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Strontium isotopes as an indicator for groundwater salinity sources in the Kirkuk region, Iraq

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HIGHLIGHTS

- This field study evaluates the salinity sources in the groundwater in Kirkuk region.
- Salinity is related to evaporates dissolving and/or mixing with oil field brine.
- Strontium isotopes proved to be a valuable tool to distinguish mixing processes.

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ABSTRACT

The Kirkuk region in northern Iraq hosts some of the largest oil fields in the Middle East. Several anticline structures enabled vertical migration and entrapment of the oil. Frequently, complex fracture systems and faults cut across the Eocene and middle Oligocene reservoirs and the cap rock, the Fatha Formation of Miocene age. Seepage of crude oil and oil field brines are therefore a common observation in the anticline axes and contamination of shallow groundwater resources is a major concern. In this study, 65 water samples were collected in the Kirkuk region to analyze and distinguish mixing processes between shallow groundwater resources, uprising oil field brines, and dissolution of gypsum and halite from the Fatha Formation. Hydrochemical analyses of the water samples included general hydrochemistry, stable water isotopes, as well as strontium concentrations and for 22 of the samples strontium isotopes ($^{87}Sr/^{86}Sr$). Strontium concentrations increased close to the anticline axes with highest concentrations in the oil field brines (300 mg/l). Strontium isotopes proved to be a valuable tool to distinguish mixing processes as isotope signatures of the oil field brines and of waters from the Fatha Formation are significantly different. It could be shown, that mixing of shallow groundwater with oil field brines is occurring close to the major fault zones in the anticlines but high concentrations of strontium in the water samples are mainly due to dissolution from the Fatha Formation.

1. Introduction

In the Kirkuk region of northern Iraq, drinking and irrigation water demand is mainly provided by shallow groundwater resources of Quaternary alluvial sediments, and the Pliocene and Upper Miocene sediments of the Bai Hassan, Mukdadia and Injana groups. The Kirkuk region also hosts some of the largest oil fields in the Middle East, accounting for almost 12% of Iraq's proven oil reserves (IEA, 2012). Vertical migration and entrapment of the oil were enabled by the ongoing evolution of the Zagros belt creating several anticline structures of which the most prominent one is the Kirkuk anticline with the Baba dome oil field. Due to vertical migration hydrocarbon accumulations can be found in host rocks at shallow depths with production zones less than 400 m below surface. The lower to middle Miocene Fatha (Lower Fars) Formation is forming the cap rock in the region (Mahdi, 2007; Buday, 1980). However, frequently complex fracture systems and faults cut across the reservoirs and the cap rock, and previous drilling logs indicate the presence of major cavities (Daniel, 1954). Consequently, crude oil and brine seepages as well as sulfur springs are often found at the surface close to the fault zones.

The seepages are a serious contamination threat to the groundwater resources located between the oil reservoirs and the surface as seepages may contain high concentrations of hydrocarbons, heavy metals, or salts, making the affected groundwater unfit for use. Such contamination of groundwater by oil field brines was shown at various hydrocarbon reservoirs worldwide (Heston, 2015; Gleason and Tangen, 2014; Zhang et al., 2009; Dutton et al., 1989; Mast, 1985). On the other hand, the detection of trace elements in groundwater can indicate or verify the presence of pathways between the reservoirs and the surface. The hydrochemical patterns might even allow distinguishing between seepage from different host formations and the cap rock, enabling to better understand the fracture system of the region.

The objective of this paper is to evaluate the origin of high salinity in shallow groundwater aquifers in the Kirkuk region which are used for

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irrigation and domestic water supply. The main aim is to distinguish between contamination from uprising oil field brines, and from brines derived from water-rock interaction in the Fatha cap rock formation, as suggested earlier (Khanaqa and Al-Manmi, 2011; Saud, 2009; Sadiq, 2008). Both can contribute to the salinity increase and thus making the groundwater unsuitable for use. For this, groundwater, spring water, and river water samples were taken and analyzed for basic hydrochemical parameters, including water isotopes (D, ^{18}O). In addition strontium concentrations and strontium isotopes ($^{87}Sr/^{86}Sr$) were determined, as it was shown that Sr isotopic ratios do not significantly change during evaporation, making them specifically useful as tracers for the interaction of surface water and groundwater (Peterman and Stuckless, 1992). Results of the hydrochemical analyses were compared to the composition of brine samples from the Kirkuk oil field. Finally, data were analyzed considering the geological conditions of the study area, in particular the tectonic and structural features, such as the extent and orientation of the main anticlines, faults and lineaments. With this, a conceptual model is proposed for the evolution of the shallow water resources of the region.

2. Study area

The study area is located in the Kurdistan Region in Northern Iraq in the Kirkuk and Erbil governments and covers about 8500 km^2 (Fig. 1). Kirkuk, the largest city in the study area and the center of Iraq's oil industry has a population of about 1 million. The climate is semi-arid with hot, dry summers and cool, rainy winters. The mean annual temperature is 21.6 °C and the mean annual precipitation 365 mm (Kottek et al., 2006). Agriculture is widespread in the region with mainly wheat and barley production, and relies heavily on irrigation using water from shallow aquifers.

3. Geological and hydrogeological setting

The Zagros Fold and Thrust Belt, an orogeny resulting from the ongoing convergence between the Arabian and Eurasian plates, stretches on a length of about 2000 km, parallel to the Iraqi-Iranian borders. Main structural features are NW trending anticlines. In the northern part of the orogeny the thrust belt is subdivided by the Main Zagros Thrust, the Mountain Front Flexure, and the Zagros Deformational Front into two regions, the High Folded Zone in the north-east and the Low Folded Zone, or Foothill Zone, in the south-west (Fig. 1A) (Zebari and Burberry, 2015). The study area is located in the Low Folded Zone and includes several anticlines. Besides the most prominent Kirkuk anticline, these are the Qara Chauq, Bai Hassan, Jambur and Kor Mor anticlines (Fig. 1B).

The cores of the anticlines are mainly formed by fractured limestone of upper Cretaceous to Tertiary age, being the host rocks of abundant oil and gas accumulations. They, which originate from Jurassic and lower Cretaceous source formations below (Pitman et al., 2004). The Fatha Formation, consisting of anhydrite, gypsum and salt, interbedded with limestone and marl (Aqrawi, 1993) forms the cap rock (Table 1). The overlying Upper Miocene and Pliocene sediments of the Injana (Upper Fars), Mukdadia and Bai Hassan Formations consist of alternating sequences of sandstones, siltstones, and claystone. Most of the study area is covered by unconsolidated Quaternary sediments (Figs. 1B and 2). Exploitable groundwater occurs in the Upper Miocene and Pliocene sediments of the Injana, Mukdadia, and Bai Hassan Formations, and in the Quaternary sediments.

Due to the tectonic activities in the region, the whole sequence of sediments is extensively fractured. Most prominent fractures and thrust faults are oriented parallel to the anticline axes and cut deep into the sediments reaching the oil reservoirs. The Kirkuk anticline Thrust Fault, e.g., reaches a length of >130 km. Several faults that do not reach the surface have been identified in drilling logs and by geophysical investigations (Daniel, 1954) (Fig. 2). Numerous faults and lineaments perpendicular to the anticlines can be identified from the geological map (Sissakian and Fouad, 2014). Further lineaments have been identified in this study by remote sensing techniques, using the digital elevation model and the auto lineament extraction method (Abdullah et al., 2010) (Fig. 3). The faults and lineaments may create pathways for formation water, brines and hydrocarbons to the shallow aquifer systems and to the surface. There is ample field evidence of methane and oil seepages at the surface, especially in the vicinity of the Kirkuk anticline fault (Fig. 4).

From a hydrogeological point of view, the north-west to south-east striking Kirkuk anticline divides the area into two sub-basins (Saud, 2009) (Figs. 1 and 2). These basins are separated by the Fatha Formation which has a low matrix permeability and outcrops in a small band on the anticline axis (Fig. 1B). However, due to the fracture and fault system perpendicular to the anticline axes, and local karstification of the Fatha Formation a hydraulic connection between the two basins can be assumed. The region is mainly drained by the Lesser Zab river, which cuts through the anticline axis north-west of Kirkuk.

4. Materials and methods

4.1. Materials

Sixty five water samples from surface water (Lesser Zab river, springs) and groundwater (Bai Hassan, Mukdadia, and Quaternary aquifer), as well as brine (formation water) from the Kirkuk and Bai Hassan oil fields (wells K 396 and BH 175 as M. Oligocene-Eocene) respectively, were collected in the study area around the Kirkuk anticline. Sampling locations were chosen based on the geographic location, e.g. distance to faults, elevation, and defined screened intervals of the wells (Fig. 2). Surface water samples were taken out from the Lesser Zab river, and directly at the discharge points of the springs. Groundwater samples were collected at operating groundwater wells. The oil field brine samples were provided by the Iraqi North Oil Company.

Before sampling, field parameters (pH, electrical conductivity (EC), and bicarbonate) were obtained. At each location two samples were collected in polyethylene bottles (250 ml). One of the two samples was filtered and acidified with HNO_3 to preserve cations. In addition, isotope samples were collected in 100 ml glass bottles sealed with teflon caps. Samples were stored in a cooler before transported to the laboratory.

4.2. Methods

The concentrations of major ions and strontium were determined by ion chromatography (Metrohm 882 compact IC plus). The relative standard deviation was 3%. The limit of quantification for strontium was 0.1 mg/l. Stable water isotopes (δ^2H and $\delta^{18}O$) were analyzed using a Picarro L2130-i Cavity Ring Down Spectrometer (CRDS) connected to a Picarro A0211 high precision vaporizer. All values are expressed in the standard delta notation in per mil against VSMOW according to Coplen (1996):

$$\delta\ \text{sample (permil)} = \left(\frac{\text{R sample}}{\text{R reference}} - 1\right) \times 1000. \quad (1)$$

First, raw data were corrected for memory effects and machine drift, then they were normalized to the VSMOW/SLAP scale. Normalization was done using the method of Gonfiantini (Gonfiantini, 1984) where values between 0 and −428 per mil for δ^2H and between 0 and −55.5 per mil for $\delta^{18}O$ were assigned to VSMOW and SLAP. For this purpose, two laboratory standards, which were calibrated directly against VSMOW and SLAP, were measured in each run. External reproducibility - defined as standard deviation of a control standard during all runs - was 0.63 per mil and 0.15 per mil for δ^2H and $\delta^{18}O$, respectively. For samples with high salinity cryogenic vacuum distillation was used prior to measurements (Ingraham and Shadel, 1992).