation index of fluoridated minerals

The average SI values of fluorite and sellaïte minerals show similar trends inside the lake (Fig. 4). However, two decreasing zones are observed in the middle of the lake. The fact that their average SI values are less than unity indicates that the lake water is under statured in respect to fluorite and sellaïte minerals with average annual values of -1.1 ± 0.2 and -0.9 ± 0.3, respectively (Table 1). In contrast, SI of fluorapatite has values that are more than unity along the entire studied basin and has an average annual value of 42.9 ± 8.5 (Table 1). That, indicates the over saturation of the lake water with fluorapatite. It is also observed that the saturation pattern decreases gradually from the western side to the eastern side of the lake (Fig. 4). This trend is compatible with the phosphorus apatite contents in Lake Edku (Khalil, 2008). It was reported that phosphorus apatite represented an average 56% of the sum of the phosphorus contents and that PO_4 was the main storage form in Lake Edku sediments. Additionally, the high contents of phosphorus apatite (320–404 ppm) detected in the eastern part of the lake were related to the continuous discharged waters from the drains (Khalil, 2008). Saturation index values of fluoridated minerals in the lake water reveal over saturation (precipitation) by the fluorapatite ($Ca_5(PO_4)_3F$) and under saturation by the fluorite (CaF_2) and sellaïte (MgF_2) in all lake water samples. Accordingly, the values of saturation index reveal the possible relationship between fluoride and phosphate and the formation and precipitation of the minerals in the lake system (Nezli et al., 2009). The relation pH–SI of correlation matrix shows the saturation index pointing toward the fluorapatite ($SI \gg 0.5$). However, the fluorite and the sellaïte decrease as the pH increases (Nezli et al., 2009) and fluorapatite dissolution rate decreases with an increasing pH (Guidry and Mackenzie, 2003). Organic phosphorus may have also coincided with precipitations of both calcium carbonate and fluorapatite (Reimers et al., 1996). This is confirmed by the high significant relations of fluorite & sellaïte ($r = 0.963$; $p = 0.000$) and fluorite & fluorapatite ($r = 0.427$; $p = 0.001$). Additionally, the formation of the fluoride minerals are strongly correlated with the chemical composition of supplying waters (sea and drainage waters) including fluoride concentration [fluorite & fluoride ($r = 0.929$; $p = 0.000$), sellaïte & fluoride ($r = 0.876$; $p = 0.000$), fluorapatite & fluoride ($r = 0.552$; $p = 0.000$)] and chlorinity [fluorite & Cl ($r = 0.368$; $p = 0.005$) and sellaïte & Cl ($r = 0.411$; $p = 0.002$)]. The

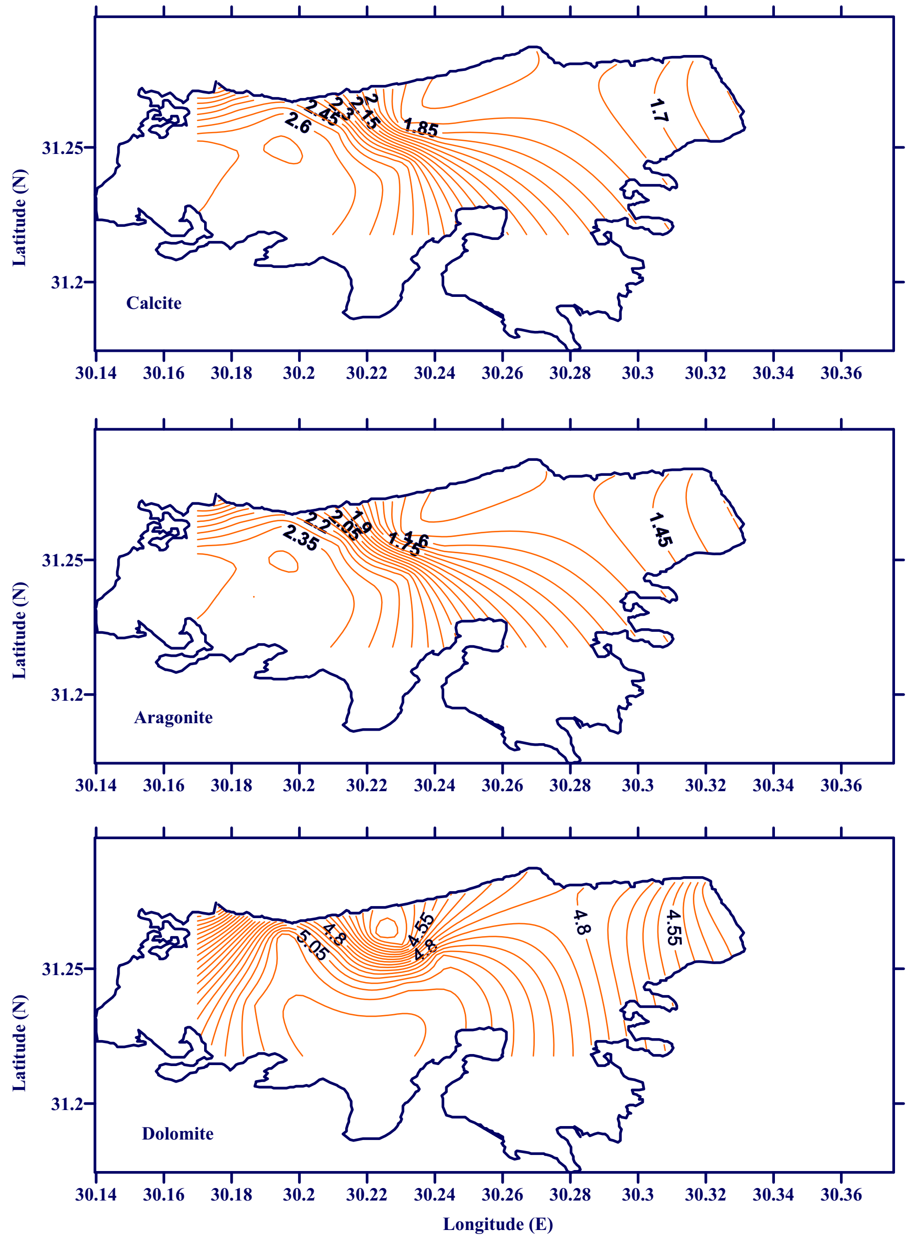

Figure 3 The contour maps of the annual average saturation index of calcite, aragonite and dolomite minerals in Lake Edku.

positive relation between F^- and fluorite ($r = 0.929$; $p = 0.000$) can explain the mass law equation relating to calcite and fluorite when both are in contact with water (Mamatha and Rao, 2010; Dey et al., 2012):

$$CaF_2(s) + HCO_3^- \rightarrow CaCO_3(s) + H^+ + 2F^-$$

Furthermore, it was recorded that in alkaline waters ($7.6 < pH < 8.7$) ionic exchanges between fluorinated minerals and the hydroxyl group (OH^-) can be performed and the solubility of fluoride can be increased (Nezli et al., 2009). It was also viewed that under high pH conditions the apatite supernatants dominantly consisted of phosphate species. The decrease in the calcite solubility in alkaline conditions could therefore be attributed to the phosphate species (Amankonah et al., 1985). This reflects that calcite is more stable in the presence of phosphate than in pure water, indicating that, precipitation of $CaCO_3$ is favored in solutions that are characterized by apatite and calcite equilibria (Amankonah et al., 1985). The precipitation of a more stable solid phase can, among other factors, reduce the calcium activity in the solution systems. Moreover, fluoride and calcium concentrations in the study area may be controlled by fluorite solubility (Salifu et al., 2012). Consequently in areas containing high calcium ion concentrations that resulted from the geochemical processes, calcium may play a critical role in the distribution of fluoride in lake water. The dissolution of fluorite may be suppressed when the concentration of Ca is above the limit for fluorite solubility, resulting in low fluoride content (Chae et al., 2007; Mamatha and Rao, 2010; Salifu et al., 2012).

The multiple regression analysis of pH, chlorinity, fluoride, carbonated and fluorinated minerals contents is measured as shown in the following equation:

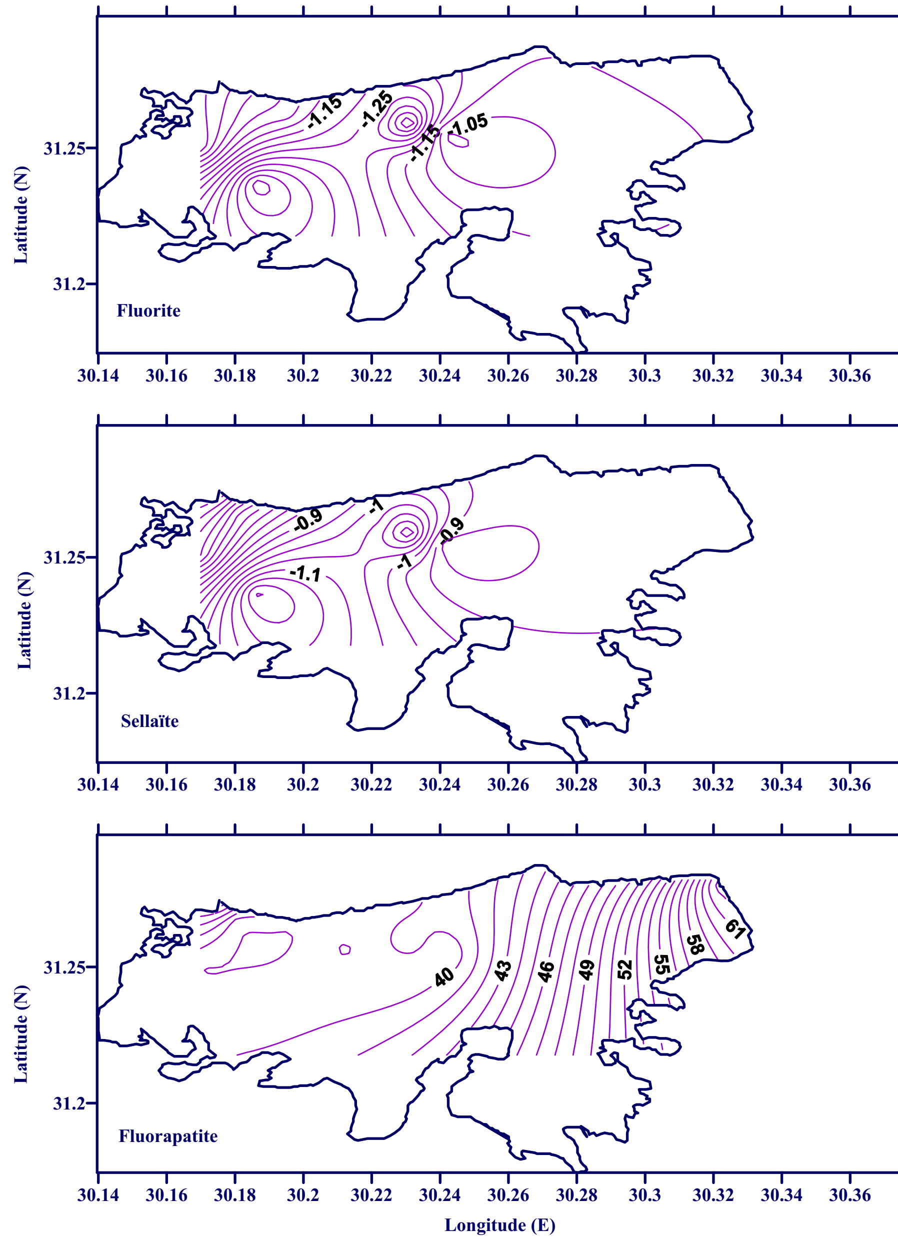

Figure 4 The contour maps of the annual average saturation index of fluorite, sellaïte and fluorapatite minerals in Lake Edku.

$$F = 1.31 + 0.50\ \mathbf{fluorite} + 0.26\ \mathbf{fluorapatite} - 0.13\ \mathbf{dolomite} - 0.12\ \mathbf{Cl} + 0.40\ \text{sellaite} \quad (R = 0.963;\ p < 0.000;\ \text{the bold values are highly significant})$$

This equation indicates the effect of fluoride in lake water on the existence of fluorinated minerals. It also shows that the fluoride content of the lake is affected by the chlorinity value (i.e. the source of waters feeding the lake basin). Generally, the fluoride content in lake is influenced by the saturation of dolomite, fluorapatite, fluorite and sellaite.

Conclusions

Lake Edku is connected to the Egyptian Mediterranean coast in its north western area through El-Maadiya inlet. The lake is affected by the drainage wastes of the main drains that are located in its eastern and southern sides. Some chemical parameters (fluoride, calcium, magnesium, carbonate, phosphorus, pH and chlorinity) were seasonally determined in the surface water of lake during 2010. The determined contents of carbonate, phosphorus, calcium, magnesium, and fluoride along Lake Edku were used in the calculations of the saturation index (SI) values. The pH ranges were on the alkaline side along the lake area. The chlorinity of Lake Edku was affected by the water type (drainage and marine waters). The seasonal ranges of chlorinity and pH during winter, spring, summer and autumn were 4.0–4.6, 0.4–16.6, 0.3–1.3 g/Kg and 0.8–4.2 and 7.2–8.8, 7.1–8.6, 7.8–8.8 and 7.2–8.3, respectively. The seasonal horizontal distribution of fluoride contents was in harmony with the chlorinity contents. This indicated the great effect of the supplied water types on the fluoride distribution in the lake region. Its seasonal levels in winter, spring, summer and autumn were 0.62–1.59, 0.44–1.53, 0.13–1.07 and 0.23–1.17 mg/l with an annual average concentration of 0.8 ± 0.1 mg/l. The average saturation index (SI) of calcite, aragonite and dolomite minerals along Lake Edku referred to the over saturation in respect to these minerals and the incapability of their dissolution. Moreover, the SI values of fluoridated minerals of the lake revealed the precipitation by the fluorapatite ($Ca_5(PO_4)_3F$) and an under saturation by the couple fluorite (CaF_2) and sellaïte (MgF_2) in all water samples. The saturation index had highlighted a plausible relationship between fluoride and phosphate minerals found in the lake system. Interestingly, the high SI of fluorapatite in Lake Edku induced low fluoride levels and accordingly minimum ecological fluoride pollution risk.

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