Contents lists available at ScienceDirect

# Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

# Impact of seawater intrusion and disposal of desalinization brines on groundwater quality in El Gouna, Egypt, Red Sea Area. Process analyses by means of chemical and isotopic signatures



C. Jahnke<sup>a,\*</sup>, M. Wannous<sup>b</sup>, U. Troeger<sup>b</sup>, M. Falk<sup>c</sup>, U. Struck<sup>c,d</sup>

<sup>a</sup> State Office for Mining, Geology and Minerals Brandenburg, Inselstraße 26, 03046, Cottbus, Germany

<sup>b</sup> Technical University Berlin, Central Institute El Gouna, Ackerstraße 76, 13355, Berlin, Germany

<sup>c</sup> Museum of Natural History, Leibniz Institute for Evolution and Biodiversity Science, Invalidenstraße 43, 10115, Berlin, Germany

<sup>d</sup> Freie Universität Berlin, Institute of Geological Sciences, Malteserstraße 74-100, Building D, 12249 Berlin, Germany

#### ARTICLE INFO

Editorial handling by Prof. M. Kersten Keywords: Egypt Red Sea Desalinization Seawater intrusion Brine disposal

# ABSTRACT

The processes of seawater intrusion, groundwater abstraction and disposal of high concentrated effluents from desalinization plants (DSP) were investigated in a coastal aquifer on the Red Sea coast of El Gouna, Egypt. The feeding wells (depths from 20 to 150 m), the product water and the residual brines of three desalinization plants were sampled for chemical analysis and were partially sampled for stable isotopes analysis ( $\delta^{18}$ O and  $\delta^{2}$ H in H<sub>2</sub>O).

The wells in the aquifer abstract mixtures of brackish groundwater (total dissolved solids TDS 5–15 g/l) and seawater from the Red Sea (TDS 42–44 g/l) that intrudes into the coastal aquifers. Primary mixing rates were determined by means of the Br/Cl ratio and ranged from 5% to > 90% seawater. The disposal of the highly concentrated residual brines from the DSPs via infiltration/injection into the used aquifer causes a locally strong increase in the salinization of the groundwater (up to 60 g/l TDS, significantly above seawater concentration) in wells that are actually feeding the DSPs (containing up to 60% brine). The influence of the brines on the groundwater could also be identified by the Br/Cl ratio in relation to salinization. Conversely, the primary source (the mixing ratio groundwater-seawater) of the brines from the DSP could also be identified by Br/Cl ratio and stable isotopes ( $\delta^{18}$ O and  $\delta^{2}$ H in H<sub>2</sub>O), which behave as conservative tracers in the reverse osmosis processes in the DSP.

The brackish groundwater shows partially gypsum saturation and supersaturation. Mixing of this groundwater with seawater additionally increases the sulphate concentration and cation exchange processes and especially the calcium concentration. The abstracted groundwater and groundwater-seawater mixtures therefore have a high potential for sulphate scaling. Calcite, as the second important phase for scaling, is generally supersaturated in groundwater, seawater and the mixtures. Consequently, the brines that are produced from these waters are highly supersaturated with respect to gypsum and calcite.

The injection/infiltration of these brines into the aquifers leads to extended zones of groundwater with increased salinity and saturation/supersaturation in respect to gypsum and probably intense gypsum precipitation.

#### 1. Introduction

The growing population and economy in the Red Sea Area of Egypt increase the water demand in a region with an arid climate and a lack of fresh water resources. Beside freshwater pipelines from the Nile Valley to the Red Sea Coast, the desalinization of seawater and brackish water in coastal aquifers are the only common options to satisfy the increasing demand (El-Sadek, 2010; Hafez and El-Manharawy, 2002; Khalil, 2004). Due to the coastal outline and the dispersed locations of tourist, industrial and urban settlements, the sizes of the desalinization plants are relatively small, with capacities of approximately 100 to approximately  $1000 \text{ m}^3/\text{d}$  (El-Sadek, 2010).

The treatment of seawater from the Red Sea has some particular problems:

• salinity with a TDS of 42.5-44.5 g/l (20-25% higher than standard

\* Corresponding author. E-mail address: Christoph.Jahnke@lbgr.brandenburg.de (C. Jahnke).

https://doi.org/10.1016/j.apgeochem.2018.11.001

Received 23 February 2018; Received in revised form 31 October 2018; Accepted 1 November 2018 Available online 02 November 2018

0883-2927/ © 2018 Elsevier Ltd. All rights reserved.



seawater  $\approx$  35.5 g/l);

- high sulphate scaling potential due to high sulphate content and a high ratio of sulphate/alkalinity (Hafez and El-Manharawy, 2002); and
- richness in biota and suspended matter, which often require a pretreatment (Hafez and El-Manharawy, 2002).

The use of brackish water in the coastal aquifers (TDS from > 2 to 10 g/l) of the Red Sea area is related to other problems:

- normally non-renewable, finite resources, often with a lack of systematic investigation;
- Salt layers underneath the coastal aquifers can lead to a strong increase in water salinity with increasing depth, and in case of abstraction from these aquifers, the upconing of high saline groundwater may occur;
- The coastal aquifers are often in hydraulic connection with the Red Sea, so seawater intrusion might be a problem in case of ground-water abstraction in the coastal aquifers (investigated in a similar environment, i.e., by Eissa et al., 2016 at the Gulf of Aqaba).

Beside the problems of the economic abstraction and treatment of the saline and/or brackish water, the disposal of the hypersaline effluent from the desalinization plants is a common problem for a sustainable use of desalinization. The long-term effect of brine discharge into the environment has not been investigated sufficiently yet. In general, some models have been developed to check the distribution of the plumes (Del Bene et al., 1994; Doneker and Jirka, 2001; Purnalna et al., 2003). Other investigations were undertaken to study the effect of the brine disposal on the marine environment (Chesher, 1975; Höpner and Windelberg, 1997; Mabrook, 1994; Morton et al., 1997). In case of some inland desalinization plants where the brine has been discharged either in open pits or directly on the surface (Mohamed et al., 2005; Someswara et al., 1990), the soil salinity increased as well as the salinity of the feeding water where the discharge points were not far from the intake locations. The salinity of the aquifers can also increase through leakage from pipelines conducting the brine (Sadhwani et al., 2005; Tularam and Ilahee, 2007) or through discharging the brine directly into the underground (Baalousha, 2006).

This study aimed to analyse and quantify the impact of the disposal of saline effluents from desalinization plants on the groundwater chemistry in an arid environment with different sources of salinity (seawater, dissolution of evaporites and disposal of brines from DSP) to show methods for differentiating the influence of those sources and to show the interactions of those sources in hydrochemical processes (brine disposal, seawater intrusion, dissolution/precipitation of minerals, and ion exchange) on different parameters.

### 2. Site description

# 2.1. Water supply in the investigation area

El Gouna town is located directly on the Red Sea 20 km north of Hurghada City (Fig. 1 a) and situated in the Eastern Desert of Egypt. It was founded as a tourist resort in 1989. The population number was estimated as 6400 in 2004, while the present population is estimated at approximately 15,000 inhabitants, depending on the tourist volume.

The climate is characterized by very hot dry summers and mild winters. The temperature can reach 40 °C between July and August and decreases to 20 °C in winter. Rainfall events, which are very rare, do not exceed a few millimetres and normally occur between October and May. A record of precipitation and resulting flash flood events from 1923 until 2014 was reported by (Hadidi, 2016). Nevertheless, the infiltration process from these events requires further investigation.

The water supply in El Gouna depends completely on the desalinization of groundwater-seawater mixtures from coastal aquifers, where they use three desalinization plants (DSPs) to produce water (Fig. 1 b). More than 50 wells divided into three groups feed the three desalinization plants, which treat approximately 11,600 m<sup>3</sup>/d. The product water is used for the drinking water supply and to irrigate gardens and green areas, which include a golf course and tree nurseries. In addition, the sewage of three wastewater treatment plants (WWTP, with a capacity of approximately 4700 m<sup>3</sup>/d) located in the investigation area is used for irrigation.

DSP-1 ("new DSP") entered service in 2011, whereas DSP-3 ("old DSP") and DSP-2 were established in 1995. The wells of the "DSP-1 (new DSP)" group (Fig. 1) feed DSP-1, which has a maximum capacity of 4000 m<sup>3</sup>/d. The maximum capacity of DSP-3 is 9500 m<sup>3</sup>/d, whereas the average production is 5–6000 m<sup>3</sup>/d. The wells of group "DSP-3 (old DSP)" surround the DSP, and a pipeline transporting water from the wells of the "mountain group" feeds DSP-3. The more highly concentrated waters from the wells of the DSP-3 group and the less concentrated waters from the mountain group pipeline are treated in different facilities at the DSP. DSP-2, which is situated in the west close to the mountain area, desalinates approximately 130 m<sup>3</sup>/d, which is used for irrigation only.

All three desalinization plants employ reverse osmosis technology. The amount of product water ranges from 35% to > 50% of the feed water, so that 4000 to  $6000 \text{ m}^3/\text{d}$  of desalinized product water and  $6000 \text{ to } 8000 \text{ m}^3/\text{d}$  of concentrated retentate (brines) are produced. Anti-scalants (e.g., salts of polycarboxylic acids) are used to prevent mineral precipitation on membranes.

Since discarding brines directly into the sea is not allowed by law, the brine outflow from the DSPs is handled in different ways. In the northern sector of El Gouna at DSP-1, a discharging well (with a depth 95–100 m) was drilled to inject the brine from the DSP into the subsurface (Fig. 1). The small amount of brines from DSP-2 is drained directly on the surface close to the DSP. At DSP-3, the residual brines are conducted into a channel, which is connected to a pipeline that ultimately leads into an artificial lagoon lying close to DSP-3. Part of the brine is conducted into ponds that are used as fish farms (after dilution with low mineralized waters).

# 2.2. Geology of the study area

The investigation area is located at the south western border of the Gulf of Suez, a continental rift structure that is separated from the Red Sea rift by the Aqaba transform fault in the south and bounded by the Red Sea hills on the west and the Sinai Massif on the east. The rifting in the Gulf of Suez evolved in the Late Oligocene and Miocene (24 Ma to 14 Ma) and is to a minor extent still active (Bosworth et al., 2005). The stratigraphy can therefore be divided into three major sedimentary sequences/units with the following lithostratigraphic formations (see Fig. 2, abbreviations corresponding to Klitzsch and Linke, 1983).

- Pre-rift Units (Pre-Oligocene)
  - o Gr Basement (Precambrian Granites) (not occurring in the investigation area and not on the map in Fig. 2: Palaeozoic, Upper Cretaceous, Lower Eocene)
- Syn-rift Units (Late Oligocene Middle Miocene)
   o Tmm Middle Miocene (continental and shallow marine)
   o Tev Evaporates of Middle and Late Miocene
- Late-rift Units (Late Miocene/Pliocene to Quaternary) o Tpl Pliocene (shallow marine and continental clastics)
  - o Q,  $Q_{G, S, W}$  Quaternary (gravel plain, sabkha deposits, alluvial fan and wadi deposits)

The topographic heights of the Abu Shar Plateau (Gebel Abu Shar, 200–400 m.a.s.l.) and the Eastern Desert Mountains to the west of the investigation area are related to rotated fault blocks of the rift basin. The NW-SE orientated blocks extend parallel to the coastline 5 km west of El Gouna. A perpendicular fault system striking NE-SW (see Fig. 2)



Fig. 1. Investigation area: facilities and well locations (coordinate system: ETRS, 1989 UTM 36N, epsg-code: 25836, also in the following maps). The classification of wells into the groups is based on the local classification.

crosses the blocks, where wadis and alluvial fans developed in the Syn-Rift and Late-Rift sequences (Wadi Bail, Wadi Abu Tareifi and Wadi Umm Diheis; see Fig. 2).

The Eastern Desert Mountains in the west of the area are formed by Precambrian crystalline basement (acidic plutons and ophiolite formations) (Greiling et al., 1988; Hadidi, 2016). The main block of the Abu Shar Plateau consists of Miocene units (Fig. 2: Tmm and Tev). The Middle Miocene unit (Tmm) is built up by a sequence of stromatolitic limestones, shallow water limestones with dolomitic hardgrounds and sandstones with intercalations of conglomerates (Linke, 1986). Thick layers of halite with intercalations of sulphates and carbonates (evaporitic unit, Tev) were deposited between the rotated fault blocks in the Middle Miocene and are located today in the deeper parts of the basin (especially offshore at depths from several 100 up to some 1000 m), playing an important role as cap rocks of hydrocarbon reservoirs. Near the surface, the Tev evaporitic unit has been washed out (consisting today of gypsum and anhydrite with intercalations of marls) and eroded, and hence the existence of outcrops is rare (Hadidi, 2016; Linke, 1986).

The area between the mountains and the shoreline builds a flat coastal plain with an elevation between 5 and 20 m.a.s.l. It consists of the Late-Rift sequences of the Pliocene and Quaternary, which are composed of alluvial fan and wadi deposits ( $Q_W$ ), gravel plain deposits ( $Q_G$ ), sabkha deposits ( $Q_s$ ) and shallow marine clastics (Tpl and Q) with thicknesses up to several 100 m (Hadidi, 2016; Klitzsch and Linke, 1983).

The water supply wells of El Gouna are drilled in the coastal plain in the Quaternary and Pliocene formations to depths of 25–150 m. The sediment record from drilling logs shows an interchange of coarse alluvial fan deposits with finer grained stream and/or beach sedimentation and shallow marine sandy muds and siltstones with carbonates. These strata can be divided into different aquifers of local character with thicknesses from 10 to 30 m that are separated by aquitards of marine mud- and siltstones with thicknesses of several metres.

# 3. Methods

# 3.1. Sampling and chemical analytics

Samples from groundwater, seawater and desalinization plants were analysed between 2014 and 2018 to investigate the hydrochemical situation and processes in the area. Information such as depth of boreholes, length of casings and position of screens was unavailable for many of the wells. In addition, the exact positions of the wells are not documented and were estimated using a GPS-handheld device during the sampling campaigns (with an accuracy of  $\pm$  several metres). Additionally, the well heads are not referenced to a vertical datum. In the feeding wells of the DSP, permanently installed submersed pumps were used for sampling. The water level in these wells could not be measured, hence hydraulic data are currently unavailable, and groundwater flow direction is indeterminable. Only assumptions about the hydrodynamics can be made and are discussed based on the hydrochemical results.

For the samples from the wells, parameters EC, T and pH were measured at each sampling location using WTW<sup> $\circ$ </sup> portable devices. Alkalinity was measured in the field using gran titration. Anion and cation samples were filtered through a 0.45 µm filter and placed into 50-ml bottles. The cation and anion samples were acidified by adding 0.2 ml of HNO<sub>3</sub> and 0.2 ml of bacteria acid C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>S, respectively.

 $NO_3^-$ ,  $SO_4^{2-}$ ,  $Cl^-$  and  $Br^-$  were analysed using a Metrohm<sup>\*</sup> 881 Compact Ion Chromatograph pro - Anion – MCS. Major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) were analysed using an Agilent<sup>\*</sup> 715 ICP-OES. All analyses were performed at a laboratory on the El Gouna campus of the Technical University of Berlin.

Stable isotope ratios of oxygen ( ${}^{18}O/{}^{16}O$ ) and hydrogen ( ${}^{2}H/{}^{1}H$ ) in H<sub>2</sub>O in water samples were measured with a PICARRO<sup>\*</sup> L1102-i isotope analyser at the Museum of Natural History in Berlin-Germany. The L1102-i is based on the WS-CRDS (wavelength-scanned cavity ring down spectroscopy) technique (Gupta et al., 2009). Measurements were calibrated by the application of linear regression of the analyses of IAEA calibration material VSMOW, VSLAP and GISP.

Representative hydrochemical analyses are presented in Appendix



Fig. 2. Geological map of the area (Klitzsch and Linke, 1983); see the text for geologic symbols/abbreviations.

A. Supplementary material, Table S - 1. The samples were taken from 44 wells that either feed the desalinization plants or are being used for direct irrigation, from residual brines and desalinated product water (drinking water) of the DSP and from seawater of the Red Sea. At 12 locations samples were taken for the analysis of stable isotopes, oxygen  $(^{18}O/^{16}O)$  and hydrogen  $(^{2}H/^{1}H)$  in H<sub>2</sub>O.

The grouping of the samples (mountain group, DSP-1, and DSP-3 wells) in Table S - 1 and the following sections follows the local classification of the wells and was not changed (see Fig. 1).

3.2. Analyses of conservative mixing processes – use of linear and nonlinear relationships

To analyse and quantify the influence of seawater and brines of the DSP on groundwater chemistry, mixing calculations were carried out based on the ratio of the conservative parameters  $Br^-$  and  $Cl^-$  and stable isotopes  ${}^{18}O/{}^{16}O$  and  ${}^{2}H/{}^{1}H$  in  $H_2O$ .

The mixing concentration  $A_m$  of a parameter A in a mixture with a fraction  $\alpha$  between two endmembers having concentrations  $A_1$  and  $A_2$  is given by

$$A_m = (1 - \alpha)A_1 + \alpha A_2. \tag{1}$$

The mixing fraction  $\alpha$  of the endmember 2 in the mixture is given by

$$\alpha = \frac{A_m - A_1}{A_2 - A_1}.\tag{2}$$

In some cases (e.g., in processes where concentration ratios behave conservatively but not the concentrations themselves), it is necessary to use concentration ratios instead of concentrations in mixing calculations. Concentration ratios therefore behave nonlinearly in mixing processes of two or more parameters, which was first discussed and outlined for isotopic ratios (Jenkins and Clarke, 1976; Langmuir et al., 1978). In a mixture of two parameters and two endmembers (A<sub>1</sub>;B<sub>1</sub>) and (A<sub>2</sub>;B<sub>2</sub>), the ratio  $A_m/B_m$  of the mixture ( $A_m$ ;B<sub>m</sub>) must be calculated as follows:

$$\frac{A_m}{B_m} = \frac{(1-\alpha)A_1 + \alpha A_2}{(1-\alpha)B_1 + \alpha B_2} = \frac{(1-\alpha)\frac{A_1}{B_1} + \alpha \frac{A_2}{B_1}}{(1-\alpha) + \alpha \frac{B_2}{B_1}} = \frac{(1-\alpha)\frac{A_1}{B_1} + \alpha \frac{B_2}{B_1}\frac{A_2}{B_2}}{(1-\alpha) + \alpha \frac{B_2}{B_1}}.$$
(3)

In Formula 3, the concentration ratio  $A_m/B_m$  of the mixture depends not only on the mixing fraction  $\alpha$  and the ratios  $A_1/B_1$  and  $A_2/B_2$  but also from the ratio  $B_2/B_1$ . The fraction  $\alpha$  of the endmember ( $A_2;B_2$ ) in the mixture ( $A_m;B_m$ ) based on concentration ratios can be obtained by rearranging Formula 3:

$$\alpha = \frac{\frac{A_m}{B_m} - \frac{A_1}{B_1}}{\frac{B_2}{B_1} \left(\frac{A_2}{B_2} - \frac{A_m}{B_m}\right) - \frac{A_1}{B_1} + \frac{A_m}{B_m}}.$$
(4)

In special cases where  $B_1 = B_2 = B_m$  (or at least as an approximation  $B_1 \approx B_2 \approx B_m$ ), Formula 4 is reduced to the linear equation

$$\alpha = \frac{\frac{A_m}{B_m} - \frac{A_1}{B_1}}{\frac{A_2}{B_2} - \frac{A_1}{B_1}}.$$
(5)

When increasing the deviation of  $B_1/B_2$  from 1, the nonlinearity of Formula 3 and Formula 4 increases, and the deviation of Formula 5 from Formula 4 also increases; hence, Formula 5 becomes increasingly incorrect.

The formula that must be used depends on the  $B_2/B_1$  ratio of the endmembers of the mixing process. For the ionic ratio Br/Cl (or v.v. Cl/Br), the nonlinear Formula 3 and Formula 4 usually have to be used due to the normal difference in concentrations of both ions in natural waters. The ratios  ${}^{18}O/{}^{16}O$  and  ${}^{2}H/{}^{1}H$  (and also the enrichment factors normalized to SMOW  $\delta^{18}O$  and  $\delta^{2}H$ ) can be used with the linear Formula 5 since the concentrations of the isotopes  ${}^{16}O$  and  ${}^{1}H$  are almost constant in natural waters ( $\approx$  the amount of water in the solution), and hence the ratio  $B_2/B_1$  in Formula 3 and Formula 4 is very close to 1.

#### 3.3. Hydrochemical modelling

Beside conservative mixing processes of tracers, chemical reactions occur that can be described by means of hydrochemical models. In this work, two hydrochemical modelling approaches were used:

- a) modelling of speciation and saturation with respect to minerals and gaseous phases of analysed samples from groundwater, seawater and DSP brines to characterize the actual state of the hydrochemical system; and
- b) modelling of reaction paths during mixing processes between intruding seawater and groundwater including
  - (1) precipitation of mineral phases and
  - (2) ion exchange between the water and the solid phases.

The hydrochemical modelling were carried out with the *PHREEQC Interactive, Version 3.3.9* software (2016). Because of the partially high salinization of the solutions with ionic strengths up to > 1 mol/l, a thermodynamic database basing on solubility data and Pitzer

interaction parameters (Pitzer, 1973) were used, which were first developed for the complete system Na–K–Ca–Mg–Cl–SO4-TIC at 25 °C and 1 atm by Harvie et al. (1984) and Harvie and Weare (1980) and are updated for ranges of temperature from 0 to 200 °C and pressures from 0 to 1000 atm based on the compilations of Appelo (2015) and Appelo et al. (2014) (included as the parameter file "Pitzer.dat" in *PHREEQC Interactive, Version 3.3.9* 2016).

# 4. Results and discussion

4.1. Hydrochemical groups and sources of groundwater in the investigation area

The groundwater in the investigation area shows a broad range of salinizations from brackish to saline, with approximately 5-60 g/l of total dissolved solids (TDS). In some wells, the salt content in the groundwater even exceeds the salinization of the Red Sea (with 37-44 g/l TDS). The groundwater analyses presented in Table S - 1 can be interpreted as mixtures of three hydrochemical groups with different source and chemical characteristics:

- a) natural brackish groundwater in the south and west of the investigation area ("mountain group": DSP-2 and mountain DSP wells),
- b) intrusive seawater from the Red Sea, and
- c) residual brines from the desalinization plants.

The DSP-1 and DSP-3 feeding wells abstract mixtures of these 3 groups.

Fig. 3 shows the hydrochemical characteristics of the analyses in a modified Piper plot (the position of  $Cl^-$  and  $HCO_3^- + CO_3^{2-}$  is changed for a better representation). In Table 1, the salinities and characteristic concentration ranges of the conservative tracers, chloride and bromide, are listed for the 3 hydrochemical groups.

The different hydrochemical groups can be characterized as follows.

### a) Natural brackish groundwater of the mountain group

The groundwater from wells located west and south of the investigation area, mostly near the topographic step between the coastal flat and the Abu Shaar Plateau, represents the normal groundwater in the region (although partially influenced by residual brines of DSP-2, as shown later). Compared to the other groups, the concentrations of



Fig. 3. Modified Piper plot with the compositions of the different hydrochemical groups in the investigation area.

#### C. Jahnke et al.

#### Table 1

Concentration ranges of chloride and bromide in the hydrochemical groups of the investigation area (the numbers in brackets show the number of analyses in this group, and the analyses are presented in Appendix A. Supplementary material, Table S - 1).

Hydrochemical group [in brackets number of analyses]	Salinity [‰] TDS [g/l]	Chloride [g/l]	Bromide [mg/l]	Ratio Br/Cl (molar)
Mountain group [29] Red See [14]	5.5–15.7	2.0–7.0	20–50	3.6*10 <sup>-3</sup> (3-4.3*10 <sup>-3</sup> )
Offshore Seawater [12, a selection of 4 analyses is presented in Table S - 1]	37 3-41 7	22.0-23.5	70-80	1 51*10 <sup>-3</sup> (1 44–1 54*10 <sup>-3</sup> )
Lagoons of El Gouna [2]	43.3-44.4	26.0-28.0	80-90	$1.4*10^{-3}$ (1.4–1.41*10 <sup>-3</sup> )
Residual brines of desalinization plants (DSP) [7]				
DSP-1 (new DSP) [1]	62.8	36.2	126	$1.55*10^{-3}$
DSP-2 (mountain DSP) [2]	13.6-22.2	6.1–9.9	48–78	$3.47*10^{-3}$
DSP-3 (old DSP) [4]	53.5–66.8	28.8-35.9	115–156	17.6–1.93*10 <sup>-3</sup>

chloride and bromide are low, although the waters are brackish, with chloride concentrations from 2000 to 7000 mg/l.

The sulphate content comprises 20 to > 40% of the anions. The concentrations of the cations in the group are quite similar, with percentages of Na + K of 40–50% and molar ratios of Mg/Ca between 0.75 and 1.1. Nevertheless, the ratios of SO<sub>4</sub>/Cl and (Ca + Mg)/(Na + K) indicate two subgroups (see the Piper-plot, Fig. 3). The concentrations of NO<sub>3</sub> show a range from 0.5 to 15 mg/l, with two outliers with concentrations up to > 50 mg/l (wells No. 16 and 17, see Table S - 1).

The molar Br/Cl ratios of the samples from the mountain group are high  $(3.1-4.3*10^{-3})$ , approximately two to three times higher than that of seawater  $(1.4-1.55*10^{-3})$ , and hence the salinization of these brackish waters cannot be derived from intruded seawater. The dissolution of evaporitic salt that occurs at greater depth in the Gulf of Suez (Miocene evaporates, see section 2.2) also cannot be the reason for the salinity because of the much lower Br/Cl ratios of evaporites. The molar Br/Cl ratios of halite range between  $1*10^{-5}$  and  $2.5*10^{-4}$ , and those of K-Mg-salts (like sylvite KCl or carnallite KMgCl<sub>3</sub>\*6H<sub>2</sub>O) are between  $4*10^{-4}$  and  $1.1*10^{-3}$  (recalculated from data collections in Braitsch, 1971; Herrmann, 1972; Herrmann, 1980). Analyses of halites from the Miocene evaporites of the Red Sea show molar Br/Cl ratios between  $2.8*10^{-5}$  and  $1.4*10^{-4}$ , with an average of  $7.9*10^{-5}$  (recalculated from analyses in Stoffers and Kühn, 1974). Sturchio et al. (1996) reported some analyses of brackish thermal groundwater from the Gulf of Suez at the western Sinai Peninsula with Br/Cl ratios of  $2.84-3.55*10^{-3}$ , comparable to that of the mountain group, and interpreted the relative enrichment of Br with the uptake and evaporative concentration of marine aerosols in the recharge area because Br enrichment is very common in marine aerosols (Sturges and Harrison, 1986; Winchester and Duce, 1967). The samples from the mountain group also show a partially thermal influence and increased temperatures up to 40 °C, while the normal temperature range of the groundwater in the coastal plain is 27 °C-32 °C (wells of the old DSP group and new DSP group).

#### b) Seawater of the Red Sea and the artificial Lagoons of El Gouna

The salinity of the Red Sea in the investigation area (37.3-41.7%) is higher than that of standard seawater (35%) (Andrie and Merlivat, 1989; Cember, 1988; Craig, 1966) and shows a typical seawater ion composition dominated by chloride, sodium and magnesium. The molar Br/Cl ratios  $(1.4-1.55*10^{-3})$  also coincide with standard seawater (Alcala and Custodio, 2008; Millero et al., 2008). In relation to the offshore Red Sea, the samples from the artificial Lagoons of El Gouna show a higher salinization. This might be a result of evaporation processes and discharge of DSP brines into the lagoons.

# c) Residual brines of desalinization plants

The brines from the DSP-1 and DSP-3 desalinization plants show chloride concentrations significantly above that for seawater but plot between seawater and the mountain group in the Piper diagram (Fig. 3). The chloride concentration of brine from DSP-2 (the DSP of the "mountain group") is much lower (from 6 to 10 g/l) and falls in the range of the brackish mountain group in the Piper plot (Fig. 3). The desalinated product water of the DSPs is a solution dominated by NaCl with chloride concentrations up to 250 mg/l. Approximately 40–50% of desalinized water is produced from the feed water, which leads to brine concentrations twice that of the feed water.

The Br/Cl ratio of the brine from DSP 1 is close to that of seawater  $(1.55*10^{-3})$ , for the brine of DSP-2, the ratio is comparable to the average of the mountain group, and the Br–Cl ratios of DSP-1 and DSP-3  $(17.6-1.93*10^{-3})$  lie between those of the mountain group and seawater. Br and Cl have the same chemical behaviour in reverse osmosis processes – they are concentrated in the residual brines in the same way and do not form mineral phases in the relevant concentration range. As a result, the Br/Cl ratio of the brines is not significantly changed during the desalinization process and is comparable to that for the water from which the brines are produced - even the total concentrations are changing. Consequently, the Br/Cl ratio can be used as a proxy (which is independent of the total concentrations) for seawater-groundwater mixing as well as the desalinization process, as shown in sections 4.2.1 and 4.3.

4.2. Mixing processes between groundwater, seawater and brines from the desalinization plants

# 4.2.1. Mixing and desalinization processes - analyses of the conservative tracers bromide and chloride

The hydrochemical groups and their mixing processes can be analysed and quantified by means of the tracers Cl and Br and their ratio (Fig. 4). Cl, Br and their ratio have been used as tracers in numerous hydrochemical studies to determine the sources and evolution of waters in different environments (e.g., Alcala and Custodio, 2008; Herrmann, 1972; Herrmann, 1980; Rittenhouse et al., 1969; Valyashko and Petrova, 1956). Cl and Br are nearly ideal tracers. They are highly soluble, do not form their own mineral phases and are not incorporated in other phases in the brackish to saline concentration range and are not involved in ion exchange or adsorption reactions in a normal pH range. As shown in sections 4.4 and 4.5, most of the other parameters are influenced by phase reactions and cation exchange and cannot be used as conservative indicators for the quantification of mixing processes without consideration of other processes.

The following mixing processes occur in the investigation area and are shown schematically in respect to chloride and the bromide/ chloride ratio in Fig. 4 A):

- Mixing process (1): brackish groundwater of the mountain group and intruded seawater;
- Mixing process (2): mixing of waters resulting from Mixing process (1) (including the endmembers) with brines of the DSP:
  - (2a) mixing of brackish groundwater of the mountain group and bines of DSP-2,
  - (2b) mixing of waters resulting from process (1) with brines of DSP-



Fig. 4. Plots of Cl vs. The ratio Br/Cl:

A) Mixing processes between the different hydrochemical groups (DSP-1, -2, -3: brines of desalinization plants; for the numbers of mixing lines, see the text) B) Reaction path for the development of the chloride concentration and the bromide/chloride ratio in the DSP brines (for DSP-3): Mixing process (1) (seawater – mountain group) and concentration of an average mixture in the desalinization process (path (4) Point C – DSP-3).



**Fig. 5.** Stable isotopes content in groundwater samples of the mountain group, Red Sea, DSP-3 brine. Meteoric waterlines: GMWL – Global Meteoric Waterline (Craig, 1961) AMWL – African meteoric waterline (Cohen et al., 1997). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3, and

(2c) mixing of seawater and waters resulting from process (1) with brines of DSP-1.

The waters of the wells of the old and new DSP groups are the results of processes (1), (2b) and (2c). Fig. 4 A) indicates that 5 sources with different salinities exist (the brackish water of the mountain group, seawater and the brines of the 3 DSPs with their different characteristics) but only two primary sources with different Br/Cl ratio: seawater with an average of  $1.51*10^{-3}$  (range  $1.4-1.55*10^{-3}$ ) and the mountain group with an average of  $3.6*10^{-3}$  (range  $3-4.3*10^{-3}$ ) (see Table 1).

The brines from the DSP are concentrated mixtures of both primary sources. Fig. 4 B) shows schematically the development of the chloride concentration and the Br/Cl ratio during the formation of the residual brines of DSP-3. Process (1) represents the mixture of groundwater from the mountain group and seawater in the abstraction wells until point (C) (compare Fig. 4 A). Process (3) represents the development of Cl and Br/Cl of the brine in the desalinization plant during reverse osmosis.

Because bromide and chloride have the same chemical behaviour in the desalinization process (they are retained in the same fraction), the Br/Cl ratio remains constant and can be used as a concentration-independent proxy for the content of both sources in the brine (seawater and water of the mountain group). The Br/Cl ratios of the analyses from DSP-3 brines of 1.76-1.78\*10<sup>-3</sup> (samples 2016) and 1.92-1.96\*10<sup>-3</sup> (samples 2018) are reached in the mixing process in point (C) at chloride concentrations of approximately 300 meq/l and 240 meq/l. Using Formula 4 with an average for the Br/Cl ratios of  $4.1 \times 10^{-3}$  for the mountain group (lowest mineralized waters, see Figs. 4) and  $1.5*10^{-3}$  for seawater, mixing ratios of 45-47% seawater (samples 2016) and 33-35% seawater (samples 2018) are achieved. The brine of DSP-1 with a Br/Cl ratio of  $1.55*10^{-3}$  is very close to that of seawater and contains after Formula 4 more than 80% seawater. The DSP-2 brine ("mountain DSP" Br/Cl  $3.47*10^{-3}$ ) is very less influenced by seawater (< 5%) and represents a concentrated mixture of the different waters of the mountain group.

# 4.2.2. Mixing and desalinization processes - analyses of stable isotopes $\delta^2 H$ and $\delta^{18}O$ in $H_2O$

Stable isotopes such as  $\delta^2 H$  and  $\delta^{18} O$  in H<sub>2</sub>O also behave as tracers in the mixing processes between groundwater and seawater and in the desalinization process. Fig. 5 shows the  $\delta^2$ H and the  $\delta^{18}$ O values of low mineralized samples from the groundwater of the mountain group (Appendix A. Supplementary material, Table S - 1, well Nos. 1, 3, 11, 12, 17, 19, 22, and 25), the Red Sea (Table S - 1, No. 56) and residual brines produced in DSP-2 and DSP-3 (Table S - 1, Nos. 51 and 52). The  $\delta^2$ H and  $\delta^{18}$ O values of the brackish groundwater from the mountain group plot below the range of the global meteoric waterline GMWL  $\delta^2$ H = 8  $\delta^{18}$ O + 10 (Craig, 1961) and the African Meteoric line AMWL  $\delta^2 H$  = 7.4  $\delta$   $^{18}O$  + 10.1 (Cohen et al., 1997) (the reasons for this deviation are not the topic of this paper, and geothermal influences can be supposed; see section 4.1a) and 4.4.2). The analyses of Red Sea water shows a deviation from SMOW ( $\delta^2$ H:11.62‰ SMOW.  $\delta^{18}$ O: 2.33‰ SMOW) that is comparable to those of other investigations (e.g., Andrie and Merlivat, 1989).

The  $\delta^2 H$  and  $\delta^{18} O$  values in the residual brine of DSP-3 plot close to

a mixing line between the Red Sea and the mountain group. Using Formula 2/Formula 5 with location 19 (Table S - 1) for the mountain group (most depleted water,  $\delta^2 H = -50.3$ ,  $\delta^{18}O = 6.4$ ) and No. 56 (Table S - 1) for seawater ( $\delta^2 H = 11.6$ ,  $\delta^{18}O = 2.3$ ), the mixing ratios for DSP-3 in 2016 and 2018 range between 46.5% and 33% seawater (calculated with  $\delta^2 H$ , which fits very well to the values obtained by means of the Br/Cl ratio in section 4.2.1) and 51% and 40% (calculated with  $\delta^{18}O$ ). The deviation in the calculation using  $\delta^{18}O$  is related to the value for well 19. Using a value of -5.5 for  $\delta^{18}O$  (which is in the range of the mountain group), the calculated mixing ratios are close to the others with 36–46% seawater. Therefore,  $\delta^2 H$  and  $\delta^{18}O$  in H<sub>2</sub>O show the same behaviour as the Br/Cl ratio in the reverse osmosis processes in the DSP and can be used as a proxy for the primary mixing ratio of seawater and groundwater. The DSP-2 brine plots again in the range of the mountain group and contains none or very little seawater.

#### 4.3. Spatial distribution of the salinization patterns

Using Formula 4 and the assumptions of section 4.2.1, the primary seawater content can be calculated based on the Br/Cl ratio for all analyses including DSP brines and mixtures of groundwater-seawater brines. Fig. 6 shows interpolated spatial distributions of the chloride concentrations (A) and the molar Br/Cl ratios (B). The interpolation was carried out based on logarithmic values by means of geostatistical methods (variogram analyses and kriging interpolation).

The distribution of chloride concentrations in Fig. 6 A) indicates seawater intrusion in the east and north of the investigation area with concentrations > 20 g/l (Red Sea 22–23 g/l Cl). The brackish groundwater in the southwest shows concentrations < 5 g/l chloride.

Due to the mixing with seawater, the concentrations increase to the north and east, reaching the concentration of the Red Sea. However, the highest chloride concentrations are not related to seawater intrusion and are found surrounding desalinization plants 1 and 3, where concentrations up to > 30 g/l chloride are observed.

The molar Br/Cl ratios in Fig. 6 B) show different patterns. The intruded seawater in the northeast has a Br/Cl ratio of  $1.51 \times 10^{-3}$ , and in the southwest, the groundwater from the mountain group has a ratio >  $3.6 \times 10^{-3}$ . The region with high Cl concentrations surrounding DSP-1 shows the Br/Cl ratio of the Red Sea, but for the high concentrated region surrounding DSP-3, the Br/Cl ratio is partially higher.

Based on the interpolated Br/Cl ratios of Fig. 6 B), the distribution of the primary seawater content can be calculated using Formula 4 (Fig. 7 A). The content of seawater shows an intrusion into the well fields of the DSP-1 and DSP-3 desalinization plants located in the north and northeast of the investigation area (however, there is a lack of sampling locations at the north-western border of the investigation area). The wells near DSP-1 extract a mixture with > 90% seawater that is additionally concentrated by the desalinization processes. The wells surrounding DSP-3 extract a broader range of mixtures with primary 50% to > 90% seawater that is also concentrated in the DSP. The wells that are influenced by infiltration or injection of brines from DSP-1 and DSP-3 are identified by means of Br and Cl concentrations (Fig. 4) and are marked in Fig. 7 A). In these regions, the chloride concentrations lie partially above that of seawater, which is related to the brine disposal (Fig. 6 A).

After calculating the seawater content in the mixtures, the chloride concentration that results from this seawater can be estimated.

The Cl concentration that makes up the difference between the measured Cl concentration (Fig. 6 A) and Cl concentration that comes from the groundwater seawater mixture (resulting from Fig. 7 A) derives from other sources. This additional Cl concentration, which is not the result of seawater intrusion, are plotted in Fig. 7 B). Surrounding DSP-1 and DSP-3, the groundwater shows high additional Cl concentrations between 2.5 and > 10 g/I that are related to the infiltration of the DSP brines. Surrounding DSP-2, a slighter increase can be seen. This is partially related to the brines of DSP-2 but might have other reasons (occurence of remains of the Tev unit and geothermal influences north of DSP-2).

# 4.4. Phase equilibria and their spatial distribution

#### 4.4.1. CaSO<sub>4</sub> phases

The Saturation index of the samples was calculated for sampling temperature with *PHREEQC Interactive, Version 3.3.9* (2016) with thermodynamic data based on the Pitzer interaction parameters (database "pitzer.dat", see section 3.3). The stable  $CaSO_4$  phase in the temperature and salinity range of the groundwater in the investigation area is gypsum  $CaSO_4*2H_2O$  because of the lower solubility compared to Anhydrite. Anhydrite is stable at higher temperatures and salinities (Blount and Dickson, 1973; Bock, 1961). Only a few samples with high



Fig. 6. A) Interpolated spatial distribution of the chloride concentrations. B) molar Br/Cl (B) in the investigation area (interpolation using kriging based on variogram analyses).



**Fig. 7.** A) Interpolated primary seawater content (%) in the solutions based on the Br/Cl ratios (Fig. 6 B) and Formula 4. B) Additional Cl content not related to seawater intrusion in the feeding wells of the DSP.



Fig. 8. A) Saturation indices of gypsum CaSO4\*2 H<sub>2</sub>O in relation to the sulphate concentration (saturation indices calculated with *PHREEQC Interactive, Version 3.3.9* (2016).

B) Interpolated spatial distribution of the saturation index of gypsum in the investigation area (interpolation using kriging based on variogram analyses).

supersaturation for gypsum are also saturated/supersaturated with anhydrite CaSO<sub>4</sub>. Data of anhydrite are therefore not presented here. Fig. 8 A) shows the saturation index SI of gypsum in relation to the sulphate concentration, and Fig. 8 B) shows the regional distribution of the SI<sub>gypsum</sub> and the regions with saturation with respect to gypsum (spatial interpolation by means of variogram analyses and kriging).

Despite the high sulphate content, the water of the Red Sea shows a subsaturation (saturation indices SI < -0.6) because of the low calcium concentration and the low activity of the 2-fold charged sulphateion at high ionic strength. The brackish groundwater of the mountain group shows an increase of SI gypsum with increasing sulphate content. At concentrations of SO<sub>4</sub> > 50 meq/l, the saturation of gypsum is almost reached (SI > -0.05). The waters of the mountain group can be differentiated in two subgroups:

- 1) sulphate concentrations < 30 meq/l and subsaturation with gypsum, and
- 2) sulphate concentrations of 30-50 meq/l and saturation.

The natural sources of gypsum in aquifers of the coastal plain area). (a) gypsum from the Miocene Evaporites (Tev unit, see Fig. 2) in the East Desert Mountains of the Gebel Abu Shar, which is transported via flash flood events and deposited in alluvial fans and wadi sediments in the coastal plain, and

b) gypsum from seawater evaporation in sabkha sediments.

An additional source for high sulphate and calcium concentrations are the DSP brines. The feeding wells of DSP-1 and DSP-3 with a clear influence of brine-infiltration are labelled in Fig. 8A) and B) (compare Fig. 7, Cl content not related to seawater > 1 g/l). A clear differentiation exists here also for sulphate; the wells that are influenced by brines of DSP-1 and DSP-2 have sulphate concentrations above that of seawater, and the wells without influence fall in the range of subgroup 2) of the mountain wells. The residual brines of the DSP have the highest supersaturation (SI<sub>gypsum</sub> > 0.1, with one exception), which is probably the result of anti-scaling chemicals preventing the precipitation of gypsum.

The spatial distribution of the saturation with respect to gypsum also shows a clear correlation to the desalinization plants (Fig. 8 B). In the surroundings of the DSP, saturation and supersaturation with gypsum is generally found. In the case of DSP-1 and DSP-3, this is clearly related to the influence of residual brines. In the case of DSP-2, in addition to the brine infiltration, geothermal processes might play a role.

# 4.4.2. Carbonate equilibria and pH

Phase equilibria of carbonate minerals are coupled equilibria between the dissolution/precipitation of carbonates, the dissolution of  $CO_2$ , the dissociation of carbon acid  $H_2CO_3$  (all depending on temperature and pressure) and possibly the influence of other acids. The analytical data, the hydrochemical relations and the spatial distribution are shown in Appendix A. Supplementary material, A-1, Table S - 1 and A-2, Figure S - 1 to Figure S - 4.

The temperatures of the samples from wells in the coastal plain (the old DSP group and new DSP group) range between 27 and 31 °C, the temperatures of superficial seawater of the Red Sea ranges with seasonal variations between 22 and 29 °C (not measured in the samples). The samples of the mountain group differ between 27 °C and 40 °C. The increased temperatures above 31 °C are related to geothermal influences on fault structures at the eastern border of the Abu Shar Plateau (see Fig. 2), in the northern area of DSP-2. Similar geothermal influences are documented from other regions of the Red Sea Rift area, i.e., for the Sinai Peninsula (Sturchio et al., 1996). The samples of the mountain group are mostly weak alkaline, and even the measured pH of some samples is < 7 (Appendix A. Supplementary material, A-2, Figure S - 1). The dissociation constant of water K<sub>w</sub> depends on temperature and pressure (values and calculation models, i.e., in the compilations from Bandura and Lvov, 2006). In the range from 0 to 200 °C and 0-1000 MPa, Kw increases with temperature at fixed pressure, and therefore the pH of neutrality (where  $[H_3O^+] = [OH^-]$  and therefore  $pH = pOH = -log(K_W)/2$  decreases. The influence of pressure in the range 1-25 atm. is low, so the values for 1 atm. plotted in Figure S - 1 are representative for the relevant well depths. With two exceptions, the pH values of the samples are  $\approx$  or > the neutral pH. The samples from the coastal plain (old DSP group and new DSP group) cover a similar pH range, and only some of the wells, influenced by DSP brines, are weak acidic below the neutral pH.

Based on the measured pH, temperature and alkalinity, the total inorganic carbon TIC  $(CO_3^{2^-} + HCO_3^- + H_2CO_3/CO_2)$  can be calculated by means of a speciation model with *PHREEQC Interactive*, *Version 3.3.9* (2016) (section 3.3) (for seawater, a temperature of 25 °C was chosen as an average). The TIC is independent of pH, but pH is controlled by the dissociation equilibria of the carbon acid (if no additional sources for acidity exist). For the groundwater samples, a decrease of pH with increasing TIC can be evidenced (Appendix A. Supplementary material, A-2, Figure S - 2), which is related to dissociation of additional carbon acid with increasing TIC:

$$\boldsymbol{CO}_2 + \boldsymbol{H}_2 \boldsymbol{O} \to \boldsymbol{H}_2 \boldsymbol{CO}_3 \to \boldsymbol{H}^+ + \boldsymbol{H} \boldsymbol{CO}_3^- \to 2\boldsymbol{H}^+ + \boldsymbol{CO}_3^{2-}.$$
 (6)

The DSP brines show the highest TIC in combination with a moderate pH  $\approx$  7.25, which is related to the progressive concentration in the DSP processes and the use of anti-scaling chemicals that prevent the carbonate precipitation.

The regional distribution of the TIC content (Appendix A. Supplementary material, A-2, Figure S - 3) indicates a natural background in the coastal plain of TIC  $\leq 2.2 \text{ mmol/kg}_{H2O}$  and confirms the

relation of increased TIC values to the infiltration zone surrounding DSP-3 and the infiltration and geothermal zone north of DSP-2. The zone of brine injection close to DSP-1 (deep discharging well, Fig. 1) does not show increased TIC, and even the general concentrations and the gypsum supersaturation clearly indicate the influence of DSP brines (sections 4.3 and 4.4.1). The source of increased TIC surrounding DSP-3 is, beside the high TIC of the brines, the oxidation of organic matter in the unsaturated zone during the infiltration process (additional water also infiltrate from the ponds of the fish farm). In case of an injection into the aquifer (DSP-1), these reactions do not occur.

With a few exceptions, the samples are saturated and supersaturated with respect to calcite CaCO<sub>3</sub> (Appendix A. Supplementary material, A-2, Figure S - 4). Dolomite is supersaturated too in all the samples (and therefore not presented here). The saturation of aragonite is strongly correlated with calcite, slightly lower (SI<sub>aragonite</sub>  $\approx$  SI<sub>calcite</sub>-0.173) and is also not presented here. For groundwater, an increase in the pH with the saturation index of calcite can be noticed, which is a result of the buffering of protons by dissolution of carbonate minerals. The dissolution of CaCO<sub>3</sub> transfers carbonate CO<sub>3</sub><sup>2-</sup> ions into the solution that consume protons and shift the pH to higher values:

$$H^{+} + CaCO_{3} \rightarrow H^{+} + Ca^{2+} + CO_{3}^{2-} \rightarrow Ca^{2+} + HCO_{3}^{-}.$$
 (7)

The increase of  $Ca^{2+}$  ions in the solution increases the  $SI_{calcite.}$  The high supersaturation of brines is the result of the anti-scaling chemicals used, preventing the precipitation of calcite.

#### 4.5. Ion exchange processes in the groundwater - seawater mixing

In 4.2 and 4.3, the mixing processes between seawater and groundwater of the mountain group and the influence of seawater were illustrated based on the conservative tracers chloride and bromide. Additional processes influence the chemistry of the non-conservative ions. Beside the dissolution and/or precipitation of mineral phases (discussed in 4.4), especially cation exchange processes occur. The exchange processes follow the principle formula (using the Gaines & Thomas Convention for heterovalent exchange, Gaines and Thomas, 1953):

$$Na^+ + 0.5Ca \cdot X_2 \leftrightarrow Na \cdot X + 0.5Ca^{2+}$$
 (X  
- exchange complex with adsorbed cations).

(8)

To analyse and quantify the mixing and reaction processes, a hydrochemical model was developed that includes mixing of brackish groundwater with seawater, cation exchange and phase equilibria with minerals. The modelling was carried out in *PHREEQC Interactive, Version 3.3.9* (2016) (see section 3.3) as a sequential batch reaction in the following sequence.

Step 1: Definition of an initial groundwater solution and an initial exchange complex

- a) Defining the initial solutions for brackish groundwater
- b) Equilibrating the exchange complex with the initial solution

Step 2: Mixing of the solutions of step 1 with seawater and reequilibrating the exchange complex

- a) Mixing of the solution from step 1b) with 5% seawater
- b) Allow the precipitation of calcite and gypsum in case of supersaturation (threshold for calcite: SI > 0.5, for gypsum: SI > 0.1).
- c) Re-equilibrating the mixed solution with the exchange complex under the conditions defined in 1b)

Step 3: Sequential repetition of step 2 until a seawater content > 99% in the mixing solution is reached. The proportion of seawater in mixing step 2 is increased at higher salinities to accelerate the model.

To cover the concentration range of the brackish groundwater and the reaction processes, different scenarios were modelled with different initial solutions and different exchange capacities. In the figures, two scenarios are shown, presenting the upper and lower concentration range of the reactive mixing processes.

- Scenario 1: lower concentration range of brackish groundwater, lower exchange capacity
  - o analyses N.18 for brackish groundwater (see Appendix A. Supplementary material, Table S 1), subsaturated with gypsum,  $SI_{gypsum} = -0.0278$ , exchange capacity 0,3 mol/l solution)
- Scenario 2: upper concentration range of brackish groundwater, higher exchange capacity
  - o analyses N.13 for brackish groundwater (see Appendix A. Supplementary material, Table S 1), groundwater close to gypsum saturation  $SI_{gypsum} = -0.01370,3 \text{ mol/l solution}$ )

The exchange capacities of 0.2 and  $0.3 \text{ mol/}l_{\text{solution}}$  in the models represent sandy sediment material with porosities between 25% and 30% and cation exchange capacities CEC between 2.5 and 5 meq/100 g sediment. For seawater, sample No. 57 was selected as an average (see Appendix A. Supplementary material, Table S - 1). For the calculations of the exchange, the Gaines & Thomas convention and the default values of the exchange coefficients in the thermodynamic data base "pitzer.dat" of PHREEQC were used (see section 3.3).

Results of scenario 2 are shown in Fig. 9A (concentrations of cations) and Fig. 9B (saturation indices and activities) depending on the seawater content of the mixture. The concentrations of the cations in the solution show a non-linear trend during the mixing process (especially calcium) because of the ion exchange processes. Supersaturation and precipitation of calcite occurs in the model (also in scenario 1) due to calcium enrichment in solution during the exchange processes. Supersaturation for gypsum and other sulphate minerals is not reached in



**Fig. 9.** Results of modelled reactive mixing scenario 2 (see text section 4.5): A) Concentration of the cations Na, Ca, Mg (in solution and adsorbed) during reactive mixing of brackish groundwater and seawater. Full lines represent concentration in solution (Na on the right axis), and dotted lines represent adsorbed concentrations.

B) Saturation indices of calcite and gypsum and activities of  $Ca^{2+}$  and  $SO_4^{2+}$  in solution during reactive mixing of brackish groundwater and seawater.

the mixture even if the concentrations of SO<sub>4</sub> and Ca are increasing during the mixing (maximum calcium concentration at a mixing ratio of  $\approx 50\%$  seawater). The reason is that the activities of the twofold charged ions are low compared to the concentrations (ratio activity/ concentration: Ca<sup>2+</sup>: 22–26%, SO<sub>4</sub><sup>2-</sup>: 7–18%), and the activity of SO<sub>4</sub> decreases with increasing ionic strength due to the seawater influence (Fig. 9B); hence, the ion activity product [Ca<sup>2+</sup>][SO<sub>4</sub><sup>2-</sup>] decreases too. Even gypsum supersaturation is normally not reached during the mixing of brackish groundwater and seawater, and the saturation indices with respect to gypsum are much higher than in seawater. Consequently, these mixtures have very high potential for sulphate scaling in the desalinization process (much higher than seawater).

The results of both modelled scenarios in relation to the analysis are shown in Appendix A. Supplementary material, 8.3 A-3, Figure S - 5 (for sodium and calcium) and Figure S - 6 (for magnesium and calcium) (modelled data recalculated from molality to meq/l). The modelled scenarios follow the concentrations range of the analyses for the wells that are not influenced by the DSP brines. Calcium is enriched in the solution with increasing sodium concentration up to seawater contents of  $\approx$  50% (Figure S - 5) due to the cation exchange. Samples with higher contents of sodium (Na > 300 meq/l, Figure S - 5) are not pure groundwater-seawater mixtures and are also influenced by the DSP brines (section 4.3, Fig. 7). Magnesium concentrations above seawater are also a clear indicator for the influence of DSP brines (Figure S - 6). Therefore, these analyses do not follow the modelled scenarios. The mixing of DSP-1 and DSP-3 brines is schematically represented by the mixing lines (2b, c) in Figure S - 5 (compare with section 4.2.1 and Fig. 4A). This leads to a further increase of the Ca, Na and Mg concentrations and shows a broad scattering depending on the composition of the DSP brine and the starting point at the groundwater-seawater mixing line. It must be considered that the DSP brines have a broad concentration range depending on the used feeding wells and that only a few samples were analysed.

# 5. Conclusions

The groundwater in the coastal aquifers of the investigation area is a mixture of brackish waters and intruded seawater. The impact of seawater intrusion on the groundwater decreases with growing distance from the coast. Seawater intrusion is forced by the continuous abstraction of the non-renewable brackish groundwater, which is a problem for the region due to its arid climate and negligible actual groundwater recharge.

The mixing ratio of seawater and groundwater in the wells can be identified using the conservative tracers Br/Cl ratio and  $\delta^{18}O$  and  $\delta^{2}H$  in H<sub>2</sub>O. The treatment of the groundwater-seawater mixtures in the desalinization plants has no influence on these tracers so that the source of the residual brine (the mixing ratio groundwater-seawater) can still be identified using them. Even if the concentrations and hydrochemical characteristics of the technical solutions differ strongly from the primary natural waters, these tracers are still reliable indicators for the initial mixing ratio.

In the coastal plain surrounding the desalinization plants DSP-1 and DSP-3, groundwater salinities above seawater concentration can be observed (up to 60 g/l TDS, Red Sea water: 37–44 g/l TDS). The Br/Cl-ratio identifies this effect as a result of the disposal of the brines from the DSP's that are infiltrated and injected into the aquifer. The leaching of evaporates, located in the deeper subsurface (halite layers of the Middle and Late Miocene), could be excluded as a reason for the high salinities in the investigated depth range of 20–150 m. Currently, numerous feeding wells at distances up to 600 m from the desalinization plants are affected, and abstract water contains up to 60% brine from the DSPs.

During mixing of groundwater and seawater, ion exchange processes occur (especially Na  $\Leftrightarrow$  Ca), which increases the Ca concentration in the solution. Even gypsum supersaturation is normally not reached in

these processes, the saturation indices with respect to gypsum in the mixtures are much higher than in seawater. Calcite as the second important phase for scaling is generally supersaturated in groundwater, seawater and the mixtures. Consequently, these mixtures have very high potential for sulphate and carbonate scaling in the desalinization process (especially for gypsum much higher than for pure seawater). The brines of the DSP are highly supersaturated with respect to gypsum and calcite. The precipitation of the minerals is prevented by the addition of anti-scalants in the reverse osmosis. Consequently, the regions of brine infiltration and injection are not only characterized by increased salinity but also by saturation and supersaturation with respect to gypsum. As a result, an intense gypsum precipitation in fact occurs in the screens of wells extracting high concentrated water, requiring a frequent wash over.

In addition to the effects of seawater intrusion and brine disposal, geothermal influences could be identified at fault structures in the western part of the investigation area (increased temperatures up to 40  $^{\circ}$ C, increased TIC, and slightly increased salinity). These effects superimpose the brine infiltration at DSP-2 and are still investigated by detailed chemical and isotopic analyses.

#### Acknowledgements

The authors would like to thank Mr. Hilal from the water supply authority of El Gouna for enabling the access into the wells on the El Gouna farm and the desalination plants. They also thank Dr. N. Tsoupanos and Mr. Bollkemper from the chemical laboratory at the TU Berlin-Campus El Gouna, Department of Water Engineering.

Many thanks go to an anonymous reviewer for his thorough reading and critical and constructive comments.

# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apgeochem.2018.11.001.

#### References

- Alcala, F.J., Custodio, E., 2008. Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal. J. Hydrol. 359, 189–207. https://doi.org/ 10.1016/j.jhydrol.2008.06.028.
- Andrie, C., Merlivat, L., 1989. Contribution des données isotopiques de deutérium, oxygène- 1 8, hélium-3 et tritium, à l'étude de la circulation de la Mer Rouge. Oceanol. Acta 12, 165–174.
- Appelo, C.A.J., 2015. Principles, caveats and improvements in databases for calculating hydrogeochemical reactions in saline waters from 0 to 200°C and 1 to 1000atm. Appl. Geochem. 55, 62–71. https://doi.org/10.1016/j.apgeochem.2014.11.007.
- Appelo, C.A.J., Parkhurst, D.L., Post, V.E.A., 2014. Equations for calculating hydrogeochemical reactions of minerals and gases such as CO2 at high pressures and temperatures. Geochem. Cosmochim. Acta 125, 49–67. https://doi.org/10.1016/j. gca.2013.10.003.
- Baalousha, H., 2006. Desalination status in the Gaza Strip and its environmental impact. Desalination 196, 1–12. https://doi.org/10.1016/j.desal.2005.12.009.
- Bandura, A.V., Lvov, S.N., 2006. The ionization constant of water over wide ranges of temperature and density. J. Phys. Chem. Ref. Data 35, 15–30.
- Blount, C.W., Dickson, F.W., 1973. Gypsum-anhydrite equilibria in systems CaSO4-H2O and CaSO4-NaCl-H2O. Am. Mineral. 58, 323–331.
- Bock, E., 1961. On the solubility of anhydrous calcium sulfate and of gypsum in concentrated solutions of sodium chloride at 25°C, 30°C, 40°C and 50°C. Can. J. Chem. 39, 1746–1751.
- Bosworth, W., Huchon, P., McClay, K., 2005. The Red Sea and Gulf of Aden basins. J. Afr. Earth Sci. 43, 334–378. https://doi.org/10.1016/j.jafrearsci.2005.07.020.
- Braitsch, O., 1971. Salt Deposits. Their Origin and Composition, Minerals, Rocks, and Inorganic Materials: Monograph Series of Theoretical and Experimental Studies, vol. 4 Springer Verlag, Berlin, Heidelberg, New York.
- Cember, R.P., 1988. On the sources, formation, and circulation of Red Sea deep water. J. Geophys. Res.: Oceans 93, 8175–8191. https://doi.org/10.1029/JC093iC07p08175.
- Chesher, R.H., 1975. Chapter 6. Biological impact of a large-scale desalination plant at key west, Florida. In: Wood, E.J.F., Johannes, R.E. (Eds.), Tropical Marine Pollution. Elsevier Oceanography Series. Elsevier, pp. 99–153. https://doi.org/10.1016/S0422-9894(08)71111-5.
- Cohen, T.S., Talbot, M.R., Awramik, S.M., Dettman, D.L., Abell, P., 1997. Lake level and palaeoenvironmental history of Lake Tanganyika, Africa, as inferred from late Holocene and modern stromatolites. Geol. Soc. Am. Bull. 109, 444–460.

Craig, H., 1966. Isotopic composition and origin of the Red Sea and salton sea geothermal brines. Science 154 (3756), 1544–1548. https://doi.org/10.1126/science.154.3756. 1544.

Craig, H., 1961. Isotopic variations in meteoric waters. Science 133, 1702–1703. Del Bene, J.V., Jirka, G., Largier, J., 1994. Ocean brine disposal. Desalination 97,

- 365–372. Doneker, R.L., Jirka, G.H., 2001. CORMIX-GI systems for mixing zone analysis of brine
- wastewater disposal. Desalination 139, 263–274. https://doi.org/10.1016/S0011-9164(01)00318-6.
- Eissa, M.A., Thomas, J.M., Pohll, G., Shouakar-Stash, O., Hershey, R.L., Dawoud, M., 2016. Groundwater recharge and salinization in the arid coastal plain aquifer of the Wadi Watir delta, Sinai, Egypt. Appl. Geochem. 71, 48–62. https://doi.org/10.1016/ j.apgeochem.2016.05.017.
- El-Sadek, A., 2010. Water desalination: an imperative measure for water security in Egypt. Desalination 250, 876–884. https://doi.org/10.1016/j.desal.2009.09.143.
- Gaines, G.L., Thomas, H.C., 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys. 21, 714–718. https:// doi.org/10.1063/1.1698996.
- Greiling, R.O., El Ramly, M.F., El Akhal, H., Stern, R.J., 1988. Tectonic evolution of the northwestern Red Sea margin as related to basement structure. Tectonophysics 153 (1-4), 179–191. https://doi.org/10.1016/0040-1951(88 https://doi.org/10.1016/ 0040-1951(88) 90014–5.
- Gupta, P., Noone, D., Galewsky, J., Sweeney, C., Vaughn, B.H., 2009. Demonstration of high-precision continuous measurements of water vapor isotopologues in laboratory and remote field deployments using wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) technology. Rapid Commun. Mass Spectrom. 23, 2534–2542.
- Hadidi, A., 2016. Wadi Bili: Example for Flash Floods in Wadis in the Eastern Desert of Egypt, a Structural Model for Evaluation of the Groundwater and the Artificial Recharge. PhD thesis. TU Technical University of Berlin, Central Institute El Gouna, Berlin.
- Hafez, A., El-Manharawy, S., 2002. Economics of seawater RO desalination in the Red Sea region, Egypt. Part 1. A case study. Desalination 153, 335–347. https://doi.org/10. 1016/S0011-9164(02)01122-0.
- Harvie, C.E., Möller, N., Weare, J.H., 1984. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-H-CI-SO4-OH-HCO3-CO3-CO2-H2O system to high ionic strengths at 25°C. Geochem. Cosmochim. Acta 48, 723–751.
- Harvie, C.E., Weare, J.H., 1980. The prediction of mineral solubilities in natural waters: the Na-K-Mg-Ca-SO4-Cl-H2O from zero to high concentration at 25°C. Geochem. Cosmochim. Acta 44, 981–997.
- Herrmann, A.G., 1980. Bromide distribution between halite and NaCl-saturated seawater. Chem. Geol. 28, 171–177.
- Herrmann, A.G., 1972. Bromine distribution coefficients for halite precipitated from
- modern sea water under natural conditions. Contrib. Mineral. Petrol. 37, 249–252.
  Höpner, T., Windelberg, J., 1997. Elements of environmental impact studies on coastal desalination plants. Desalination 108, 11–18. https://doi.org/10.1016/S0011-9164(97)00003-9.
- Jenkins, W.J., Clarke, W.B., 1976. The distribution of 3He in the western Atlantic ocean. Deep-Sea Res. Oceanogr. Abstr. 23, 481–494. https://doi.org/10.1016/0011-7471(76)90860-3.
- Khalil, E.E., 2004. Water strategies and technological development in Egyptian coastal areas. Desalination 165, 23–30. https://doi.org/10.1016/j.desal.2004.06.003.
- Klitzsch, E., Linke, H.W., 1983. Photogeological Interpretation Map. CONOCO coral Inc., Cairo, A.R.E.
- Langmuir, C.H., Vocke Jr., R.D., Hanson, G.N., Hart, S.R., 1978. A general mixing equation with applications to Icelandic basalts. Earth Planet Sci. Lett. 37, 380–392. https://doi.org/10.1016/0012-821X(78)90053-5.
- Linke, H.W., 1986. Golf von Suez Geologie und Tektonik (Doctoral Thesis). Technical University of Berlin, Department of Mining and Geoscience, Berlin.
- Mabrook, B., 1994. Environmental impact of waste brine disposal of desalination plants, Red Sea, Egypt. Desalination 97, 453–465. https://doi.org/10.1016/0011-9164(94) 00108-1.
- Millero, F.J., Feistel, R., Wright, D.G., McDougall, 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.
- Mohamed, A.M.O., Maraqa, M., Al Handhaly, J., 2005. Impact of land disposal of reject brine from desalination plants on soil and groundwater. Desalination 182, 411–433. https://doi.org/10.1016/j.desal.2005.02.035.
- Morton, A.J., Callister, I.K., Wade, N.M., 1997. Environmental impacts of seawater distillation and reverse osmosis processes. Desalination 108, 1–10. https://doi.org/10. 1016/S0011-9164(97)00002-7.

PHREEQC Interactive, Version 3.3.9. USGS Geological Survey.

- Pitzer, K.S., 1973. Thermodynamics of electrolytes. I. Theoretical basis and general equations. J. Phys. Chem. 77, 268–277.
- Purnalna, A., Al-Barwani, H.H., Al-Lawatia, M., 2003. Modeling dispersion of brine waste discharges from a coastal desalination plant. Desalination 155, 41–47. https://doi. org/10.1016/S0011-9164(03)00237-6.
- Rittenhouse, G., Fulton, R.B., Grabowski, R.J., Bernard, J.L., 1969. Minor elements in oilfield waters. Chem. Geol. 4, 189–209. https://doi.org/10.1016/0009-2541(69) 90045-X.
- Sadhwani, J.J., Veza, J.M., Santana, C., 2005. Case studies on environmental impact of seawater desalination. Desalination 185, 1–8. https://doi.org/10.1016/j.desal.2005. 02.072.
- Someswara, N., Venkateswara, T.N.V., Babu, G., Venu, K., 1990. Impact of reject water from the desalination plant on ground water quality. Desalination 78, 429–437.
- Stoffers, P., Kühn, R., 1974. Geochemische und petrographische Untersuchungen an Evaporit-Bohrkernen aus dem Roten Meer. Kali Steinsalz 8, 290–299.

- Sturchio, N., Arehart, G.B., Sultan, M., Sano, Y., AboKamar, Y., Sayed, M., 1996. Composition and origin of thermal waters in the Gulf of Suez area, Egypt. Appl. Geochem. 11, 471–479. https://doi.org/10.1016/0883-2927(96)00025-X. Sturges, W.T., Harrison, R.M., 1986. Bromine in marine aerosols and the origin, nature
- Sturges, W.T., Harrison, R.M., 1986. Bromine in marine aerosols and the origin, nature and quantity of natural atmospheric bromine. Atmos. Environ. 20 (1967), 1485–1496. https://doi.org/10.1016/0004-6981(86)90020-X.
- Tularam, G.A., Ilahee, M., 2007. Environmental concerns of desalinating seawater using

reverse osmosis. J. Environ. Monit. 9, 805-813. https://doi.org/10.1039/B708455M.

- Valyashko, M.G., Petrova, E.M., 1956. Geochemistry of bromine in the processes of salt deposition and the use of the bromine content as a genetic and prospecting criterion. Geochemistry 6, 570–589.
- Winchester, J.W., Duce, R.A., 1967. The global distribution of iodine, bromine, and chlorine in marine aerosols. Naturwissenschaften 54, 110–113. https://doi.org/10. 1007/BF00640572.