Geochemistry of Sabkhas in Abu Ghraib, Western Baghdad, Iraq

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Abstract
The study aims to detail the chemistry of Sabkha located in Abu-Ghraib, western Baghdad to know the content of the rare elements distributed. Sabkhas are found in dry areas with significant evaporation rates. The quantity of dissolved salts rises as water evaporates from the shallow basins, eventually causing salt to crystallize. The creation of the distinctive salt pans and crusts on the top is greatly influenced by this process. The trace elements (Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Sn, Ba, Ta, Tl, Pb, Th, U, I, and Br) beside the major oxides were analyzed using XRF technique. There are no clear significant differences in the distribution of the elements between the two Sabkhas in the village of Kadim Alaa’ab and the village of Haj Shiaa. Sabkhas are characterized by limited oxygen supplies in the brine, high temperatures, and precipitation of evaporite minerals including chlorides, sulfates, and sulfides. Halite predominates in the Sabkha sediments due to the association of chloride with Na₂O. The CaO is distributed forming calcite, dolomite and gypsum as well as a small amount of clay minerals. The association of trace elements, especially Ni, Rb, Ta, Tl and Br, is mainly concentrated with clay minerals, followed by their concentration in silica, especially Y, Zr and Th. As for halite, it is not associated with trace elements.

Keywords: Sabkha; Geochemistry; Salts; Evaporite; Dry arid

1. Introduction

Sabkhas are depressions in which water collects in regions characterized by arid and semi-arid climatic conditions, meaning areas where salt flats are formed (Awadh et al., 2021). The continental Sabkha is formed in a sedimentary basin with internal drainage that leads to the accumulation of salts. This phenomenon is attributed to the proximity of groundwater to the surface (Friedman, 1978; Hsü, 2013;). Sabkha means salinization of the soil, which in itself is a phenomenon that arises due to the high level of shallow groundwater (Quraishi et al. 2013; Awadh and Muslim, 2014; Awadh et al., 2016), and the poorly permeable soil prevents water from leaching during conventional irrigation, so it is not rinsed (Awadh and Al-Hamdani, 2019). Compared to regular seawater, the salt concentration in the Sabkha and water is typically several times higher. Although potassium chloride, magnesium chloride, and calcium sulfate can also be present, sodium chloride is frequently the predominant salt. Due to the restricted oxygen availability in the brine, redox processes occur in the Sabkhas sediments. Sulfates,

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sulfides, and organic materials are among the chemical species that interact during these reactions. These redox processes depend heavily on the microorganisms that live in the sediments. According to a report by USAID (2004), rising water tables and their effect on soil salinity have contributed to land degradation, resulting in an annual loss of 5% of cultivated land. In arid and semi-arid climates, high temperatures lead to the evaporation of water, which leads to the gradual deposition of salts over time, and the accumulation of a large amount of salt on the soil surface (Al-Hamdani et al., 2016; Awadh, 2018; Boschetti et al., 2020; Awadh et al., 2022). Some studies determined the origin of salts in Iraq and their mineral components, in addition to estimating the salt reserves, including the study of (Jassim and Al-Badri 2019). One of Iraq's largest and most famous Sabkhas is the Sunaisla Sabkha, a closed continental Sabkha in the Jazira region, western Iraq. It was formed by the accumulation of rainwater that washes the soil surrounding the Fatha and Injana Formations, which later mixed with groundwater (Abdul Amir, 2005; Awadh and Ahmed, 2013). It has been shown that the Sebkha Sunaisla consists mainly of halite comprising 97% of this composition (Abdul Amir, 2005). The study of Sabkha is helpful to know the extent to which the soil is affected by salts, to determine the type of salts, and to demonstrate the possibility of reclaiming lands for agriculture and benefiting from salt in various fields. The study area is located in Abu Ghraib, west of Baghdad (Fig. 1). The study aims to determine the chemistry of Sabkha.

Fig. 1. Location map of the study area; A is the Shiaa village; B is the Kadim Alaa’ab village

2. Materials and Methods

2.1. Sampling

The fieldwork included an exploratory trip during which the villages of Kadim Alaa'ab and Haj Shiaa were chosen as an area of interest representing Sabkhas (Fig. 2). The field work was carried out from December 2021 to March 2022. Thirty soil samples, 20 from the village of Haj Shiaa and the remaining ten from the village of Kadim Alaa'ab, were collected from a depth of 1 to 30 cm with an interval of 100 m using the systematic sampling method. Nylon bags were used to transfer the samples to the lab, where they were processed for the necessary analyses. The sampling sites were determined using GPS, where 11 samples were chemically analyzed using XRF and XRD techniques (Table 1).
Fig. 2. Sampling sites in the studied areas; A: red circles are the sample location in Haj Shiaa village and B, blue circles are the sample location in the Kadim Alaa’ab in Abu Ghraib village, western Baghdad.

Table 1. Coordinates and methodology of samples from the Haj Shiaa and Kadim Alaa’ab villages. The x is the type of analysis performed.

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2.2 Mineralogical and Geochemical Analysis

The soil samples were analyzed for mineralogy, and major oxides (SiO$_2$, Al$_2$O$_3$, CaO, MgO, Fe$_2$O$_3$, Na$_2$O, K$_2$O, Cl, SO$_3$, LOI), and trace elements (Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Te, I, Cs, Ba, La, Ce, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, and U) using XRD and XRF techniques, respectively. The analyses were achieved in the Department of Geology, College of Science at the University of Baghdad.

3. Results and Discussion

3.1. Sabkha Mineral Composition

In mineral precipitation, chemical interactions frequently cause different minerals to precipitate in Sabkhas. The evaporation and concentration of dissolved ions can result in evaporite minerals such as halite, anhydrite, and gypsum.

The mineralogical species of non-clay and clay minerals are presented in Figs 3 and 4; the mineral content is presented in Table 2. Halite made up 48.1 to 80.2% of the overall mineralogical composition of the Sabkha, with an average of 63.4%. The average (%) concentrations of feldspar (7.0), quartz (5.7), calcite (6.5), gypsum (5.8), anhydrite (7.6), dolomite (2.3), chlorite (4.8), illite (6.2), and Kaolinite (7.9) form the detail mineral species of the Sabkhas studied. Clay minerals are materials have ability to adsorb trace elements on their surfaces (Awadh, S.M. and Yousif, 2015).
Fig. 3. X-ray diffractogram of Sabkha soil shows the non-clay minerals with kaolinite, sample No. 6 SH

Fig. 4. X-ray diffractogram of Sabkha soil shows clay minerals, sample No. 6 SH
he average (%) of CaO (10.3, 11.26), MgO (0.92, 0.52) and LOI (9.92, 10.2), respectively (Table 3). A good correlation exists with K2O (0.61) and MgO (0.9). Conversely, in Kadim Alaa’ab, the correlation coefficients for silica with Al2O3 and MgO are 0.96 and 0.97, respectively (Table 4). This observation is attributed to the prevalence of quartz and chlorite in the Sabkha. The presence of Mg is evidence of the derivation of the sediments from basic and ultra-basic igneous rocks rich in magnesium (Krauskopf, 1967). Low alumina content (2.7-5.32%, av. 3.87% and .05-3.67%, av. 2.12%) in the two study areas (Haj Shiaa and Kadim Alaa’ab), respectively, reflecting how much clay minerals existed. The CaO distribution in both areas is illustrated in Fig. 5b and 6b. The MgO distribution in both areas is displayed in Figs 5d and 6d. Due to calcite presence, a good correlation exists between CaO and LOI (0.69) in the Haj Shiaa reflecting calcareous Sabkha soil. The MgO distribution in both areas is displayed in Figs 5d and 6d as it participated in forming the dolomite and clay minerals. The K2O distribution in both areas is shown in Figs 5c and 6e as its averages (%) in Haj Shiaa (1.31) and Kadim Alaa’ab (0.95) involved in clay minerals and feldspar. An evident positive correlation was recorded between K2O with each of silica (0.96), Alumina (0.99) and LOI (0.77), as shown in Table 4. This is attributed to clay minerals in samples 1KA and 9KA.

Table 2. Mineral components (%) of non-clay and clay minerals in the Sabkha

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<td>9.5</td>
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<tr>
<td>Min</td>
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<td>2.5</td>
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<tr>
<td>Max</td>
<td>80.2</td>
<td>19.1</td>
<td>10.7</td>
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<tr>
<td>Av</td>
<td>63.4</td>
<td>10.6</td>
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*Hal= halite; Gyp= gypsum; Anh=anhydrite; Cal= Calcite; Qtz= quartz; Feld=feldspar; Dol= dolomite; Chl= chlorite; Ili= illite; Kao= kaolinite

3.1. Geochemistry of Major Oxides

The results of the major components (SiO2, Al2O3, CaO, MgO, Fe2O3, Na2O, K2O, Cl, SO3, and LOI) of the Sabkha in Haj Shiaa and Kadim Alaa’ab were presented in Table 3. The correlation coefficient software programmer was utilized to elucidate the associations among the various variables, and the outcomes were subsequently analyzed. Contour maps (Figs 5a and 6a) were utilized to illustrate the distribution of silica in the two designated study regions. This distribution depended on the amount of silica, which ranges between 11.23 and 20.13%, with an average of 14.42%, and from 10.22 to 18.39%, with an average of 14.64%, respectively (Table 3). The presence of silica in Haj Shiaa exhibits a positive correlation with both Al2O3 (0.61) and MgO (0.9). Conversely, in Kadim Alaa’ab, the correlation coefficients for silica with Al2O3 and MgO are 0.96 and 0.97, respectively (Table 4). This observation is attributed to the prevalence of quartz and chlorite in the Sabkha. The presence of Mg is evidence of the derivation of the sediments from basic and ultra-basic igneous rocks rich in magnesium (Krauskopf, 1967). Low alumina content (2.7-5.32%, av. 3.87% and .05-3.67%, av. 2.12%) in the two study areas (Haj Shiaa and Kadim Alaa’ab), respectively, reflecting how much clay minerals existed. Figs 5b and 6b present the alumina distribution in both areas. No clear correlation was shown between silica and K2O due to the high amount of quartz; in contract, alumina correlated with an intermediate relationship with K2O, indicating the presence of many clay minerals. Alumina is included in the chemical composition of illite and feldspar (Tobia and Shangola, 2019; Veena et al., 2014). In the Haj Shiaa and Kadim Alaa’ab, the average (%) of CaO (10.3, 11.26), MgO (0.92, 0.52) and LOI (9.92, 10.2), respectively (Table 3). The CaO distribution in both areas is illustrated in Figs 5c and 6c. Due to calcite presence, a good correlation exists between CaO and LOI (0.69) in the Haj Shiaa reflecting calcareous Sabkha soil. The MgO distribution in both areas is displayed in Figs 5d and 6d as it participated in forming the dolomite and clay minerals. The K2O distribution in both areas is shown in Figs 5c and 6e as its averages (%) in Haj Shiaa (1.31) and Kadim Alaa’ab (0.95) involved in clay minerals and feldspar. An evident positive correlation was recorded between K2O with each of silica (0.96), Alumina (0.99) and LOI (0.77), as shown in Table 4. This is attributed to clay minerals in samples 1KA and 9KA.
Potassium enters as one of the exchange ions in clay minerals or may adsorb to the surfaces of their plates (Goldshmidt, 1970).

Table 3. Major oxides (%) in Sabkhas of the Haj Shiaa and Kadim Alaa’ab

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<td>CaO</td>
<td>MgO</td>
<td>FeO₂</td>
<td>Na₂O</td>
<td>K₂O</td>
<td>Cl</td>
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<td>29.76</td>
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Table 4. Correlation coefficient of major oxides in the Haj Shiaa and Kadim Alaa’ab

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<td>-0.97</td>
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Alumina is included in the chemical composition of illite and feldspar (Tobia and Shangola, 2019; Veena et al., 2014). In the Haj Shiaa and Kadim Alaa’a, the average (%) of CaO (10.3, 11.26), MgO (0.92, 0.52) and LOI (9.92, 10.2), respectively (Table 3). The CaO distribution in both areas is illustrated in Figs 5c and 6c. Due to calcite presence, a good correlation exists between CaO and Lol (0.69) in the Haj Shiaa, reflecting calcareous Sabkha soil. The MgO distribution in both areas is displayed in Figs 5d and 6d as it participated in forming the dolomite and clay minerals. The K₂O distribution in both areas is shown in Figs 5e and 6e as its averages (%) in Haj Shiaa (1.31) and Kadim Alaa’ab (0.95) involved in clay minerals and feldspar. An apparent positive correlation was recorded between K₂O with each of silica (0.96), Alumina (0.99) and LOI (0.77), as shown in (Table 4). This is attributed to clay minerals in samples 1KA and 9KA. Potassium enters as one of the exchange ions in clay minerals or may adsorb to the surfaces of their plates (Goldshmidt, 1970). The SO₃ content (%) in both areas has (9.37 and 9.52) (Table 3), represented by Na content on average is 22.8% and 23.27%, illustrated in Figs 5g and 6g, respectively. In the same way, Cl is usually dominated in the studied area due to being linked to Na in halite. The average Cl (%) contents seem closely as 26.24 in the Haj Shiaa area and 26.72 in the Kadim Alaa’a area. Chloride values are drawn to show their distribution in both areas (Figs 5h and 6h). Eventually, it is fruitful to illustrate the whole chemistry of Sabkha in both studied areas to give a powerful glance to the reader’s understanding; this illustration is given in Fig.7).

3.2. Geochemistry of Trace Elements

Trace elements are defined as those whose trace concentrations are often insufficient to form independent minerals, but they are included in the composition of minerals due to the closeness of their radii and ionic charges with the main elements. They have complex behavior during sedimentary processes by several factors such as weathering, sorting, adsorption, diagenesis, transportation and metamorphic processes (Condie et al., 1980; Nesbitt et al., 1995). Ten or fewer major elements comprise 99% or more of the system, leaving the other 80 elements as traces (White, 2018). The trace elements (Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Sn, Ba, Ta, Ti, Pb, Th, U, I, and Br) were also analyzed.

3.2.1. Halite-related trace elements

Halite is represented by a highly correlated (0.99) between Na₂O and Cl (Table 7). The correlation coefficient shows that halite in the studied areas is an independent salt, and none of the trace elements is associated with it (Table 7). The trace elements are negatively correlated to halite (Na₂O and Cl) as Na₂O and Cl are correlated with each of V (0.68) (-0.73), Mn (-0.76) (-0.78), Ni (-0.76) (-0.78), Zn (-0.79) (-0.82), Ga (-0.75) (-0.77), As (-0.72) (-0.74), Rb (-0.81) (-0.83), Y (-0.72) (-0.74), Zr (-0.74) (-0.75), and Ba (-0.76) (-0.78) (Table 7).

In the Haj Shiaa area, Table 5 shows the range and average (ppm) of V (18-46, 29), Mn (274-56, 427), Ni (48-100, 74), Zn (34-59, 41), Ga (4-7, 6), As (1-2, 1), Rb (5-8, 7), Y (5-9, 7), Zr (26-50, 37), and Ba (41-109, 87). Trace elements (V, Cr, Cu, Zn, Ga, Y, Zr, Nb, Ba and Pb) have lower concentrations than the international soil standard. Trace elements (Ni and Sr) are of higher concentrations than the international soil standard.

In the Kadim Alaa’ab area, the range and average (ppm) of V (14-38, 28), Mn (292-426, 357), Ni (28-84, 62), Zn (22-46, 37), Ga (3-7, 5), As (0-3, 1), Rb (2-10, 7), Y (2-10, 7), Zr (12-61, 43), and Ba (42-132, 98) (Table 6). Trace elements (V, Mn, Cu, Zn, Ga, Se, Y, Zr, Nb, Ba and Pb) have lower concentrations than the international soil standard. Trace elements (Cr, Ni, and Sr) are of higher concentrations than the international soil standard.
Fig. 5. Spatial distribution of chemical component in the Sabkha in the Haj Shiaa village.
Fig. 6. Spatial distribution of chemical component in the Sabkha in the Kadim Alaa’ab village.
Fig. 7. Bar chart represents the Sabkh chemistry in the studied areas.

Table 5. Trace elements concentration (ppm) in the Sabkha soil (Haj Shiaa area) compared to international references.

| Trace elements | Haj Shiaa | | | | | | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | 2A SH | 3 SH | 6 SH | 11 SH | 14 SH | 17 SH | 20 SH | Min | Max | Av | ²soil | ³PAAS | ⁴UCC |
| Ti | 1066 | 1760 | 1644 | 306 | 2167 | 1814 | 1563 | 306 | 2167 | 1474 | - | 5000 |
| V | 18 | 29 | 26 | 46 | 22 | 36 | 27 | 18 | 46 | 29 | 76 | 150 |
| Cr | 16 | 44 | 34 | 60 | 48 | 65 | 27 | 16 | 65 | 42 | 53 | 35 |
| Mn | 27 | 44 | 39 | 59 | 558 | 561 | 469 | 305 | 426 | 274 | 561 | 427 | 560 |
| Ni | 48 | 73 | 71 | 100 | 76 | 86 | 64 | 48 | 100 | 74 | 20 | 55 | 20 |
| Cu | 12 | 17 | 15 | 22 | 17 | 16 | 10 | 10 | 22 | 16 | 25 | 50 |
| Zn | 34 | 40 | 38 | 59 | 39 | 39 | 38 | 34 | 59 | 41 | 41 | 85 | 71 |
| Ga | 4.0 | 7.0 | 7.0 | 7.0 | 6.0 | 6.0 | 4.0 | 4.0 | 7.0 | 6.0 | 19 | 20 |
| As | 1.0 | 2.0 | 1.0 | 2.0 | 1.0 | 1.0 | 1.0 | 1.0 | 2.0 | 1.0 | - | - |
| Se | 0 | 1.0 | 0 | 4.0 | 3.0 | 1.0 | 0 | 0 | 4.0 | 1.0 | 10 |
| Rb | 5.0 | 8.0 | 7.0 | 8.0 | 7.0 | 8.0 | 6.0 | 8.0 | 7.0 | 8.0 | 160 | 112 |
| Sr | 211 | 311 | 336 | 322 | 251 | 361 | 289 | 211 | 361 | 297 | 240 | 200 |
| Y | 5.0 | 7.0 | 6.0 | 9.0 | 7.0 | 7.0 | 5.0 | 9.0 | 7.0 | 29 | 27 |
| Zr | 26 | 39 | 33 | 50 | 43 | 39 | 29 | 26 | 50 | 37 | 240 | 210 | 190 |
| Nb | 1.0 | 1.0 | 1.0 | 2.0 | 1.0 | 3.0 | 1.0 | 1.0 | 3.0 | 1.0 | 13 | 19 | 25 |
| Mo | 5.0 | 4.0 | 4.0 | 17 | 15 | 15 | 12 | 4.0 | 17 | 10 |
| Sn | 0 | 0 | 0 | 2.0 | 5.0 | 10 | 0 | 0 | 10 | 2.0 |
| Ba | 41 | 108 | 105 | 108 | 109 | 82 | 57 | 41 | 109 | 87 | 554 | 650 | 550 |
| Ta | 35 | 34 | 35 | 36 | 37 | 38 | 38 | 34 | 38 | 36 |
| TI | 1.0 | 1.0 | 0 | 1.0 | 2.0 | 2.0 | 1.0 | 0 | 2.0 | 1.0 |
| Pb | 7.0 | 10 | 9.0 | 10 | 9.0 | 2.0 | 8.0 | 2.0 | 10 | 8.0 | 20 | 20 | 20 |
| Th | 4.0 | 0 | 5.0 | 6.0 | 8.0 | 6.0 | 5.0 | 0 | 8.0 | 5.0 | 14.6 | 10.7 |
| U | 2.0 | 0 | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 | 0 | 2.0 | 2.0 | 3.1 | 2.8 |
| Br | 89 | 223 | 214 | 279 | 299 | 295 | 359 | 89 | 359 | 251 |
| I | 4.0 | 2.0 | 0 | 4.0 | 0 | 0 | 0 | 0 | 4.0 | 1.0 |


PAAS; Post Archean Australian Shale, UCC; Upper Continental Crust.
Table 6. Trace elements concentration (ppm) in the Sabkha soil (Kadim Alaa’ab area) compared to international references

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PAAS; Post Archean Australian Shale, UCC; Upper Continental Crust.

3.2.2. Carbonates-related trace elements

Carbonates mean calcite and dolomite. The trace elements are correlated to calcite as they have a reasonable correlation coefficient appearing between CaO with each of Cu (0.77), As (0.74), and I (0.66). Manganese (Mn) is correlated with dolomite as it has a good correlation coefficient with Mg (0.6) (Table 7).

In the Haj Shiaa area, Table 5 shows the range and average (ppm) of Cu (10-22, 16) and I (0-4, 1). In the Kadim Alaa’ab area, the range and average (ppm) of Cu (4-17, 12), and I (0-5, 1) (Table 6).

3.2.3. Clay minerals-related trace elements

The trace elements (Ni, Rb, Ta, Ti, and Br) are incorporated within the clay minerals. They have good relationships with K2O (0.72, 0.65, 0.7, 0.71, and 0.77) and Al2O3 (0.77, 0.58, 0.7, 0.6, and 0.71). They have disarranged relations with SiO2 (0.68, 0.5, 0.68, 0.11, and 0.6) because silica is of multi-sources and belongs to quartz and feldspar. (Table 7).

In the Haj Shiaa area, Table 5 shows the range and average (ppm) of Ta (34-38, 36), Ti (0-2, 1), and Br (89-359, 251). In the Kadim Alaa’ab area, the range and average (ppm) of Ta (33-38, 36), Ti (0-2, 1), and Br (75-385, 175) (Table 6).

3.2.4. Quartz-related trace elements

The trace elements (Y, Zr, and Th) are linked to the quartz as they have a good correlation coefficient with silica (0.69, 0.68, and 0.7), respectively (Table 7). In the Haj Shiaa area, Table 5 shows...
the range and average (ppm) of (Th) (0-8, 5). In the Kadim Alaa’a’b area, the range and average (ppm) of (Th) (2-7, 4) (Table 6).

Table 7. Correlation coefficient of major and trace elements in both study areas (Haj Shiaa and Kadim Alaa’a’b).

5. Conclusions

The Sabkha ecosystems have a complicated chemistry that is impacted by several variables. These distinctive areas offer essential insights into geochemical processes and are crucial habitats for specialized creatures adapted to severe environments and high salinity. Redox reactions happen in the sediments of Sabkas due to the limited oxygen supply in the brine. Several chemical species interact during these reactions, including chloride, sulfates, sulfides, and organic compounds. Chloride and Na2O contribute the highest amount in the Sabkha sediments, which makes halite the common mineral. The most significant amount of CaO formed calcite, and the other part was incorporated in dolomite after its association with MgO, and there is a small quantity associated to form gypsum, anhydrite and clay minerals. The behavior of the trace elements showed that they are not related to the halite. The concentrations of V, Cr, Cu, Zn, Ga, Y, Zr, Nb, Ba, and Pb are below the international soil standard. Nickel and Sr are two trace elements with higher quantities than the soil’s international standard. Trace elements (Ni, Rb, Ta, Ti and Br) are incorporated into the clay minerals having good relations with K2O and with Al2O3. The trace elements (Y, Zr and Th) are associated as it has a good correlation coefficient with silica. The trace element is associated with calcite, while manganese is associated with dolomite.

Acknowledgements

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References


