Egyptian Journal of Aquatic Research (2015) 41, 31–39

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National Institute of Oceanography and Fisheries

Egyptian Journal of Aquatic Research

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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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Received 18 November 2014; revised 13 February 2015; accepted 13 February 2015
Available online 31 March 2015

KEYWORDS

Water samples;
Fluoride distribution;
Mineral species;
Saturation index;
Lake Edku;
Egypt

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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Peer review under responsibility of National Institute of Oceanography and Fisheries.

http://dx.doi.org/10.1016/j.ejar.2015.02.004
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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

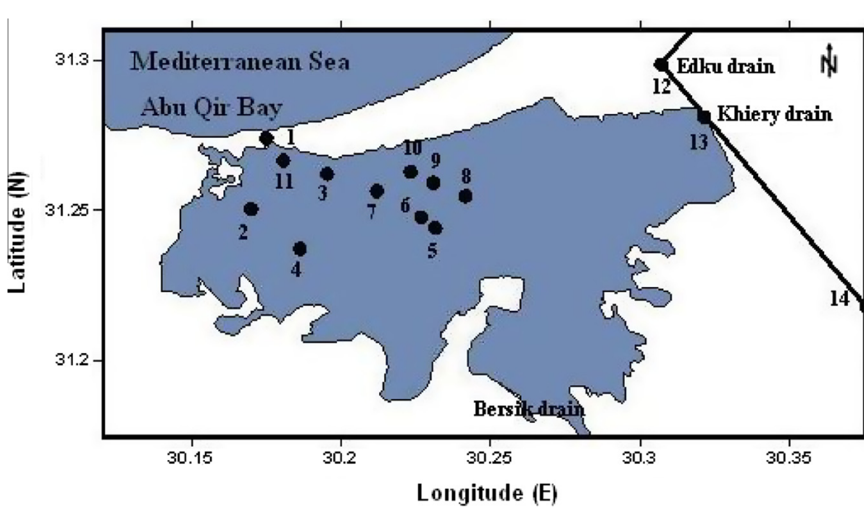

Figure 1 Sampling location in Lake Edku.