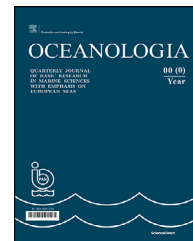


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.journals.elsevier.com/oceanologia](http://www.journals.elsevier.com/oceanologia)

## ORIGINAL RESEARCH ARTICLE

# Combining multivariate statistical analysis to shed light on distribution and interaction of halogens in two economic ports along Red Sea Coast in Egypt

Gehan M. El Zokm, Ghada F. El-Said\*, Abeer A.M. El Sayed

National Institute of Oceanography and Fisheries, NIOF, Egypt

Received 14 February 2021; accepted 29 September 2021

Available online 14 October 2021

## KEYWORDS

Halogens;  
Seawater;  
Sediment;  
Multivariate analysis;  
Mabahiss and Safaga  
bays;  
Red Sea

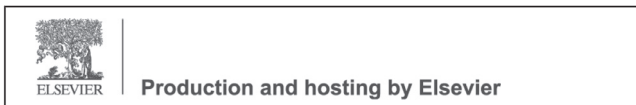
**Abstract** Mabahiss Bay and Safaga Bay are two important ports along the Red Sea coast of Egypt. The present study is the first to monitor halogen concentrations in these two ports. Certain halogens (F, Cl, Br and I) in coastal waters and sediments exhibited different behaviors. Fluoride (1.92–8.31 mg/L and 0.34–1.24 mg/g), chloride (20.76–22.68 g/L and 0.38–8.31 mg/g), bromide (95.90–151.84 mg/l and 6.66–50.61 mg/g), and iodide (2.77–39.19  $\mu$ g/L and 1.71–3.76  $\mu$ g/g) appeared in the seawater and sediments of Mabahiss Bay, respectively. In Safaga Bay, F, Cl, Br and I yielded ranges of (1.80–10.15 mg/L and 0.14–0.74 mg/g), (21.47–22.57 g/L and 0.68–1.42 mg/g), (15.98–146.51 mg/L and 6.13–74.59 mg/g) in seawater and sediments, respectively. In Mabashis Bay exclusively, the bromide and iodide levels in seawater increased significantly, and the sediments were vice versa. The average fluoride value in the two ports' seawater was higher than that in the unpolluted Mediterranean Sea. In contrast, the average bromide content in Mabahiss Bay seawater exceeded the Mediterranean Sea level. The seawater chloride content of the two ports was within the Mediterranean seawater's value, but the iodide concentration was lower than that of the unpolluted seawater. The application of different multivariate statistical techniques showed that halogen's distribution and halogen's geochemical characteristics control interaction in each region, ground flux, and proximity to human sources.

© 2021 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

\* Corresponding author at: National Institute of Oceanography and Fisheries, NIOF, Egypt.

E-mail addresses: [gehanelzokm@yahoo.com](mailto:gehanelzokm@yahoo.com) (G.M. El Zokm), [ghadafarouk25@yahoo.com](mailto:ghadafarouk25@yahoo.com), [ghadafarouk25@gmail.com](mailto:ghadafarouk25@gmail.com) (G.F. El-Said), [perry201277@hotmail.com](mailto:perry201277@hotmail.com) (A.A.M. El Sayed).

Peer review under the responsibility of the Institute of Oceanology of the Polish Academy of Sciences.



<https://doi.org/10.1016/j.oceano.2021.09.007>

0078-3234/© 2021 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

Seawater is the main source of iodine (I), and the iodine concentration in seawater ranges from 40 to 60  $\mu\text{g/L}$ . Approximately 70% of the iodine in the earth's crust is bound to ocean sediments (Muramatsu and Wedepohl, 1998). Fluorine (F) was mobilized during marine carbonate diagenesis. However, it is fixed in newly formed carbonate, apatite, or clay minerals. Bromide and chloride are traceable chemicals in hydrology because they do not absorb negatively charged ions in the solid phase; thus, they are widely used to study the movement of water in marine sediments. Like iodine, bromine may volatilize from the marine environment and be carried to the land's surface. An increase in the I/Cl and Br/Cl ratios indicates an increase in iodine and bromine content, which is caused by prohibited substances flowing from external outlets to the surface of the marine environment. Limited information on halogens' geochemistry in the soil indicates that the adjacent sea influences the concentrations of chlorine, bromine, and iodine in the soil. In contrast, the content of fluorine in the soil depends on its content in the parent material. In some areas, the source of halogen pollutants significantly participates in its environmental concentration. The high electronegativity of fluorine makes it the most reactive element and enables it to form compounds with almost all elements except inert gases. However, the electronegativity (eV) of halogen decreases in the order of  $F (3.9) > Cl (3.0) > Br (2.8) > I (2.5)$ . Fluoride in seawater exists in the form of  $MgF^+$  (46%),  $F^-$  (51%), and  $CaF^+$  (2%) (Liteplo et al., 2002). Fluorine replaces any other halide ions in its compound (Brescia et al., 1975). Fluoride is found in nature as fluorite, fluorapatite, cryolite, fluorite and sellaite and carbonate-fluorapatite (El-Said et al., 2015, 2020, 2021; Masoud and El-Said, 2011), while human fluoride sources are such as coal combustion, oil refining, steel manufacturing, aluminum smelting, textile by-products, brick production, and phosphate fertilizer plants (Masoud and El-Said, 2011). Many fluoride compounds such as beryllium fluoride and aluminum fluoride are used industrially as phosphatase inhibitors (Masoud and El-Said, 2011). In environment, the anthropogenic sources of fluoride have been considered a major source among them. Bromine is produced as a by-product of many industries including pesticides, disinfectants, dyes, textiles, cosmetics (El-Said et al., 2020). Iodine and chloride are also produced from burning of coal or fuel oil for power generation and iodine is used in the pharmaceutical industry (Harlove and Aranovich, 2018).

The four halogens commonly occur as the X ion (Harlove and Aranovich, 2018). Iodine also exists in the form of the iodate anion ( $IO_3^-$ ) in oxidizing alkaline media (such as seawater). Iodine's low electron affinity results in the occurrence of  $I_2$  in the environment. Fluorine, chlorine, and a small amount of bromine are lithophilic due to their accumulation in silicate minerals. However, iodine is chalcophilic rather than lithophilic in character (Harlove and Aranovich, 2018). Chlorine is the most abundant halogen in sedimentary formation waters with concentrations ranging from  $<100$  to  $>250000$  mg/L (Worden, 1996), followed by bromine with a range of  $(1 < Br > 6000$  mg/l). Chlorine and bromine exhibit strong systemic covariation, suggesting that they are subject to the same control mechanisms

(Worden, 1996). Fluorine only shows relatively high concentration at higher chlorine and bromine concentrations, indicating that the same processes can control fluorine, chlorine, and bromine. Iodine is not related to any other halogen, indicating that a unique process controls iodine. The key processes affecting halogen concentration are seawater evaporation and dilution, water-salt interaction, and organic sources' input.

The Red Sea is a semi-enclosed basin representing one of the marginal seas of the Indian Ocean. The Red Sea is a unique, large marine ecosystem with coral reef systems spreading across its coastline. In addition to its unique, attractive environment, the Red Sea is a significant trading navigational route (Attia and Ghrefat, 2013). Hurghada and Safaga are important ports along the Egyptian Red Sea coast serving industrial activities, petroleum activities, marine sports, and fishers societies (El-Geziry et al., 2020; Nour et al., 2018; Nour and Nouh, 2020). Hurghada is considered the largest Egyptian resort city in the Red Sea.

This study provides a framework to understand halogen distribution in two Red Sea ports in Egypt. It examines the concentrations of F, Br, Cl and I in seawater and marine sediments relative to environmental parameters. This study also aimed to demonstrate the utility of multivariate analysis for evaluating and interpreting large data sets for environmental parameters, identifying pollution sources, and obtaining better concepts of halogen interactions at the two ports.

## 2. Material and methods

### 2.1. Sampling area

Fourteen sampling sites (M1–M14) were selected in the northern part of Mabahiss Bay (Figure 1). The sampling area extends from latitude  $27.29^\circ$  to  $27.32^\circ$  and longitude  $33.73^\circ$  to  $33.77^\circ$  (Figure 1). Mabahiss Bay occupies an area of approximately 35 km<sup>2</sup> near the southern end of the Suez Gulf north of Hurghada, and granitic mountains in the Eastern Desert bound its coast. The coastal area contains several dry valleys and is covered by Pleistocene reefal limestone, gravels, and sands (Attia and Ghrefat, 2013). The wide range of depths in the study area reflects the irregularity in this area's bottom topography (Attia et al., 2012). The offshore islands and the submerged coral system serve to dissipate wave energy during stormy conditions. Fishing is the main impact in this area, especially fishing with nets on reef flats and lagoons (Selim, 2007). Many *Parupeneus* (goatfish), polychaetes, sponges, gastropod shells (*Strombus* and *Lambus*), seagrass, and seaweed inhabit this reef flat. There are some activities in Hurghada area, especially, the export of Egyptian phosphate, packed of cement and alchortz ore (Abouhend and El-Moselhy, 2015). Besides, the construction of major shipyards to build fishing vessels and brine discharge for mega desalination plants has affected this region.

Fifteen sampling locations (S1–S15) represent the northern and central parts of Safaga Bay. The study ranged from the Ras Abu Soma Peninsula to the fortress area north of Safaga Island (Figure 1). Safaga Bay is on the Red Sea west side with a maximum depth of 70 m (Abd EL Wahab et al., 2011). The bay is bordered by a narrow dry coastal plain

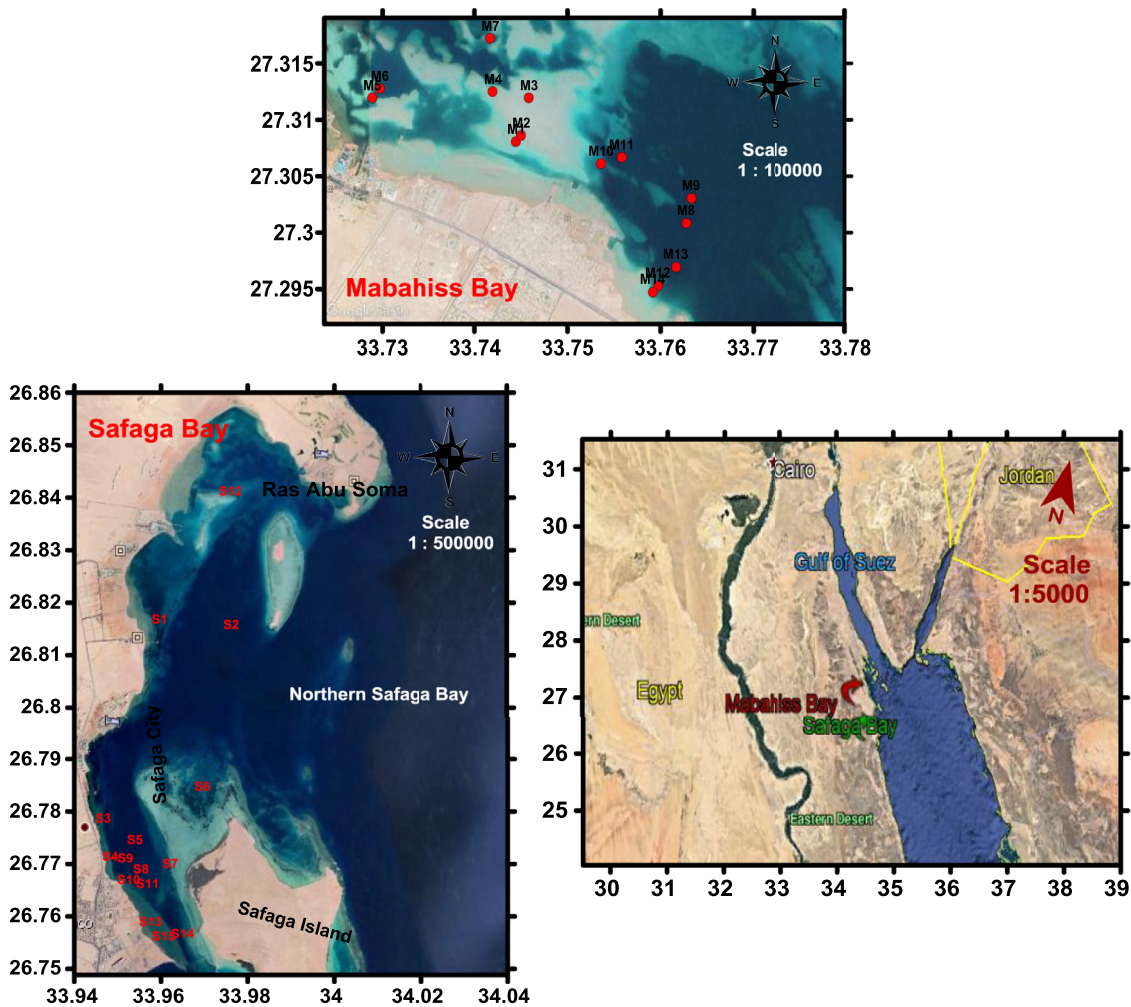


Figure 1 Sampling sites in Mabahiss and Safaga bays along the studied area.

on the west, while the eastern and southern areas are bordered by steep slopes, and the northern area borders the well-known Ras Abu Soma Peninsular. Safaga Bay can be subdivided into the northern and western sides. The sampling area extends from latitude 26.75° to 26.84° and longitude 33.94° to 33.98° (Figure 1). Additionally, this area plays an important role in Egyptian international trade, characterized by transport volumes with frequent loading and unloading. The port includes passenger and freight terminals for bauxite, coal, grain, quartz, and orthoclase (El-Metwally et al., 2017; Mansour et al., 2011). Safaga area is also affected by heavy oil spills due to crude oil extraction and shipping activities (Abouhend and El-Moselhy, 2015).

## 2.2. Sampling and preparation of seawater and sediment samples

Twenty-nine triplicate inshore surface seawater (w) and sediment (s) samples were collected from various sites in Mabahiss Bay (14 sites, M1–M14) and Safaga Bay (15 sites, S1–S15) during 2018 (Figure 1). Duplicate seawater samples were collected using Niskin bottle from a depth range 10–24 m and preserved in 1-liter stoppered, dark polyethylene bottles, which were transferred in iceboxes to the National

Institute of Oceanography and Fisheries lab. The other 29 bottles were immediately used to analyze  $CO_{3w}$ ,  $HCO_{3w}$ ,  $Ca_w$ ,  $Mg_w$ ,  $B_w$ , and  $SO_{4w}$ . Sediment samples from each sampling site at different depths were collected using a Van Veen grab sampler and were kept in colorless polyethylene bags at  $-20^{\circ}C$  until they were air-dried in the lab. Sediment samples were spread on a clean plastic plate and then air-dried at room temperature. The particle size of the air-dried sediment sample was estimated (Folk, 1974).

The sediment samples were crushed to a fine powder and then digested with an acid mixture (3 mL  $HNO_3$ , 2 mL  $HClO_4$ , and 1 mL HF) at  $70^{\circ}C$  in closed Teflon containers. The filtered digested sediment samples were preserved in colorless well-closed plastic bottles for  $Ca_s$ ,  $Mg_s$ ,  $B_s$ , and  $SO_{4s}$  determination. The extracted halogen solutions were obtained from the fusion of  $Na_2CO_3$  with fine sediment powder (Jeffery, 1975; Mohamed, 1999; Saenger, 1972).

## 2.3. Analysis of water and sediment samples

The values of temperature ( $T_w$ ;  $^{\circ}C$ ), pH, salinity ( $S_{\text{‰}}$ ), and total dissolved salts (TDS; g/L) in seawater samples were measured in the field using portable equipment (CTD YSI: 566). Fluoride content in seawater and extracted sediment

solution was measured using the established zirconium-Alizarin Red S method (El-Said and El-Sikaily, 2013). The chloride content in seawater was calculated from the salinity value (Strickland and Parsons, 1972). The bromide content in seawater and extracted sediment solution was determined using the titrimetric method (Grasshoff, 1976). The catalytic reduction method using the Ce(IV)-As(III) reaction was applied to determine the iodine concentration in seawater and extracted sediment solution (APHA-AWWA-WPCF, 1999). The calcium and magnesium content in seawater and digested sediment samples, the carbonate and bicarbonate content in water and sediment samples were determined using the titrimetric method (APHA-AWWA-WPCF, 1999; Balázs et al., 2005; Strickland and Parsons, 1972). Reactive phosphorus in seawater was determined (APHA-AWWA-WPCF, 1999). Silicate was measured in seawater using the calorimetric method (Strickland and Parsons, 1972). The turbidimetric method was applied to estimate  $\text{SO}_4$  in seawater and digested sediment samples (APHA-AWWA-WPCF, 1999). The curcumin colorimetric method was used to determine the amount of boron in seawater and digested sediment samples (APHA-AWWA-WPCF, 1999). Mohr's method determined the chloride contents in sediments (APHA-AWWA-WPCF, 1999; Manual of Methods of Analysis of Foods, 2005). The total phosphorus (TP) content in sediment samples was determined (Aspila et al., 1976). Total carbonates (%  $\text{CO}_3$ ) and total silicate (%  $\text{SiO}_4$ ) in sediment samples were estimated (Molnia, 1974).

#### 2.4. Quality control and quality assurance

The used glassware was cleaned with detergent and steeped in 10%  $\text{HNO}_3$ . For each determined parameter, a calibration procedure was examined for five external standards. An external standard must be close to but above the method detection limit. The detection limit and limit of quantification values for fluoride, iodide, phosphorus, silicate, and sulfate were 0.1 and 0.3 mg/L, 9.0 and 24.0  $\mu\text{g/L}$ , 0.04 and 0.13  $\mu\text{g/L}$ , 0.01 and 0.035  $\mu\text{g/L}$  and 1.0 and 3.0 mg/L, respectively. Other concentrations should correspond to the range of parameter concentrations expected in the environmental samples. The work calibration curve was verified in each work shift by measuring one or more calibration standards. Each standard has a recovery rate of approximately 90%. The precision of the data was set as the coefficient variation (CV). CV determined to be at a value of 10% was through three duplicate analyses of one sample.

#### 2.5. Statistical analysis

Multivariate analyses are recommended for monitoring and environmental studies (Abdel Ghani et al., 2013; El-Said, 2013; El Zokm et al., 2020a, 2020b; Soliman et al., 2018; Tokatli et al., 2014). They can help ecologists discover the structure of many data properties and predict a relatively prior objective. These discoveries make it easier to understand the structure and function of very complex theoretical studies. IBM-SPSS Statistics version 22 and STATISTICA version 12.0 software were used. In this study, data structures were explained using four multivariate statistical

techniques: correlation matrix with a correlation coefficient ( $r$ ), multiple regressions with a multiple regression coefficient ( $R$ ), principal component analysis (PCA), and cluster analysis (CA) at a  $p \leq 0.05$  significance level. These techniques were applied to quantitatively analyze a sample of 27 variables distributed in seawater and sediment samples in each area.

### 3. Results and discussion

#### 3.1. Hydrographical and chemical parameter's distribution in surface seawater

The specific hydrographic parameters in Mabahiss Bay and Safaga Bay ranges of temperature ( $T_w$ ), salinity ( $S_{\text{‰}}$ ), TDS and pH are 20.7–23.0°C, 37.50–40.96‰, 33.22–36.28 g/L and 7.78–7.98, and 23.2–26.7°C, 38.78–40.77‰, 37.35–36.11 g/L and 8.13–8.23, respectively. The average values of  $S_{\text{‰}}$  in Mabahiss Bay and Safaga Bay are lower than those reported for the Egyptian Red Sea Coast (39.63–40.22‰; Fahmy, 2003). The decrease in the detected pH values from those of the unpolluted Egyptian Red Sea Coast (8.06–8.22; Fahmy, 2003) is also due to the discharge from tourist resorts and desalination plants, in addition to the agricultural and industrial wastes. The TDS of Mabahiss Bay and Safaga Bay (Supplementary Table 1) are relatively similar and smaller than the TDS recorded for the open sea (39.420 g/L; Jones et al., 1999); however, Mabahiss Bay's  $\text{pH}_w$  tends to be neutral. The pH values are influenced by the water temperature ( $\text{pH} \& T_w$ :  $r = -0.6673$ ,  $p < 0.007$ ) in Safaga Bay.

The distribution of certain chemical parameters ( $\text{Ca}_w$ ,  $\text{Mg}_w$ ,  $\text{P}_w$ ,  $\text{HCO}_{3w}$ ,  $\text{CO}_{3w}$ ,  $\text{SO}_{4w}$ ,  $\text{B}_w$  and  $\text{Si}_w$ ) in Mabahiss and Safaga Bay's seawater are also determined (Supplementary Table 1). The chemical parameters take the order of  $\text{TDS} > \text{SO}_{4w} > \text{Mg}_w > \text{Ca}_w > \text{HCO}_{3w} > \text{CO}_{3w} > \text{B}_w > \text{Si}_w > \text{P}_w$  in the two bays. The calcium contents in the surface waters of Mabahiss Bay and Safaga Bay range from 256.5–432.9 and 256.5–625.2 mg/L, with an average of 333.1 and 397.6 mg/L, respectively, which are lower than the content reported in the Mediterranean Sea (459 mg/L; Jones et al., 1999). Whereas magnesium levels give ranges 1770.0–2470.2 and 1215.6–2324.3 mg/L and average levels 2124.2 and 1831.8 mg/L in Mabahiss Bay and Safaga Bay, respectively, are higher than those reported for open seawater and the Mediterranean Sea (Millero et al., 2008; Shapiro et al., 2018). The magnesium content of these two ports is higher than the specified value in the Mediterranean Sea (1211 mg/L; Jones et al., 1999), which may be due to human activity in the area. The abundance of magnesium in the seawater of Mabahiss Bay and Safaga Bay is closely related to the decomposition of minerals such as *sabkhas* in Safaga Bay ( $\text{Mg}_w \& \text{CO}_{3w}$ ,  $r = 0.7402$ ,  $p < 0.002$ ; and  $\text{Mg}_w \& \text{SO}_{4w}$ ,  $r = 0.6757$ ,  $p < 0.006$ ) and the salinity of the flow of freshwaters.

The  $\text{mMg}/\text{Ca}$  values of both Mabahiss and Safaga Bays are 7.9–14.21 and 4.16–11.01, respectively, which are higher than two of the records of non-biological, carbonate deposition in seawater in the form of aragonite + high-magnesium calcite (El-Said et al., 2016a; Ries, 2010).

In Safaga Bay, the strong correlation between  $Mg_w$  and  $CO_{3w}$  ( $r = 0.7402$ ,  $p < 0.002$ ) and  $SO_{4w}$  ( $r = 0.6757$ ,  $p < 0.006$ ) may reflect the formations of  $MgCO_3$  and  $MgSO_4$  compounds. The average values of active phosphorus in Mabahiss (0.04–20.81  $\mu\text{g/L}$ ) and Safaga (2.97–10.41  $\mu\text{g/L}$ ) bays are 7.19 and 6.78  $\mu\text{g/L}$ , respectively. These two ports seem to be somewhere between moderate eutrophic (4.65  $\mu\text{g P/L}$ ) and high eutrophic (9.30  $\mu\text{g P/L}$ ) coastal waters (Fahmy, 2003; Fahmy et al., 2016). The calculated ecological risk assessment of phosphorus ( $RQ_p$ ; El Nemr and El-Said, 2017) indicated that phosphorylation distress occurred in both ecological regions.

The  $HCO_{3w}$  average content of the surface water of Mabahiss Bay (29.67–180.56 mg/L) and Safaga Bay (78.08–146.40 mg/L) is lower than the publicly reported value of 169 mg/L; Jones et al., 1999) and above the specified level in the Mediterranean Sea coast in Egypt (97.88 mg/L; El-Said et al., 2016a). The presented data's correlation matrix concluded that the amount of boron in the seawater of Mabahiss Bay is related to the outflow's water quantity ( $S_{\%} \& B_w$ ;  $r = -0.6421$ ,  $p < 0.024$ ), the ion pair formation of borate complexes with the abundant Mg, and its deposition and adsorption or use in this area's sediment texture ( $Mg_w \& B_w = -0.6769$ ,  $p < 0.016$ ; Kot, 2009). Sulfate shows dramatic changes in Mabahiss (5535.7–9862.2 mg/L) and Safaga (4775.5–10913.3 mg/L) bays. The sulfate content along these two ports is higher than the sulfate content in the open Mediterranean Sea area (2700 mg/L; Jones et al., 1999). The high sulfate in Mabahiss Bay and Safaga Bay might be associated with disintegrated sabkhas minerals, landfill operations and terrigenous fluxes (Mansour et al., 2013). The high correlation coefficient between silicon and  $B_s$  in the seawater of Mabahiss Bay ( $r = 0.7914$ ,  $p < 0.002$ ) might be related to the biological activity of boron in cyanobacteria and diatoms (Kot, 2009). The average  $Si_w$  contents of Mabahiss Bay (65.73–244.38  $\mu\text{g/L}$ ) and Safaga Bay (55.21–326.97  $\mu\text{g/L}$ ) are 149.88 and 180.31  $\mu\text{g/L}$ , respectively.

### 3.2. Halogens' distribution in surface seawater

The distribution of halogens in seawater (w) gives the same order of  $Cl_w > Br_w > F_w > I_w$  in both Mabahiss Bay and Safaga Bay (Supplementary Table 1). Fluoride in Mabahiss Bay (1.92–8.31 mg/L) and Safaga Bay (1.80–10.15 mg/L) give average values of 4.18 and 5.30 mg/L, respectively, which is higher than those established in unpolluted seawater (1.3 mg/L; El-Sarraf et al., 2003). The current fluoride concentrations in Mabahiss Bay and Safaga Bay are within the range previously determined in the Red Sea (4.7±0.3 mg/L; El-Said, 2005). The chloride in Mabahiss Bay's seawater (21.90±0.65 g/L) and Safaga Bay (21.94±0.37 g/L) show relatively similar contents. The chloride concentrations in both bays are also relatively similar to those established in the open Mediterranean Sea (21.94 g/L; Jones et al., 1999) and lower than those recorded in the Egyptian Red Sea coast (22.2–22.7 g/L) due to its anion abundance in seawater. The bromide content in Mabahiss Bay (95.90–151.84 mg/L) is higher than that recorded in Safaga Bay (15.98–146.51 mg/L) with average values of 114.56 and 61.57 mg/L, respectively. The increased Br in Mabahiss Bay may be associated with water-soluble release and leached Br from

sediment to seawater-sediment interface (Harlov and Aronovich, 2018). However, in the earth's crust, rocks containing more than 70–80% Br are present in non-sediment rocks. The Br in Mabahiss Bay (114.56±17.24 mg/L) is also higher than that reported in the Mediterranean Sea and Lake Mariout (74.1 and 18.91 mg/L; Jones et al., 1999; El-Said et al., 2020). The variation of chloride is also related to seawater's evaporation in semi-enclosed areas and tropical regions (Jones et al., 1999). The iodide values show variable higher contents in Mabahiss Bay (2.77–39.19  $\mu\text{g/L}$ ) than those recorded in Safaga Bay (2.50–12.96  $\mu\text{g/L}$ ) with average values of 17.33 and 5.05  $\mu\text{g/L}$ , respectively. Iodide contents in the two bays are lower than that reported in seawater (50  $\mu\text{g/L}$ ; Jones et al., 1999).  $I^-$  plays an important role in the oxidation or reduction reactions in geochemical systems and strongly adsorb to mineral surfaces. The average levels of chloride, bromide, and iodide in seawater in Mabahiss Bay are higher than those recorded in Safaga Bay.

A correlation analysis revealed the relationship between halogens and studied environmental parameters in seawater and sediments of the two ports.

In Mabahiss Bay, there are high interactions relating to  $F_w \& Cl_s$  ( $r = 0.9071$ ,  $p < 0.00$ ),  $Cl_w \& F_s$  ( $r = -0.6382$ ,  $p < 0.026$ ), and  $Br_w \& Cl_s$  ( $r = -0.7107$ ,  $p < 0.010$ ). Halogens are incorporated into the earth's crust, bio-organic matter, and minerals presented; however, Cl is abundant in the oceanic crust as an amphibole mineral with 0.5 mg/g (Jones et al., 1999). The high correlation of  $Cl_w \& Mg_w$  ( $r = 0.681$ ,  $p < 0.015$ ) may accompany the mobilization of Cl and Mg in amphiboles containing iron or magnesium ions (Jones et al., 1999). The release of chloride, magnesium, bromide ( $Br_w \& Ca_w$ ;  $r = -0.6747$ ,  $p < 0.016$ ) and iodide ( $I_w \& CO_{3w}$ ;  $r = 0.815$ ,  $p < 0.001$ ) probably refer to the decomposition of sabkhas minerals and organisms fragments along with landfills and land flows. Iodine is present in the anionic  $I^-$  form and oxyanionic species such as iodate ( $IO_3^-$ ) depending on pH, oxidation potential and biological activities in seawater (Jones et al., 1999). The moderate negative correlation of  $F_s \& Mg_w$  ( $r = -0.6013$ ,  $p < 0.039$ ) may be referred to the precipitation of the  $MgF^+$  ion pair and the sparingly soluble magnesium complex (El-Said et al., 2015). The high correlations of  $B_w \& Cl_w$  ( $r = -0.6421$ ,  $p < 0.024$ ) and  $F_s \& B_w$  ( $r = 0.8112$ ,  $p < 0.001$ ) may be related to anthropogenic sources and boron's geological cycle (Kot, 2009). The release of Cl from minerals such as sabkhas and feldspar during the hydration process and the deposition of fluoroboron compounds such as (ferrucite ( $NaBF_6$ ) and avogadrite ( $(K,Cs)BF_4$ ), along with the adsorption of boron on minerals such as Al and Fe oxide, and calcareous and clay minerals in marine sediments may also be associated with high relationships between  $B_w \& Cl_w$  and  $F_s \& B_w$  (Kot, 2009).

In Safaga Bay, the relationship between the parameters defined in the correlation matrix reflects that the chlorine content in the seawater is related to the water chemistry process, landfill discharge and human activities. The relationship of  $Cl_w \& B_w$  ( $r = 0.6067$ ,  $p < 0.016$ ),  $Cl_w \& Cl_s$  ( $r = 0.6151$ ,  $p < 0.015$ ),  $Cl_w \& CO_{3w}$  ( $r = 0.6034$ ,  $p < 0.017$ ),  $I_w \& SO_{4w}$  ( $r = 0.7196$ ,  $p < 0.002$ ),  $Br_s \& I_s$  ( $r = 0.6553$ ,  $p < 0.008$ ), and  $I_w \& Si_w$  ( $r = -0.7727$ ,  $p < 0.001$ ) may indicate dissolution and/or deposition of boron, chloride, bromide, and iodide in certain marine minerals, as well as the incorporation of these elements into organic compounds,

organic matter in sediments and organic-rich sediments. (Harlove and Aranovich, 2018; Kot, 2009). Bromine and chlorine are mixed with organic matter of coal, kerogen, and petroleum (Harlove and Aranovich, 2018). The high correlations of  $B_w \& S_{\%}$  ( $r = 0.6089$ ,  $p < 0.016$ ),  $B_w \& Cl_w$  ( $r = 0.6067$ ,  $p < 0.016$ ), and  $B_w \& CO_{3w}$  ( $r = -0.6168$ ,  $p < 0.014$ ) also possibly refer to the anthropogenic and geologic origin of boron in Safaga Bay.

The horizontal distribution of halogens in Mabahiss and Safaga Bay's seawater and sediments shows different trends (Figures 2 and 3). In Mabahiss Bay, the fluoride in the seawater and sediments gradually decreases towards the sea. The contents of chloride, bromide, and iodide show the same distribution. The halogen's content in seawater decreases in seawater's direction and increases in the opposite direction in sediments. In Safaga Bay, the distribution of halogen contents declines from the shore toward the seawater and in the opposite direction of the sediments.

### 3.3. Chemical parameters' distribution in sediment

The chemical parameters determined in Mabahiss and Safaga Bay are listed in descending order:  $CO_{3s} > Mg_s > Ca_s > SiO_{4s} > SO_{4s} > B_s > P_s$  and  $CO_{3s} > Ca_s > Mg_s > SiO_{4s} > SO_{4s} > B_s > P_s$ , respectively (Supplementary Table 2). Mabahiss Bay has higher average  $Ca_s$ ,  $Mg_s$ ,  $CO_{3s}$  and  $B_s$  levels than those in Safaga Bay. These high recorded values in Mabahiss Bay may be due to the presence of sabkhas minerals containing soluble sulfate and chloride salts and carbonate minerals (Bahafzullah et al., 1993). The average boron content in Mabahiss Bay is relatively similar to the average content recorded in clay sediments (2.30 mg/g; Kot, 2009), while the boron content in Safaga Bay is lower than the average. In contrast, the  $SiO_{4s}$ ,  $SO_{4s}$  and  $P_s$  contents in the sediment subarea of Safaga Bay are higher than that of Mabahiss Bay. The weak correlation between  $SO_{4s}$  and  $HCO_{3w}$  ( $r = 0.5274$ ,  $p < 0.043$ ) and  $SO_{4s} \& T_w$  ( $r = 0.5348$ ,  $p < 0.040$ ) may be related to the influence of temperature and sulfate content on the microbial activity in Safaga Bay sediments (Sawicka et al., 2012). The moderate correlations of  $Ca_s \& T_w$  ( $r = 0.6371$ ,  $p < 0.026$ ) and  $P_s \& pH$  ( $r = 0.7226$ ,  $p < 0.008$ ) may reflect the influence of water temperature on calcium carbonate dissolution and the release of phosphorus during calcite formation in Mabahiss Bay sediment (El-Said et al., 2016b).

### 3.4. Halogens' distribution in sediment

The halogen distribution in sediments (s) give the same order of  $Br_s > Cl_s > F_s > I_s$  in the two bays (Supplementary Table 2 and Figures 2 and 3). Mabahiss Bay shows a slightly higher average fluoride content (0.63 mg/g) than that established for the earth's crust (0.55 mg/g; Harlove and Aranovich, 2018), while Safaga Bay exhibits lower content (0.38 mg/g; Harlove and Aranovich, 2018). The halogen current results of  $Cl_s$ ,  $Br_s$ , and  $I_s$  in Mabahiss Bay and Safaga Bay are higher than those reported for the earth's crust (0.24 mg/g, 0.88  $\mu\text{g/g}$ , and  $I = 0.7 \mu\text{g/g}$ ; Harlove and Aranovich, 2018). The moderate negative association of  $F_s \& Mg_w$  ( $r = -0.6013$ ,  $p < 0.039$ ) slightly reflects

the precipitation of the  $MgF^+$  ion pair and the soluble Mg complex (El-Said et al., 2015). The high correlations of  $B_w \& Cl_w$  ( $r = -0.6421$ ,  $p < 0.024$ ) and  $F_s \& B_w$  ( $r = 0.8112$ ,  $p < 0.001$ ) may be related to the anthropogenic source and geological cycle of boron (Kot, 2009). The release of Cl could result from minerals such as: sabkhas, and feldspar during the hydration process and the deposition of fluoride-boron compounds like ferrucite ( $NaBF_6$ ) and avogadrite ( $(K,Cs)BF_4$ ) and the adsorption of boron on minerals such as aluminum oxide, iron oxide, calcareous and clay minerals in marine sediments (Kot, 2009). The fluoride content in Safaga Bay gives high relationships of  $F_s \& CO_{3s}$  ( $r = -0.6474$ ,  $p < 0.009$ ),  $F_s \& B_s$  ( $r = 0.6477$ ,  $p < 0.009$ ), and  $F_s \& Si_s$  ( $r = 0.6474$ ,  $p < 0.009$ ). These relationships may release fluoride from fluorite minerals and form calcium carbonate in alkaline media, in addition to decomposing carbonate and crystalline rock fragments (Dehbandi et al., 2017; El-Said et al., 2016a).

## 4. Multivariate analysis

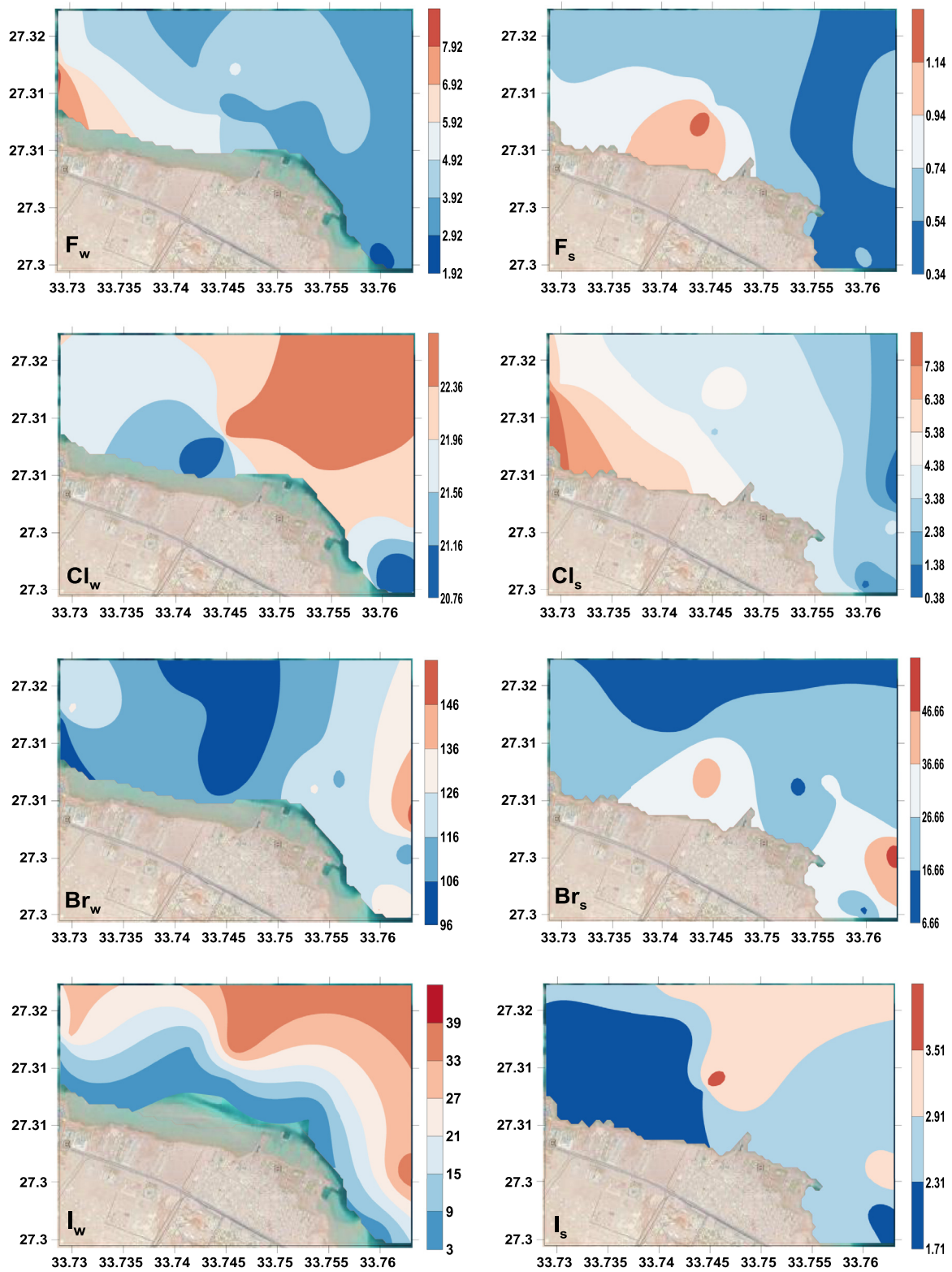
### 4.1. Box and whisker plot

Figures 4 and 5, present the box and whisker plots of the studied parameters between the two ports. Figure 4 represents the plot for  $SO_{4w}$  (mg/L),  $HCO_{3w}$  (mg/L),  $CO_{3w}$  (mg/L),  $Ca_w$  (mg/L),  $Mg_w$  (mg/L),  $B_w$  (mg/L),  $Si_w$  ( $\mu\text{g/L}$ ), and  $P_w$  ( $\mu\text{g/L}$ ) in seawater of Mabahiss (M) and Safaga Bays (S) by the box and whisker method. The boxes show the 25<sup>th</sup> percentile (first quartile) and the 75<sup>th</sup> percentile (third quartile), and the whiskers represent the lowest and the highest coefficients. In contrast, the line inside the boxes expresses the median (second quartile). Figure 5 is the plot of  $Ca_s$  (mg/g),  $Mg_s$  (mg/g),  $SO_{4s}$  (mg/g),  $CO_{3s}$  (%),  $SiO_{4s}$  (%),  $B_s$  (mg/g), and  $P_s$  ( $\mu\text{g/g}$ ) in marine sediments of Mabahiss (M) and Safaga Bays (S) drawn using the box and whisker method, where the first, second and third quartile are illustrated.

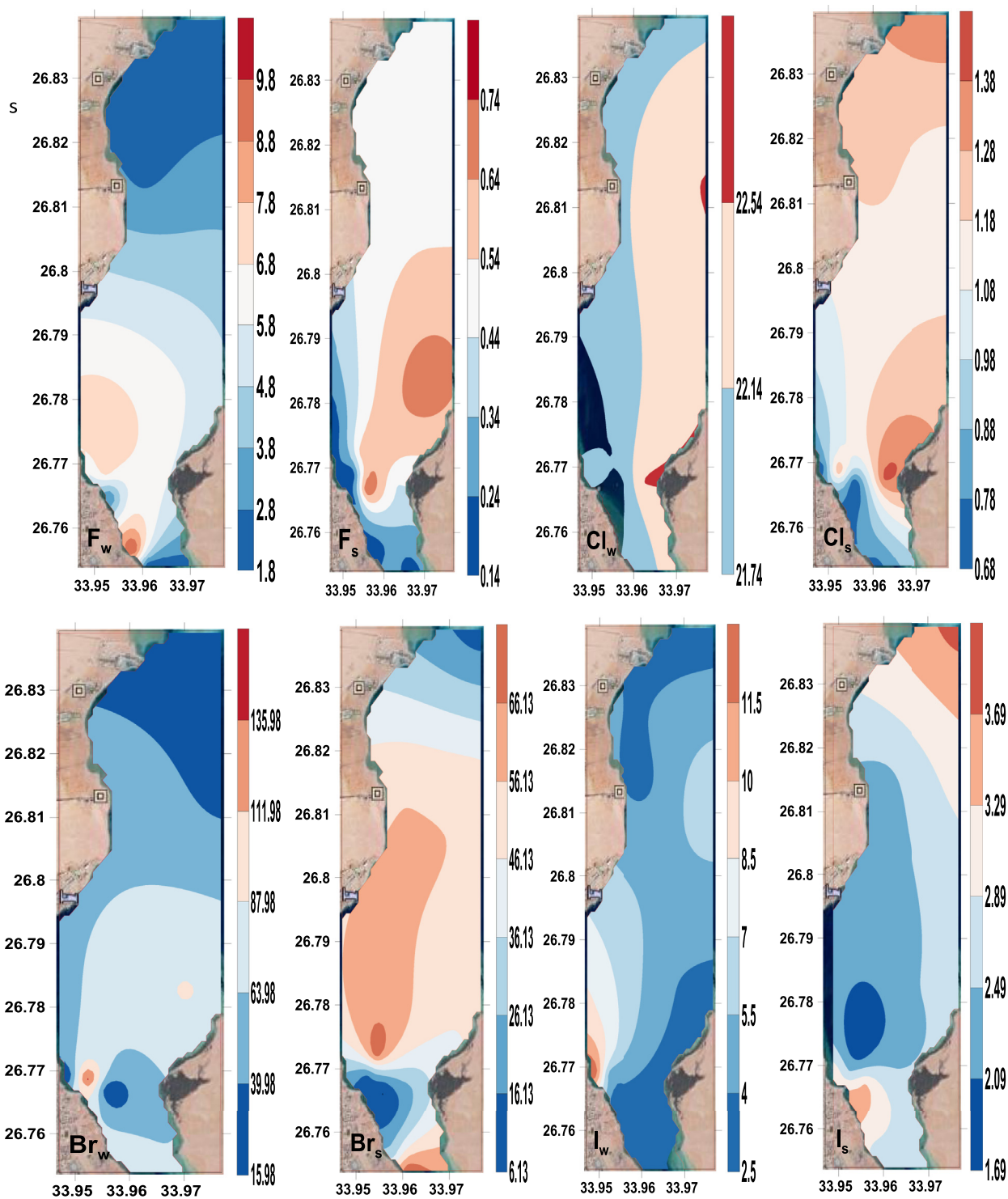
### 4.2. Multiple regression analysis

The multiple regression equation for halogen is listed as the dependent parameter. At the same time, other variables are defined as independent parameters in the surface seawater and sediments of the Mabahiss and Safaga bays (Table 1). The seven equations of Mabahiss Bay and the eight equations of Safaga Bay were constructed. Based on these equations, halogen's chemistry and other features in the two ports can be deduced.

A striking feature is that there is no regression equation for chloride in Mabahiss Bay, even between chloride and salinity, which indicates the stability of the chloride content in this region (Harlove and Aranovich, 2018). The dissolved chloride salts seems to mainly influence the chloride in seawater of the shallow Mabahiss Bay in sabkhas minerals. The multiple regression equations for the variable distribution of halogens in Mabahiss Bay may relate to marine organisms biological activities, decomposition of organic matter, formation/dissolution of carbonate minerals, and the partial dissolution of quartz particles transported to the sea from the surrounding desert during sandstorms. In Safaga Bay, the type of pollutants in this region's wastewaters play an important role in the chemistry of specific



**Figure 2** Distribution of F, Cl, Br, and Cl in seawater and sediment (mg/L and mg/g, respectively) and I ( $\mu$ /L and  $\mu$ g/g, respectively) in Mabahiss Bay.



**Figure 3** Distribution of F, Cl, Br, and I in seawater and sediment (mg/L and mg/g, respectively) and I ( $\mu\text{L}$  and  $\mu\text{g/g}$ , respectively) in Safaga Bay.

halogen contents (Attia and Ghrefat, 2013; Nour and El-Sorogy, 2018; Nour and Nouh, 2020). In the four equations describing the halogen reaction in Safaga Bay, the high pollution state and high phosphorus content indicate that the study area suffers from high phosphorus pollution (Abou El-Anwar et al., 2019). Fluoride in the two bay's sediments is usually affected by calcium, controlled by the adsorption

balance on the sediments and the solubility or precipitation of fluorite ( $\text{CaF}_2$ ) and carbonate minerals (El-Said et al., 2015). In most of the bay's equations, each halogen's unique interaction with other halogens reveals similar chemical properties between them, especially F, Cl, and Br. Halogens form a class of compounds called inter-halogen compounds, in which halogen atoms are covalently bonded to



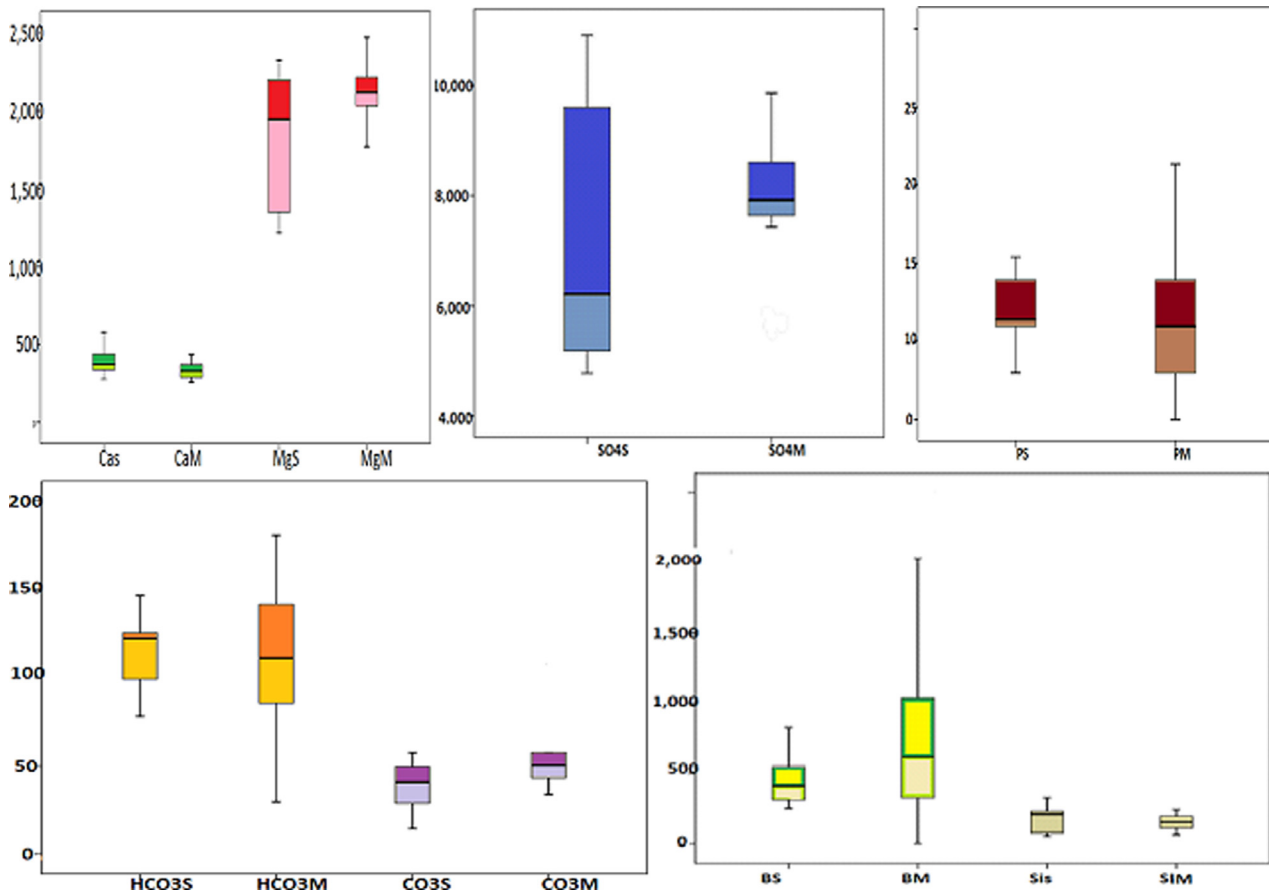


Figure 4 Box and whisker plot for chemical parameters in seawater of Mabahiss (M) and Safaga (S) bays.

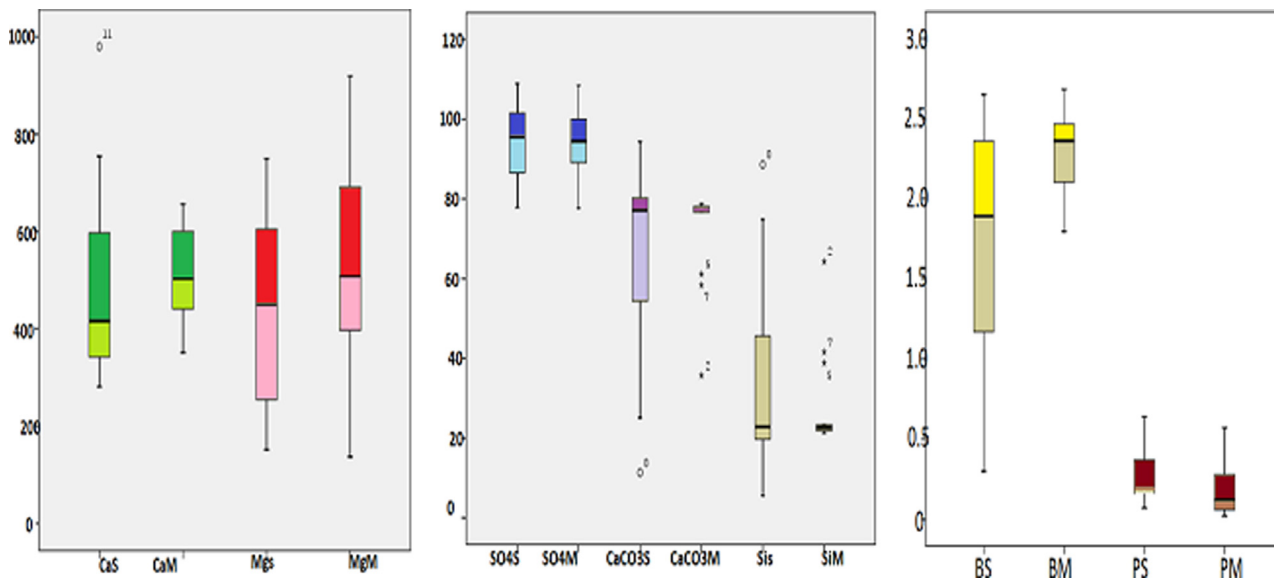


Figure 5 Box and whisker plot for chemical parameters in sediments of Mabahiss (M) and Safaga (S) bays.

each other to form Lewis bases, such as  $\text{BrCl}$  and  $\text{ICl}_4$ . Interestingly, most of the two port's halogens have important interactions with coastal water and sediment's environmental parameters.

### 4.3. Cluster analysis (CA)

In recent years, CA has had efficacious applications in assessing spatiotemporal changes in coastal seawater and

**Table 1** The multiple regression analyses of halogens as dependent variables and other parameters in seawater and sediment in Mabahiss and Safagaa Bays.

Dependent variable		Multiple regression equation	R <sup>2</sup>
		<b>Mabahiss Bay</b>	
Fluoride	Seawater	$F_w = -13.2 + 0.84 Cl_s + 0.42 Br_w + 0.42 SO_{4w} - 0.37 Ca_s - 0.31 I_s - 0.02 Depth - 0.22 SO_{4s} + 0.11 T_w + 0.16 F_s$	0.9999
	Sediment	$F_s = -0.1 + 0.69 B_w - 0.48 Depth + 0.51 SO_{4s} - 0.07 B_s + 0.16 HCO_3 + 0.24 I_w - 0.14 Ca_w + -0.01 pH + 0.38 Si_w + 0.16 F_w$	0.9999
Chloride	Seawater	No regression	0.0000
	Sediment	$Cl_s = 35.8 + 0.93 F_w - 0.36 Br_w - 0.18 SO_{4w} + 0.17 Ca_s - 0.12 pH_w + 0.30 Br_s + 0.21 Si_w + 0.10 Depth + 0.09 P_w + 0.05 Mg_w$	0.9999
Bromide	Seawater	$Br_w = 99.2 - 1.56 Cl_s - 0.17 Ca_w - 0.44 Si_s + 0.90 F_w + 0.42 B_s + 0.10 Br_s - 0.22 Mg_s + 0.08 B_w$	0.9999
	Sediment	$Br_s = -0.09 - 1.54 Si_w + 1.36 I_s + 0.18 B_w + 0.71 Cl_s - 0.67 SO_{4w} + 0.75 B_s + 0.34 Ca_s - 0.21 I_w - 0.15 S\%$	0.9999
Iodide	Seawater	$I_w = -76.7 + 0.80 CO_{3w} + 0.46 P_w - 0.33 SO_{4s} - 0.09 B_s - 0.15 \%CO_{3s} + 0.28 T_w - 0.15 Br_w$	0.9999
	Sediment	$I_s = 6.1 + 0.64 Si_s + 1.09 I_w - 0.42 F_w + 1.10 Br_s + 0.70 Si_w + 0.85 Depth - 0.74 S\% + 0.41 Mg_w + 0.33 B_s + 0.05 pH_w$	0.9999
		<b>Safag Bay</b>	
Fluoride	Seawater	$F_w = 510 - 0.55 B_w + 0.86 HCO_{3w} + 0.36 Br_w + 0.44 B_s + 0.75 P_w + 0.59 Ca_w + 0.38 Ca_s - 0.82 pH_w - 0.48 T_w - 0.23 Mg_s + 0.17 SO_{4s} - 0.09 Si_s - 0.03 F_s$	0.9999
	Sediment	$F_s = 2.75 - 0.83 B_s + 1.64 Si_s + 0.59 Ca_s + 0.18 P_s - 0.46 SO_{4s} - 1.19 Si_w - 1.03 I_s - 0.49 Br_w - 0.84 SO_{4w} - 0.30 Mg_s - 0.13 Cl_s + 0.13 Depth + 0.22 I_w$	0.9999
Chloride	Seawater	$Cl_w = -0.19 + 1.01 S\%$	0.9999
	Sediment	$Cl_s = 15.13 + 0.69 Cl_w + 0.97 CO_{3w} - 0.53 Mg_s + 0.37 P_w - 0.06 F_s - 0.40 pH_w + 0.21 Ca_s + 0.09 B_s - 0.20 HCO_{3w} - 0.39 Br_w + 0.19 SO_{4s} - 0.34 Mg_w$	0.9999
Bromide	Seawater	$Br_w = -1139.77 + 2.42 CO_{3w} - 0.05 pH - 1.55 Mg_w + 0.66 SO_{4s} - 0.44 Mg_s - 0.27 B_s + 0.81 S\% - 0.59 Cl_s + 0.33 HCO_{3w} - 0.07 I_w + 0.04 I_s - 0.02 F_w$	0.9999
	Sediment	$Br_s = -1682.1 - 0.95 I_s + 0.91 B_w - 0.19 T_w - 0.47 S\% + 0.05 Si_s - 0.43 Ca_w - 0.16 Mg_s + 0.33 SO_{4w} + 0.43 pH - 0.28 B_s - 0.19 F_s - 0.14 SO_{4s}$	0.9998
Iodide	Seawater	$I_w = -135.7 - 0.55 Si_w - 0.55 Br_w - 0.14 F_s + 0.80 SO_{4w} - 0.65 Mg_w - 0.32 B_s - 0.15 B_w + 0.20 pH_w - 0.12 Ca_s + 0.17 T_w - 0.03 Depth - 0.02 HCO_{3w} + 0.01 Ca_w$	0.9999
	Sediment	$I_s = -33.77 - 0.27 Br_s - 0.31 Br_w - 0.28 F_w - 0.80 F_s - 0.66 \%CO_{3s} - 0.306 Cl_s + 0.356 Ca_s - 0.72 Si_w + 0.285 pH_w - 0.24 Depth - 0.57 SO_{4w} - 0.197 P_w$	0.9999

identifying pollution sources (El-Said, 2013). In this study, cluster analysis is performed using hydrological methods, and the chemical parameters are represented in a dendrogram (Figure 6). However, the dendrograms aM and aS and bM and bS recombine the 16 and 15 parameters in Mabahiss and Safaga Bay's seawater and sediments, respectively. On the other hand, cM and cS represent the station's assembly in the bays of Mabahiss and Safaga, respectively.

In Mabahiss Bay, the presence of fluoride in seawater is mainly affected by pH and boron content (Figure 6aM and bM). This observation may indicate that precipitation of fluoroboron compounds such as  $NaBF_6$  and  $(K,Cs)BF_4$  (Kot, 2009). In this bay, fluoride contains the minerals from fluorapatite, phosphate, and sabkhas in marine sediments. In Mabahiss Bay, the bromide content is affected by the content of bicarbonate in seawater. The release of bromide and/or its deposition in sabkhas minerals may influence the content of marine sediments.

In the seawater of Safaga Bay, marine organisms can absorb fluoride and iodide or release them from sediments rich in organic matter, landfills, and land flows (Figure 6aS). The halogen content in the Safaga Bay sediments can be cova-

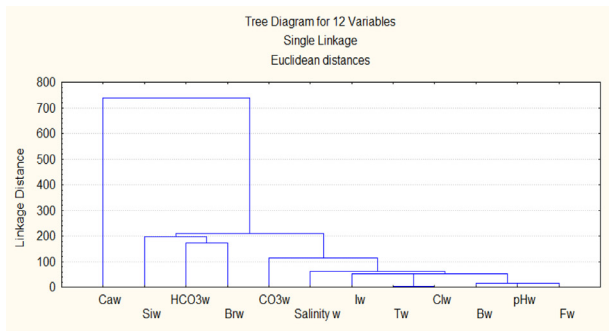
lently bonded to each other to form Lewis bases, such as  $BrCl$  and  $ICl_4$  (Schmidt et al. 2020). Fluoride can also replace other halogens in its minerals (Figure 6bS). Water-soluble halogens may be released and leached during the process of mineralization and weathering, resulting in their local abundance (Harlove and Aranovich, 2018).

The cM and cS tree diagram show the combined station assembly due to the distribution of various parameters in seawater and sediments and human activities, landfills, and land flows in Mabahiss and Safaga bays, respectively.

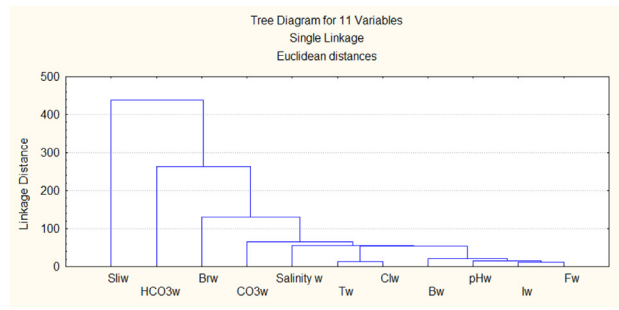
#### 4.4. Principal component analysis (PCA)

PCA/FA is applied to parameter to classify seawater and sediments (14 and 15 stations in Mabahiss and Safaga ports, respectively) (Supplementary Table 3). The six PCs explain 83.17% and 78.65% of Mabahiss and Safaga Bays' total variance, respectively. The calculated data shows that the loading parameter sets are different in the two regions, so each region is discussed separately.

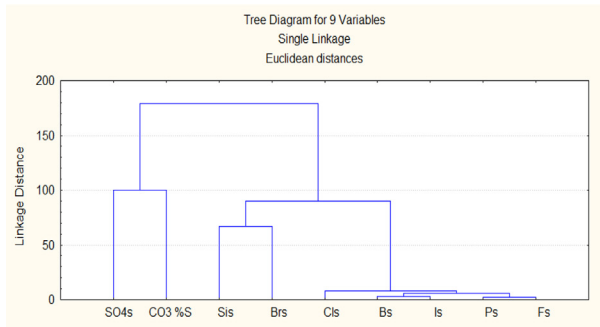
For Mabahiss Bay, PC1 accounts for 18.81% of the total variance. It has a higher positive load on  $Cl_w$  (0.919),



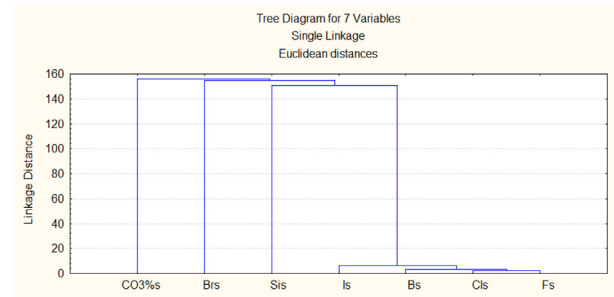
(aM)



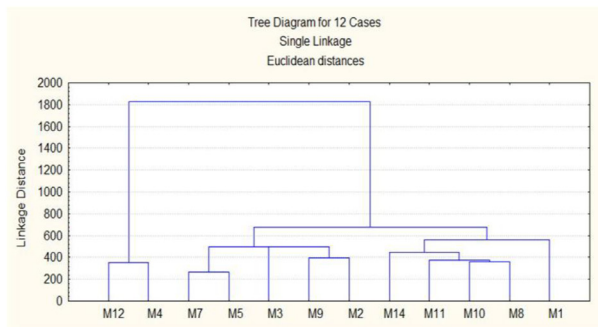
(aS)



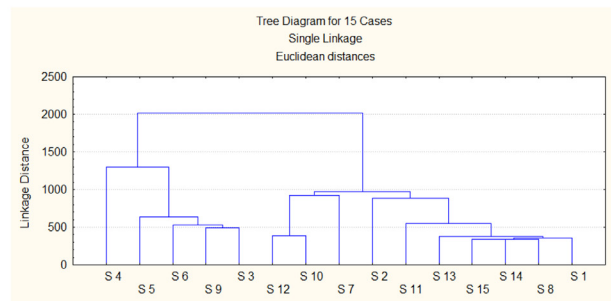
(bM)



(bS)



(cM)



(cS)

**Figure 6** Cluster analysis of Mabahiss and Safaga bays: variables in water samples (aM and aS; the cluster grouping of  $SO_{4w}$  is missed), variables in sediment samples (bM and bS) and stations grouping (cM and cS).

$S\%_o$  (0.919), and  $Mg_w$  (0.793), and a negative load on  $B_w$  ( $-0.815$ ).  $F_s$  ( $-0.831$ ) and  $Mg_s$  ( $-0.667$ ). This factor can be referred to as the salinity factor and mineral deposition factor because the hydrolysis of  $MgCl_2$  causes Mg to be fixed in hydrous silicate minerals, including chlorite. The chloride content influences the boron concentration in seawater, and B/Cl is its geochemical distribution (Moneer et al., 2012). PC2 contributes to 17.59% of the total variance with high positive loads on  $Si_s$  (0.848) and moderate positive loads on pH (0.668) and  $Br_s$  (0.672), however high negative loads may be associated with B ( $-0.848$ ),  $HCO_{3w}$  ( $-0.739$ ) and  $Si_w$  ( $-0.887$ ). Therefore, this factor is mainly due to diagenetic systems, such as dissolved silica content and feldspar diagenesis (Worden, 1996). PC3 is articulated by  $Ca_w$  (0.832),  $Ca_s$  ( $-0.597$ ),  $P_w$  (0.831), and  $T_w$  ( $-0.768$ ) at 14.16%, and

this factor may be combined with Ca as a special geochemical reaction element, especially in the formation of Ca-Hydroxyapatite ( $Ca(PO_4)(OH)$ ). PC4 contributes 12.72% of the  $F_w$  (0.951),  $SO_{4w}$  (0.635), and  $Cl_s$  (0.884) of the positive load. This factor may be due to the Lewis acid-base reaction and the degradation of the sabkhas minerals. PC5 shows 10.03%, where  $I_s$  ( $-0.792$ ) and  $\%CO_{3s}$  (0.700) are loaded. PC6 contributes 9.86% to  $I_w$  (0.833) and  $CO_{3w}$  (0.754) and  $SO_{4s}$  ( $-0.772$ ). This factor may relate to the degradation of sabkhas minerals and seawater's biological activity (Jones et al., 1999).

For Safaga Bay, PC1 shares 15.57% of the total variance with  $HCO_{3w}$  (0.625),  $Mg_s$  (0.650),  $Br_w$  ( $-0.637$ ),  $Ca_w$  ( $-0.629$ ),  $Mg_w$  ( $-0.620$ ) and  $CO_{3w}$  ( $-0.897$ ). Bromide in seawater mainly exists as  $CaBr_2$  and  $NaBr$  (Harlove and Ara-

novich, 2018). This factor can be considered the carbonate and bicarbonate balance. The evaporation of seawater causes halite to recrystallize and form dissolved bromides, such as NaBr (a better dissolved salt than NaCl) (Worden, 1996). The share of PC2 in  $P_w$  ( $-0.776$ ), pH ( $-0.778$ ),  $T_w$  (0.880), and  $SO_{4s}$  (0.651) is 13.85%. This factor involves human made sources. PC3 contributes to 13.15% of the total variance of  $F_s$  (0.822),  $CO_{3w}$  ( $-0.857$ ),  $B_s$  (0.806) and  $Si_s$  (0.857). This factor may contribute to the sediment's nature as fluorine is the most reactive halogen (Ichikuni, 1979). PC4 accounts for 13.12%, which is related to  $I_w$  (0.928),  $SO_{4w}$  (0.856) and  $Si_w$  ( $-0.901$ ). PC5 clarifies 11.97% of the data, where  $Cl_w$  (0.938),  $S_{‰}$  (0.938), and  $Cl_s$  (0.728) are loaded, and the chloride content controls this factor. PC6 has 10.98% which takes part with depth (0.658),  $Br_s$  (0.844), and  $I_s$  ( $-0.807$ ), dealing with the biological activities of marine organisms, and decomposition of organic materials, as well as human activities. This factor may be related to the Br compound in leaded gasoline.

## 5. Conclusion

The horizontal distribution profile of the halogens in seawater and sediment showed the same order of  $Cl_w > Br_w > F_w > I_w$  and  $Br_s > Cl_s > F_s > I_s$ , respectively, in both Mabahiss Bay and Safaga Bay. Interestingly, this study presented the difference in the origin of halogens in the examined bays due to the diverse geochemical distribution of sediments, landfills, land flows and sources of human activities. However, fluoride in seawater in Safaga Bay showed higher mean content than that in Mabahiss Bay and vice versa for bromide and iodide. Specific high levels of fluoride and bromide may indicate anthropogenic sources such as tourism activities, fishing, urbanization, plastic waste, shipyards, anti-corrosion and anti-fouling coatings, surface water and landfills.

On the other hand, multivariate statistical analyses reflected the different distribution of halogens in the bays. From the application of these analyses in the present study, the following conclusions were drawn, in particular. The results of these five statistical methods were complementary. The box plot and whisker method described the different distribution of halogens and specific parameters in seawater and sediments in the Bays of Mabahiss and Safaga. The correlation matrix, CA, and PCA identified the two bays' parameters sources, while multiple regression analyses mainly discussed the interaction between variables. Depending on the configuration, the cluster analysis evaluated nearby stations, and these stations may have the same source of supply. The multivariate statistical analyses in this study also revealed the geological origin of the halogens in the Mabahiss Bay sediments. In contrast, the halogens in Safaga Bay appeared to be controlled by terrestrial flows and anthropogenic sources. The Safaga Bay contains a passenger terminal and a terminal for loading and unloading bauxite, coal, grain, quartz, and feldspar. Accordingly, the statistical analyses used in the current study confirmed the relationship of human activity sources of and geochemical characteristics to the origin of the halogen changes in the study area. This conclusion forces us to use more than one statis-

tical method in the future in predicting the levels of pollutants in the environment as well as their sources.

## Acknowledgments

The authors are grateful to Prof. dr. Mahmoud Ismail, Marine Geology Laboratory, National Institute of Oceanography and Fisheries, NIOF for providing the samples used in this study.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.oceano.2021.09.007>.

## References

- Abd El Wahab, M., Melegy, A., Hela, S., 2011. Distribution and enrichment of heavy metals in recent sediments of Safaga Bay. *Egypt. Mar. Georesources Geotechnol.* 29, 364–375. <https://doi.org/10.1080/1064119X.2011.586014>
- Abdel Ghani, S.A., El Zokm, G., Shobier, A., Othman, T., Shreadah, M., 2013. Metal pollution in surface sediments of Abu-Qir Bay and Eastern Harbour of Alexandria. *Egypt. J. Aquat. Res.* 39 (1), 1–12. <https://doi.org/10.1016/j.ejar.2013.03.001>
- Abou El-Anwar, E.A., Mekky, H.S., Abdel Wahab, W., 2019.  $P_2O_5$ –F–U Characterization and Depositional Environment of Phosphatic Rocks for the Duwi Formation, Qussier – Safaga Region, Red Sea Coast. *Egypt. J. Chem.* 62 (12), 2213–2228. <https://doi.org/10.21608/ejchem.2019.11366.1728>
- APHA-AWWA-WPCF (American Public Health Association), 1999. *Standard Methods for the Examination of Water and Waste Water*, 20th edn., American Publ. Health Assoc., Washington, DC, USA.
- Abouhend, A.S., El-Moselhy, Kh.M., 2015. Spatial and seasonal variations of heavy metals in water and sediments at the Northern Red Sea Coast. *Am. J. Water Resour.* 3 (3), 73–85. <https://doi.org/10.12691/ajwr-3-3-2>
- Aspila, K.I., Agemian, H., Chau, A.S.Y., 1976. A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst* 101, 187–197. <https://doi.org/10.1039/AN9760100187>
- Attia, O.E.A., Abu Khadra, A.M., Nawwar, A.H., Radwan, G.E., 2012. Impacts of human activities on the sedimentological and geochemical characteristics of Mabahiss Bay, North Hurghada, Red Sea. *Egypt. Arab. J. Geosci.* 5, 481–499. <https://doi.org/10.1007/s12517-010-0193-3>
- Attia, O.E.A., Ghrefat, H., 2013. Assessing heavy metal pollution in the recent bottom sediments of Mabahiss Bay, North Hurghada, Red Sea. *Egypt. Environ. Monit. Assess.* 185, 9925–9934. <https://doi.org/10.1007/s10661-013-3302-4>
- Bahafzullah, A., Fayetf, L.A., Kazi, A., Al-Saify, M., 1993. Classification and distribution of the Red Sea coastal Sabkhas near Jeddah-Saudi Arabia. *Carbonates Evaporites* 8 (1), 23–38. <https://doi.org/10.1007/BF03175160>
- Balázs, H., Opara-Nadib, O., Beesea, F., 2005. A simple method for measuring the carbonate content of soil. *Soil. Sci. Soc. Am. J.* 69, 1066–1068. <https://doi.org/10.2136/sssaj2004.0010>
- Brescia, F., Arents, J., Meislich, H., Amos, T., 1975. *Fundamental of Chemistry: A Modern Introduction*, 3rd edn. Academic Press, Inc., New York.

- Dehbandi, R., Moore, F., Keshavarzi, B., 2017. Provenance and geochemical behavior of fluorine in the soils of an endemic fluorosis belt, central Iran. *J. African Earth Sci.* 129, 56–71. <https://doi.org/10.1016/j.jafrearsci.2016.12.016>
- El-Geziry, T.M., Dabbous, A.S., Abdallah, A.M., 2020. General pattern of sea level in Safaga and Qusseir Harbours on the Egyptian Red Sea coast. *Arab. J. Geosci.* 13, 436. <https://doi.org/10.1007/s12517-020-05447-y>
- El-Metwally, M.E.A., Madkour, A.G., Fouad, R.R., Mohamedein, L.I., Nour Eldine, H.A., Dar, M.A., El-Moselhy, Kh.M., 2017. Assessment the leachable heavy metals and ecological risk in the surface sediments inside the Red Sea ports of Egypt. *Int. J. Mar. Sci.* 7 (23), 214–228. <https://doi.org/10.5376/IJMS.2017.07.0023>
- El Nemr, A., El-Said, G.F., 2017. Assessment and ecological risk of heavy metals in sediment and molluscs from the Mediterranean Coast. *Water Environ. Res.* 89 (3), 195–210. <https://doi.org/10.2175/106143016x14798353399458>
- El-Said, G.F., 2005. Distribution of Fluoride Content in Some Localities of Egyptian Coastal Water Ph.D. Thesis. Chemistry Department, Faculty of Science, University of Alexandria, Alexandria, Egypt.
- El-Said, G.F., El-Sikaily, A., 2013. Chemical composition of some seaweed from Mediterranean Sea coast. *Egypt. Environ. Monit. Assess.* 185, 6089–6099. <https://doi.org/10.1007/s10661-012-3009-y>
- El-Said, G.F., 2013. Bioaccumulation of key metals and other contaminants by seaweeds from the Egyptian Mediterranean Sea Coast in relation to human health risk. *Hum. Ecol. Risk Assess.* 19, 1285–1305. <https://doi.org/10.1080/10807039.2012.708253>
- El-Said, G.F., El-Sadaawy, M.M., Moneer, A.A., Shaltout, N.A., 2015. The effect of fluoride on the distribution of some minerals in the surface water of an Egyptian lagoon at the Mediterranean Sea. *Egypt. J. Aquat. Res.* 41 (1), 31–39. <https://doi.org/10.1016/j.ejar.2015.02.004>
- El-Said, G.F., Shaltout, N.A., Moneer, A.A., El-Sadaawy, M.M., Morsy, A.M.H., 2016a. The precipitation of fluoride, calcium and magnesium minerals from Egyptian Mediterranean Sea coast in relation to discharged waters. *Desalin. Water Treat.* 57, 2113–2124. <https://doi.org/10.1080/19443994.2014.979243>
- El-Said, G.F., Khalil, M.Kh., Draz, S.E.O., 2016b. Anomalous distribution of fluoride and phosphorus forms in surface sediments along eastern Egyptian Mediterranean Sea coast. *Environ. Sci. Pollut. Res.* 23, 14240–14253. <https://doi.org/10.1007/s11356-016-6552-1>
- El-Said, G.F., El Zokm, G.M., El Sayed, A.A., El Ashmawy, A.A., Shreadah, M.A., 2020. Anomalous fluctuation of halogens in relation to the pollution status along Lake Mariout. *Egypt. J. Chem.* Article ID 8102081, 1–20. <https://doi.org/10.1155/2020/8102081>
- El-Said, G.F., El-Sadaawy, M.M., Shaltout, N.A., Moneer, A.A., 2021. Spatiotemporal distribution of some dissolved salts and minerals in Lake Edku connected to Mediterranean Sea: in relation to different pollutant inputs. *Environ. Monit. Assess.* 193, 155. <https://doi.org/10.1007/s10661-021-08935-0>
- El-Sarraf, W.M., Masoud, M.S., Harfoush, A.A., El-Said, G.F., 2003. Fluoride distribution and the effect of some ions along Alexandria coastal Mediterranean seawater of Egypt. *J. Environ. Sci.* 15 (5), 639–646.
- El Zokm, G.M., Ibrahim, M.I.A., Mohamed, L.A., El-Mamoney, M., 2020a. Critical geochemical insight into Alexandria coast with special reference to diagnostic ratios (TOC/TN & Sr/Ca) and heavy metals ecotoxicological hazards. *Egypt. J. Aquat. Res.* 46 (1), 27–33. <https://doi.org/10.1016/j.ejar.2019.12.006>
- El Zokm, G.M., Ismail, M.M., El-Said, G.F., 2020b. Halogen content relative to the chemical and biochemical composition of fifteen marine macro and micro algae: nutritional value, energy supply, antioxidant potency, and health risk assessment. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-020-11596-0>
- Fahmy, M.A., 2003. Water quality in Red Sea coastal waters (Egypt): Analysis of spatial and temporal variability. *Chem. Ecol.* 19 (1), 67–77. <https://doi.org/10.1080/0275754031000087074>
- Fahmy, M.A., Abdel Fattah, L.M., Abdel-Halim, A.M., Aly-Eldeen, M.A., Abo-El-Khair, E.M., Ahdy, H.H., Hemeilly, A., Abu El-Soud, A., Shreadah, M.A., 2016. Evaluation of the quality for the Egyptian Red Sea Coastal waters during 2011-2013. *J. Environ. Prot.* 7, 1810–1834. <https://doi.org/10.4236/jep.2016.712145>
- Folk, R.L., 1974. *Petrology of Sedimentary Rocks*. University of Texas, Austin, TX, USA.
- Grasshoff, K., 1976. *Methods of Seawater Analysis*. Verlag Chemie, Weinheim and New York, 317 pp.
- Harlove, D.E., Aranovich, L., 2018. The Role of Halogens in Terrestrial and Extraterrestrial. In: *Geochemical Processes, Surface, Crust, and Mantle*. Springer Geochemistry, Springer International Publishing AG, Switzerland, 1030 pp.
- Ichikuni, M., 1979. Uptake of fluoride by aragonite. *Chem. Geol.* 27 (3), 207–214. [https://doi.org/10.1016/0009-2541\(79\)90039-1](https://doi.org/10.1016/0009-2541(79)90039-1)
- Jeffery, P.G., 1975. *Chemical Methods of Rock Analysis*, second edn., Pergamon Press, New York, NY, USA.
- Jones, B.F., Vengosh, A., Rosenthal, E., Yechieli, Y., 1999. Chapter 3: Geochemical Investigations. In: Bear, J., Cheng, A.H.-D., Sorek, S., Ouaza, D., Herrera, I. (Eds.), *Seawater Intrusion in Coastal Aquifers-Concepts, Methods and Practices, Theory and Applications of Transport in Porous Media*, Volume 14. Springer Science+Business Media, Dordrecht, The Netherlands, 625 pp.
- Kot, F.S., 2009. Boron sources, speciation and its potential impact on health. *Rev. Environ. Sci. Biotechnol.* 8, 3–28. <https://doi.org/10.1007/s11157-008-9140-0>
- Liteplo, R., Gomes, R., Howe, P., Malcom, H., 2002. *Environmental Health Criteria 227*. World Health Organization (WHO), Geneva.
- Mansour, A.M., Askalany, M.S., Madkour, H.A., Assran, B.B., 2013. Assessment and comparison of heavy-metal concentrations in marine sediments in view of tourism activities in Hurghada area, northern Red Sea. *Egypt. J. Aquat. Res.* 39, 91–103. <https://doi.org/10.1016/j.ejar.2013.07.004>
- Mansour, A.M., Nawar, A.H., Madkour, H.A., 2011. Metal pollution in marine sediments of selected harbours and industrial areas along the Red Sea coast of Egypt. *Ann. Naturhist. Mus. Wien Ser. A113*, 225–244.
- Manual of Methods of Analysis of Foods*, 2005. Fruit and Vegetable Products: Directorate General of Health Services. Ministry of Health and Family Welfare, Government of India, New Delhi, 57 pp.
- Masoud, M.S., El-Said, G.F., 2011. Behavior of some chloride, carbonate, phosphate, sulphate and borate additive salt–NaCl aqueous solution systems in the absence and presence of NaF. *Desalin. Water Treat.* 29, 1–9. <https://doi.org/10.5004/dwt.2011.1169>
- Millero, F.J., Feistel, R., Wright, D.G., McDougal, T.J., 2008. The composition of standard seawater and the definition of the reference-composition salinity scale. *Deep-Sea Res. Pt. I* 55, 50–72. <https://doi.org/10.1016/j.dsr.2007.10.001>
- Mohamed, A.A., 1999. *Natural Pigments and Iodine Contents in Certain Marine Macroalgae*. Helwan University, Egypt, 202 pp.
- Molnia, B.F., 1974. A rapid and accurate method for the analysis of calcium carbonate in small samples. *J. Sed. Petrol.* 44 (2), 589–590.
- Moneer, A.A., El-Sadawy, M.M., El-Said, G.F., Radwan, A.A., 2012. Boron human health risk assessment relative to the environmental pollution of Lake Edku. *Egypt. J. King Saud Univ. (JKAU): Mar. Sci.* 23 (2), 41–55. <https://doi.org/10.4197/Mar.23-2.3>
- Muramatsu, Y., Wedepohl, K.H., 1998. The distribution of iodine in the earth's crust. *Chem. Geol.* 147 (3–4), 201–216. [https://doi.org/10.1016/S0009-2541\(98\)00013-8](https://doi.org/10.1016/S0009-2541(98)00013-8)

- Nour, H.E., El-Sorogy, A., Abdel-Wahab, M., Almadani, S., Al-faifi, H., Youssef, M., 2018. Assessment of sediment quality using different pollution indicators and statistical analyses, Hurghada area, Red Sea coast, Egypt. *Mar. Pollut. Bull.* 133, 808–813. <https://doi.org/10.1016/j.marpolbul.2018.06.046>
- Nour, H.E., Nouh, E., 2020. Comprehensive pollution monitoring of the Egyptian Red Sea coast by using the environmental indicators. *Environ. Sci. Pollut. Res.* <https://doi.org/10.1007/s11356-020-09079-3>
- Ries, J.B., 2010. Review: Geological and experimental evidence for secular variation in seawater Mg/Ca (calcite-aragonite seas) and its effects on marine biological calcification. *Biogeosciences* 7, 2795–2849. <https://doi.org/10.5194/bg-7-2795-2010>
- Saenger, P., 1972. A rapid spectrophotometric method for the determination of bromine in seawater and in the ash of marine algae. *Helgoländer wissenschaftliche Meeresuntersuchungen* 23 (1), 32–37. <https://doi.org/10.1007/BF01616309>
- Sawicka, J.E., Jørgensen, B.B., Bruchert, V., 2012. Temperature characteristics of bacterial sulfate reduction in continental shelf and slope sediments. *Biogeosciences* 9, 3425–3435. <https://doi.org/10.5194/bg-9-3425-2012>
- Schmidt, B., Ponath, S., Hannemann, J., Voßnacker, P., Sonnenberg, K., Christmann, M., Riedel, S., 2020. In situ synthesis and applications for polyinterhalides based on BrCl. *Chem. Eur. J.* 26, 15183–15189. <https://doi.org/10.1002/chem.202001267>
- Selim, A.E.M., 2007. *Sedimentation Threats to Red Sea Corals : An Ecological Study of Reefs in the Hurghada region.* Egypt, Ph.D. Thesis. Hull University, England, 207 pp.
- Shapiro, O.H., Kartvelishvily, E., Kramarsky-Winter, E., Vardi, A., 2018. Magnesium-rich nanometric layer in the skeleton of *Pocillopora damicornis* with possible involvement in fibrous aragonite deposition. *Front. Mar. Sci.* 5, Article 246. <https://doi.org/10.3389/fmars.2018.00246>
- Soliman, N.F., El Zokm, G.M., Okbah, M.A., 2018. Risk assessment and chemical fractionation of selected elements in surface sediments from Lake Qarun, Egypt using modified BCR technique. *Chemosphere* 191, 262–271. <https://doi.org/10.1016/j.chemosphere.2017.10.049>
- Strickland, J.D.H., Parsons, T.R., 1972. *A Practical Handbook of Seawater Analysis*, second ed., Fisheries Research Board of Canada. *Bulletin 167*, Ottawa, Canada, 311 pp.
- Tokatli, C., Çiçek, A., Emiroğlu, Ö., Arslan, N., Köse, E., Dayoğlu, H., 2014. Statistical approaches to evaluate the aquatic ecosystem qualities of a significant mining area: Emet stream basin (Turkey). *Environ. Earth Sci.* 71, 2185–2197. <https://doi.org/10.1007/s12665-013-2624-4>
- Worden, R.H., 1996. Controls on halogen concentrations in sedimentary formation waters. *Mineral. Mag.* 60 (399), 259–274. <https://doi.org/10.1180/minmag.1996.060.399.02>