Applied Geochemistry 66 (2016) 114-128

Contents lists available at ScienceDirect

Applied Geochemistry

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

# Noble gases reveal the complex groundwater mixing pattern and origin of salinization in the Azraq Oasis, Jordan



Tillmann Kaudse <sup>a, c, \*</sup>, Refaat Bani-Khalaf <sup>b</sup>, Randa Tuffaha <sup>b</sup>, Florian Freundt <sup>a</sup>, Werner Aeschbach-Hertig <sup>a, c</sup>

<sup>a</sup> Institute of Environmental Physics, Heidelberg University, 69120 Heidelberg, Germany

<sup>b</sup> Water Authority of Jordan, Laboratories and Quality Department, 8th Circle, Industrial Area, Khansa'a Street, P.O. Box 2412, 11183 Amman, Jordan

<sup>c</sup> Heidelberg Center for the Environment, Heidelberg University, 69120 Heidelberg, Germany

## ARTICLE INFO

Article history: Received 9 March 2015 Received in revised form 29 November 2015 Accepted 2 December 2015 Available online 11 December 2015

Keywords: Noble gases Azraq Jordan Groundwater mixing Salinization

## ABSTRACT

Azraq Oasis in the eastern Jordanian desert is an important freshwater resource of the country. Shallow groundwater reserves are heavily exploited since the 1980s and in consequence the groundwater table dropped significantly. Furthermore, some wells of the major well field drilled into the shallow aquifer show an increasing mineralization over the past 20 years. A previous study using conventional tracers did not result in a satisfactory explanation, from where the salt originates and why only a few wells are affected. In this study, the application of dissolved noble gases in combination with other tracer methods reveals a complex mixing pattern leading to the very localized salinization within the well field. It is found that primarily the wells affected by salinization 1) contain distinctly more radiogenic <sup>4</sup>He than the other wells, indicating higher groundwater age, and 2) exhibit <sup>3</sup>He/<sup>4</sup>He ratios that argue for an imprint of deep fluids from the Earth's mantle.

However, the saline middle aquifer below is virtually free of mantle helium, which infers an upstream from an even deeper source through a nearby conductive fault. The local restriction of the salinization process is explained by the wide range of permeabilities of the involved geologic units. As the wells abstract water from the whole depth profile, they initially pump water mainly from the well conductive top rock layer. As the groundwater table dropped, this layer fell progressively dry and, depending on the local conductivity profile, some wells began to incorporate more water from the deeper part of the shallow aquifer into the discharge. These are the wells affected by salinization, because according to the presented scheme the deep part of the shallow aquifer is enriched in both salt and mantle fluids.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Azraq is situated in the northeastern Jordanian desert, about 90 km east of the capital Amman. Azraq used to be an oasis up to the early 1990s, with an extensive system of lakes and marshland fed by several springs (Nelson, 1985). At that time the oasis hosted a vivid ecosystem and was an important stop-over for migrating birds. In the early 1980s, however, the AWSA well field was drilled close to the oasis to supply the urban areas of Amman and Zarqa with drinking water. The groundwater abstraction from this well field of 15–20 million cubic meters per year (MCM/a) and a

E-mail address: Tillmann.Kaudse@iup.uni-heidelberg.de (T. Kaudse).

growing water demand for irrigation purposes in the vicinity of the oasis and the northern parts of the Azraq basin (in total 45 MCM/a) caused the groundwater table to drop by almost 1 m per year since then, and the springs fell dry in 1991 (Al-Momani et al., 2006).

Not only is overpumping a hazard for the Azraq ecosystem, but also the threat of deteriorating groundwater quality grows. While the AWSA well field produced high quality drinking water with little mineralization during the first years of operation, some of its wells show a rising salinity over the years (compare Fig. 1). This issue was addressed in a study conducted by the Water Authority of Jordan (Al-Momani et al., 2006), but the source of the salt could not be determined with certainty. The present study, applying dissolved noble gases as the main tracers, aims at shedding new light on the complex groundwater intermixing processes and the origin of salinization in the central part of the Azraq basin.



<sup>\*</sup> Corresponding author. Institute of Environmental Physics, Heidelberg University, 69120 Heidelberg, Germany.



## 2. Hydrogeologic setting

Azraq Oasis lies in a tectonic depression within the Azraq surface catchment basin, which extends into Syria and covers an area of about 12,800 km<sup>2</sup>. Most precipitation occurs in the northern highlands around the mountain Jabal ad-Druze (compare the regional map in Fig. 2). The basin has no perennial rivers, but during storm events large amounts of water can be transported by wadi run-off from the highlands into the central playa (*Sabkha* in Arabic), where most of it evaporates.

In general, three major aquifer systems are present in the Azraq basin, which are shown in the cross-section in Fig. 3. The Ram and Kurnub sandstone aquifers of Cambrian to Lower Cretaceous age form the deepest aquifer system, which is present in almost the whole of Jordan. The upper limit of the deep aquifer is more than 1200 m below the surface in Azraq; hence, this aquifer is not exploited in this area. It is overlain by the formations of the Cenomanian to Turonian Lower Ajlun group (A1/6). These marl and limestone units are considered to act as an aquitard, separating the sandstone aquifers beneath from the Amman-Wadi Sir limestone



**Fig. 2.** The location of the Azraq Oasis in Jordan. The recharge areas of the shallow and middle aquifer systems are given in blue. The position of the cross-section in Fig. 3 is indicated by a red line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Geologic cross-section in west–east direction, as indicated in Fig. 2. The shallow, middle and deep aquifer systems are displayed in blue, while the aquicludes are brown. The vertical displacement at the Fuluq fault is obvious. As the Kurnub aquifer (K) is located differently east and west of the Fuluq Fault, it is emphasized as being part of the deep aquifer system west of the Fuluq fault and connected to the middle aquifer east of it. Adapted from Margane et al. (2002). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

aquifer above (B2/A7, Upper Turonian to Campanian-Maastrichtian). In Azraq this aquifer is often named the middle aquifer. It is recharged in the Jordan highlands in the west (see Fig. 2), and the hydraulic head gradient drives the groundwater flow in eastern and northeastern direction towards the Azraq oasis and beyond (Margane et al., 2002). Its mineralization is generally high in Azraq, so this aquifer is not utilized there as well. The middle aquifer is confined by the several hundred meter thick bituminous marl of the Muwaqqar formation (B3) of Maastrichtian to Paleocene age.

The upper aquifer system (often termed the shallow aquifer) consists of four units: the Umm Rijam chalky limestone (B4, Paleocene to Eocene) right above the B3 aquiclude, the Wadi Shallala formation (B5, Eocene), the Harrat ash-Shaam basalt shield (Oligocene to present time), covering the northern part of the basin, and, in the center of the basin, the Quaternary sediments of the Sirhan formation. Groundwater recharge to the upper aquifer occurs dominantly in the northern part of the Azraq basin at the slopes of the mountain Jabal ad-Druze (Fig. 2). The general flow direction is towards the central oasis, where this study is focused (see map in Fig. 4). Under undisturbed conditions, two major spring fields fed the lakes of the oasis, thereby being the natural discharge of the upper aquifer in the Azraq Basin, but nowadays groundwater abstraction is the only discharge.

Due to the generally good water quality, the shallow aquifer in the Azraq basin is heavily exploited for agricultural as well as domestic purposes. The transmissivity of the fractured basaltic top layer is generally very high within the AWSA well field (up to  $65,000 \text{ m}^2/\text{day}$ ), but varies strongly among the individual wells (Ayed, 1996; citing Humphreys and Sons, 1982). The lower part of the shallow aquifer, the B4 formation, is an aquifer, too, but its transmissivity is significantly lower than that of the basalts (the maximum is  $660 \text{ m}^2/\text{day}$ ). The B5, located between the basalt and B4 units, acts as an aquifer in the southern part of the basin, but is considered an aquitard in the area of the former oasis and, namely, in the AWSA well field, where its thickness is around 70 m. In the



**Fig. 4.** Overview of the vicinity of the Azraq Oasis. In brown the central mud pan (*Sabkha*) is displayed, the farm land in green and the surface basalt shield in grey. The saline AWSA wells are indicated by orange (cluster III) and brown (cluster IV) dots, the others by red (cluster I) and yellow (cluster II) dots. Farm wells are shown in green, the deep wells NDW-7 in blue and NDW-5 in purple. The approximate boundary of the salt water body in the center is indicated as an orange, dotted line. The major faults are named and drawn as black lines, other lineaments are displayed as grey lines. Road data from OpenStreetMap. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

central playa the Sirhan formation is the top-most layer. It is divided into two subunits: The youngest consists of wadi deposits, gravels and silts of the mud pan with large amounts of evaporites resulting from evaporation of the former lakes. Thus, the shallow groundwater up to a depth of about 60 m in this subunit is highly mineralized. The second subunit of the Sirhan formation comprises cemented lacustrine sediments and hosts a freshwater body. The presence of denser brackish water stratified above a freshwater body suggests a confining clay layer within the Sirhan formation (El-Waheidi et al., 1992). The Azraq depression is owed to the subsidence of the Hamza Graben system, which runs in NW–SE direction. Its formation created a dense network of fractures in and around the oasis. The Fuluq Fault is the eastern boundary of the graben and the major tectonic structure in the area with a vertical displacement up to more than 3000 m (see the cross-section in Fig. 3). As a result, the strata west of the Fuluq Fault dip towards the fault and are considerably thicker compared to the corresponding units east of the fault. A major difference of the stratification east of the Fuluq Fault regards the Kurnub formation, which is considered to be a

part of the middle aquifer there, whereas it belongs to the deep aquifer system west of the fault. To illustrate this feature, the Kurnub is emphasized in the cross-section in Fig. 3.

The Fuluq Fault passes about 10 km to the northeast of the central playa and the well field. Many more faults and minor lineaments are known or inferred under alluvial deposits (compare Fig. 4).

## 3. The salinization problem and previous studies

When the AWSA well field was drilled in the early 1980s into the shallow aquifer (both the basalt and the limestone units, compare the lithologic borehole data in Table 1S (Supporting Material)) the mineralization of all wells was low (EC mostly in the range of 400–600  $\mu$ S/cm). Since then some of the wells have shown a rising salt content (namely AWSA 3, 12, 13, and 15), while others have kept their low mineralization (compare Fig. 1). This different behavior is surprising, because the wells are located within an area of only a few square kilometers. In the map in Fig. 4 the AWSA well field and its surrounding is displayed in detail, where the orange and brown dots represent the wells with elevated salinity and the red and yellow ones those with a more or less constant salt content.

The salinization problem was extensively addressed by a study conducted by the Water Authority of Jordan (WAJ) in 2002 using traditional tracer methods (Al-Momani et al., 2006). Three possible mechanisms of the increasing salinization in the AWSA well field were discussed:

- The continuous pumping in the AWSA well field changed the hydraulic gradient and a back-flow of saline, shallow groundwater from the central mud pan towards the well field commenced.
- Transient conditions due to increased abstraction rates led to changes in the local groundwater flow path. The groundwater consequently came into contact with other geochemical environments, which altered the mineral composition of the water.
- 3. Due to the drawdown of the groundwater table in the shallow aquifer an upward leakage from the middle aquifer (B2/A7) and/ or the B3 aquitard takes place.

The first possibility is ruled out by the above mentioned study because the hydraulic head gradient at the time of data collection (in 2002) was very low, but still drove the groundwater generally from the well field area towards the *Sabkha*. This fact is confirmed by El-Naqa (2010).

According to Al-Momani et al. (2006), the second explanation, where the transient conditions in the upper aquifer led to a significant change in the groundwater geochemistry, seems to be the most likely one. This assumption is supported by the fact that the increase of some constituents is not accompanied by a change in stable isotopes, which suggests that the origin of the groundwater has not changed, but the water has experienced different geochemical conditions, possibly due to changes in its flow path. The authors, therefore, deem it unlikely that water from other sources admixes into the well field.

The third possibility, an upstream of brackish water from the middle aquifer through conductive faults, however, could not be ruled out by the Al-Momani et al. (2006) study.

The groundwater regime of the Azraq basin has been modeled by several authors (Holden, 1998; Abdulla et al., 2000; Al-Kharabsheh, 2000; Aljazzar, 2003; Abu-El-Sha'r and Rihani, 2007; Schmidt et al., 2008). All of these models describe the change of the piezometric head distribution in the Azraq basin quite well, but none of them is capable to explain the complex groundwater behavior in the Azraq Oasis. This may result from the fact that changes of the groundwater movement and interaction of the several water species present in the area take place on a relatively small spatial scale, while all models employ a more or less coarse grid resolution. In addition, experimental data, especially from the middle and deep aquifers as well as the agricultural wells around the playa, are too rare to facilitate an adequate model description of the groundwater system.

Several geoelectric surveys in the *Sabkha* shed light on the saltwater/freshwater interface in the upper Sirhan formation (El-Waheidi et al., 1992; El-Naqa, 2010; Yogeshwar et al., 2013). They found the boundary between the highly and lowly conductive zones to be quite sharp and several kilometers away from the well field. The approximate saltwater/freshwater interface extracted from these publications is shown in the map in Fig. 4. It should be noted, however, that only the data of Yogeshwar et al. (2013) provide a resolution high enough to exactly determine the interface (locations of the saltwater/freshwater interface from their two profiles are indicated as grey rhombi upon the orange line), a possible deviation of more than 1 km should be considered for the remaining indicated line. Nevertheless, El-Naqa (2010) estimated the brackish water regime to reach the AWSA well field in 500–2000 years at present abstraction rates.

## 4. Sampling and analytical methods

The samples for this study were collected during three field trips in 2009, 2010 and 2012. Wells of the AWSA well field were sampled on all campaigns, though not all of them every time. In total, 23 samples from 11 wells of the AWSA well field are considered. Most of the wells are drilled to a depth of about 200 m, except AWSA 11 (62 m), AWSA 16 (160 m), AWSA 18 (171 m) and AWSA 20 (117 m). All AWSA wells have no casing, which means they can abstract water from all penetrated depths.

In order to obtain data from all sources of salinity considered by Al-Momani et al. (2006), samples from five shallow brackish agricultural wells around the *Sabkha* were taken as examples of the hypersaline part of the upper aquifer, and from two deep boreholes which tap the middle aquifer in this area. The agricultural wells are constructed in a simpler way than the AWSA wells and the total depth is not known, but it can be expected that they reach only several 10 m deep due to drilling costs. Two of them were equipped with a pump which runs only occasionally (F3975, F3741), two others were not in use anymore (F3960, Moh). The remaining farm well comprised a hole dug to the groundwater table with a pump lowered into the water (F3731).

Both wells tapping the middle aquifer were drilled as exploration boreholes and neither had a pump installed. NDW-5 represents groundwater east of the Fuluq Fault; it reaches the very top layer of the Kurnub unit, which is considered part of the middle aquifer east of the Fuluq Fault, but is screened also at depths of the shallow aquifer. NDW-7 is located west of the fault, just within the playa (compare Fig. 4); its screen lies within the middle aquifer.

In addition to the wells in the central part of the basin, three wells in the north, close to the Syrian border, were sampled. They abstract water only from the basalt part of the shallow aquifer and define the baseline conditions of the groundwater in the recharge area in the north before it flows towards the well field.

All wells were analyzed in the field for discharge temperature, electric conductivity (EC), pH and dissolved oxygen using a multiparameter probe 340i (WTW GmbH, Weilheim, Germany). However, an exception are the wells without a pump, where water samples were collected using a bailer. In these cases the water temperature, pH and  $O_2$  content were not possible to determine reliably. The temperature sensor has an analytical precision of 0.2 K, the pH meter of 0.01, and the oxygen sensor of 0.01 mg/L.

The 2009, 2010 samples were measured for stable isotopes of hydrogen and oxygen in water molecules ( $\delta^2$ H and  $\delta^{18}$ O) on a Finnigan MAT 252 mass spectrometer (Thermo Fisher, Massachusetts, USA) at the Institute of Environmental Physics in Heidelberg, Germany. Samples of the 2012 campaign were analyzed on a Picarro L2120-I (Picarro, Santa Clara, California, USA) at the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover. Germany. While the  $\delta^{18}$ O results matched within the error range over the sampling campaigns, the  $\delta^2$ H showed a systematic offset. Because  $\delta^2 H$  and  $\delta^{18} O$  generally exhibit a strong correlation, it seems unlikely that transient conditions would lead to a change of only  $\delta^2$ H and not of  $\delta^{18}$ O. We, therefore, assume that the shift in  $\delta^2$ H between 2009/10 and 2012 is due to a systematic offset between the laboratories. Since the precision of the Picarro  $\delta^2 H$  measurement is better than that of the mass spectrometric analysis, we adjust the values of the 2009 and 2010 sampling campaigns to the 2012 data by adding the average  $\delta^2$ H shift of the corresponding wells to the 2009 and 2010 data ( $-2.84 \pm 0.32\%$ and  $-1.09 \pm 0.31\%$ , respectively).

Carbon samples were sterilized by silver nitrate (0.1 g per 500 mL sample) in the field. After extraction with hydrochloric acid,  $\delta^{13}$ C was analyzed on the same MAT 252 mass spectrometer mentioned above. Radiocarbon analysis was performed at the Klaus-Tschira-Laboratory AMS facility of the Curt-Engelholm Zentrum (Mannheim, Germany). Tritium activities (<sup>3</sup>H) of the 2010 samples were analyzed by low-level counting at the Institute of Environmental Physics in Heidelberg, Germany, with a detection limit of 2 TU. Radon activity, being a measure of the local radium content of the aquifer material, was analyzed during the 2012 sampling campaign after each sampling day using a RAD7 radon detector (Durridge, Billerica, Massachusetts, USA).

Water for the anion and cation composition analysis was filtered with a 0.22  $\mu$ m filter before being bottled in 50 mL glass bottles. The cation sample was acidified with 150  $\mu$ L of concentrated nitric acid to a pH below 2 to prevent any precipitation of solute, for this might affect the measurement reliability weeks later in the laboratories of the Institute of Earth Sciences, Heidelberg University. The cations were measured on a Varian Vista MPX (Agilent Technologies, California, USA), while the anions were analyzed on a ICS 1100 (Dionex, California, USA) using a 25  $\mu$ L loop, a separating column AS23, and eluent solvent containing 4.5 mmol Na<sub>2</sub>CO<sub>3</sub> and 0.8 mmol NaHCO<sub>3</sub>. Alkalinity, i. e. predominantly HCO<sub>3</sub><sup>-</sup> in the pH range of the sampled water, was measured by titration using a test kit by Salifert (Duiven, The Netherlands) on site.

Two different methods to sample for noble gases in the groundwater were applied. In wells equipped with a pump, the water was collected in copper tubes mounted in aluminum racks, which are closed air-tight on both sides with stainless steel clamps (Beyerle et al., 2000). At the four wells without pump, noble gas samples were collected using passive diffusion samplers (Sanford et al., 1996; Sheldon, 2002; Aeschbach-Hertig and Solomon, 2013). They consist of two copper tubes, pinched off at the outer end, which are connected by a PVC tube. Gases dissolved in groundwater can diffuse through the PVC membrane into the inner volume of the sampler. After sufficient time an equilibrium between the gases within the sampler and the surrounding groundwater establishes. This equilibration time has been determined experimentally for the diffusion sampler design used here to be well below 48 h (Wieser, 2006). Following the exposition in the well for at least two days, the diffusion samplers were rapidly retrieved and closed using pneumatic pliers. This way noble gas samples from the farm wells F3960 and Moh as well as from NDW-5 (diffusion samplers located at 684 m below ground surface) and from several depths (50, 100, 150, 200, 250, 300, 544 and 569 m) of NDW-7 were obtained. Because the maximum depth accessible with the bailer was only 250 m, noble gas samples from below this depth are not accompanied by other tracer data.

Noble gas samples were analyzed on a MM5400 mass spectrometer (GV Instruments, Manchester, UK, today Thermo Fisher, Massachusetts, USA) at the Institute of Environmental Physics in Heidelberg, Germany. The general principles of the setup and the measurement, calibration, and evaluation procedures are described by Beyerle et al. (2000); deviations and improvements are found in Friedrich (2007), Wieser (2011), and Kaudse (2014).

## 4.1. Noble gas component separation

Noble gases dissolved in groundwater consist of several components. Equilibration of percolating groundwater with the soil air results in noble gas patterns primarily depending on the ambient temperature. Knowing the equilibrium component of the total noble gas composition in groundwater enables one to reconstruct the mean annual air temperature at the time of recharge called noble gas temperature (NGT) (Aeschbach-Hertig and Solomon, 2013). An additional noble gas component, called excess air, results from the entrapment and partial dissolution of air bubbles in the soil pores. These two components dominate the noble gas composition in case of neon, argon, krypton and xenon.

Several models have been developed to explain the processes leading to excess air (Aeschbach-Hertig et al., 2008; Aeschbach-Hertig and Solomon, 2013). In this study the CE excess air model (Aeschbach-Hertig et al., 2000) is employed because it is capable of describing excess air as well as degassing patterns (Aeschbach-Hertig et al., 2008). Inverse modeling is used to determine the model parameters describing the equilibrium and excess air components in the samples (Aeschbach-Hertig et al., 1999; Ballentine and Hall, 1999). As the application of the CE model led to difficulties such as parameter correlations and high uncertainties in some cases, the data was further treated by Monte Carlo simulations to improve the reliability of the results (100,000 simulations for each sample). We followed the Monte Carlo evaluation guidelines by Jung et al., (2013) and Jung (2014). Atmospheric pressure at the groundwater table in the recharge area (which determines the atmosphere-derived noble gas concentrations in the water) was assumed as 920 mbar, which corresponds to about 800 masl, both for the shallow aquifer (recharge at Jabal ad-Druze) and the middle aquifer (recharge in the western highlands). In case of the shallow aquifer this assumption is justified by a very thick unsaturated zone in the recharge area of more than 400 m at the Jordanian/Syrian border (Margane et al., 2002).

Helium, however, has several additional sources in the subsurface. <sup>4</sup>He is produced in the Earth's crust in alpha decays of elements of the uranium and thorium decay chains present in every mineral. It accumulates in groundwater and can be employed as a qualitative groundwater age indicator (Solomon, 2000; Aeschbach-Hertig et al., 2002). This crustal He also contains a small amount of <sup>3</sup>He produced in the subsurface by neutron capture and subsequent decay of <sup>6</sup>Li to <sup>3</sup>H, which then disintegrates to <sup>3</sup>He. But due to the low lithium abundance in typical sedimentary rock this process is usually almost negligible (James and Palmer, 2000).

Mainly in localities with tectonic activity, deep mantle fluids characterized by high <sup>3</sup>He contents can be transported to shallow depth by conductive faults and influence the helium isotope signature of the shallow groundwater. Helium originating from the Earth's crust and mantle is often summarized as terrigenic helium. Another source of <sup>3</sup>He can be the decay of tritium contained in the water, producing the so-called tritiogenic <sup>3</sup>He. This component can be significant in young groundwater affected by the bomb peak, where it enables precise dating of young groundwater with the <sup>3</sup>H–<sup>3</sup>He method (Schlosser et al., 1988).

The three helium reservoirs – atmosphere, crust and mantle – differ largely in their helium isotope ratio. The atmosphere has a  $^{3}$ He/ $^{4}$ He ratio of 1.384  $\times$  10<sup>-6</sup> (Clarke et al., 1976); this value is termed R<sub>A</sub>. Because of the predominant production of <sup>4</sup>He in the crust, the crustal  $^{3}\text{He}/^{4}\text{He}$  ratio is  $R_{C}$   $\approx$  2  $\times$  10  $^{-8}$   $\approx$  0.015  $R_{A}$ (Mamyrin and Tolstikhin, 1984). Within the mantle several helium reservoirs have been identified: Mantle material which upwells in spreading zones of the crust (MORB: mid-ocean ridge basalt) typically has a  ${}^{3}\text{He}/{}^{4}\text{He}$  ratio of about  $R_{M} \approx 1.1 \times 10^{-5} \approx 8 R_{A}$ (Graham, 2002). In volcanic hot spots,  ${}^{3}\text{He}/{}^{4}\text{He}$  ratios up to 50 R<sub>A</sub> were found (Class and Goldstein, 2005; Graham, 2002) and are often interpreted as signals of a lower mantle or the mantle-core boundary. Although seismic data suggest a mantle hotspot beneath Jordan (Chang and van der Lee, 2011), the highest helium ratio found in lavae in the Golan Heights is 7.8 R<sub>A</sub> (Torfstein et al., 2013), indicating a MORB-like helium isotope signature of the local mantle material. 8 RA is, therefore, considered as the helium isotope ratio of the mantle endmember in this study. The wide range of helium isotope ratios enables a distinction of the influence of the different reservoirs on the sampled groundwater.

The total contribution of non-atmospheric <sup>3</sup>He and <sup>4</sup>He (terrigenic + tritiogenic) is calculated by subtracting the modeled atmospheric share of <sup>3</sup>He and <sup>4</sup>He, respectively, (i. e. equilibrium + excess air) from the total measured helium isotope amounts. Considerations based on measured tritium and apparent <sup>3</sup>H–<sup>3</sup>He ages are used to put some constraints on the presence of tritiogenic <sup>3</sup>He.

## 5. Results

## 5.1. Definition of well clusters found in the AWSA well field

In the following plots, the different sampling campaigns are recognizable by specific symbols: 2009: filled triangles, 2010: filled circles and 2012: open circles. The AWSA wells are labeled only by their number, while the other wells are marked with their full names.

The salinization behavior of the AWSA well field is mirrored in the terrigenic helium distribution. Fig. 5a clearly shows that those wells having an elevated salt content are also enriched in terrigenic helium (the corresponding data is found in Table 1 and Table 2S (Supporting Material)). Moreover, four clusters can be distinguished, which are marked in different colors in the plots:

Cluster I: low salinity and negligibly low terrigenic  ${}^{4}$ He (AWSA 11, 16, 18 and 20, red)

Cluster II: low salinity, but some terrigenic <sup>4</sup>He (AWSA 4, 5 and 6, yellow)

Cluster III: medium salt content and the highest terrigenic <sup>4</sup>He amount (AWSA 3, 12 and 13, orange)

Cluster IV: highest mineralization, but only medium terrigenic <sup>4</sup>He content (only the single well AWSA 15, brown)

The fact that the AWSA wells of cluster I coincide with the samples from the northern wells (grey triangles), regarded as baseline water, suggests that groundwater flowing south from Jabal ad-Druze is present in the center of the basin where it mixes with other water masses. As an elevated <sup>4</sup>He signal indicates older groundwater, its presence suggests that the saline wells of clusters III and IV as well as the cluster II wells have an admixed component of old groundwater. However, no simple correlation between salt content and helium concentration (i. e. share of old groundwater mixed into the saline wells) can be recognized.



**Fig. 5.** The samples from the AWSA well field constitute four clusters, when their electric conductivity is related to several other tracers. a) The definition of the clusters is according to their individual combinations of terrigenic <sup>4</sup>He and EC as described in the text. b) Wells of cluster II, III and IV discharge warmer water, suggesting an origin from deeper layers. c) A similar clustering is visible in the pH diagram, although the data splits into two branches for the years 2010 (closed circles) and 2012 (open circles), respectively (explanation in the text). Yet, if each year is considered individually, the brackish wells (cluster III and IV, orange and brown) have lower pH values than cluster I water (red). Higher pH values indicate water originating from the alkaline basalt aquifer. d) The depleted oxygen content in the cluster II, III and IV wells argues for older water, i.e. coming from deeper layers. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 5.2. Basic parameters and water chemistry

Shown in Fig. 5b, c and d are the discharge temperature, pH and dissolved oxygen content of the AWSA wells in relation to the EC (the according data is listed in Table 2S (Supporting Material)). Interestingly, the clusters deduced from Fig. 5a can be recognized again. The water temperatures of the cluster I wells are two to 4 K cooler than those containing a significant amount of terrigenic

Table	1
	_

Helium isotope ratios (in multiples of the atmospheric isotope ratio  $R_A$ ), Ne/He ratios, the calculated terrigenic <sup>4</sup>He amounts and noble gas temperatures.

Weil         Year <sup>3</sup> He/ <sup>4</sup> He R <sub>A</sub> Δ <sup>3</sup> He/ <sup>4</sup> He R <sub>A</sub> Δ Ne/He         Δ Ne/He         Terr. <sup>4</sup> He cSTP/g         Δ Terr. <sup>4</sup> He cSTP/g         NCT *C         Δ NCT *C           AWSA 3         2000         0.830         0.026         0.701         0.007         2.005E-07         2.404E-09         2.54         0.24           AWSA 4         2009         0.554         0.033         0.702         0.007         1.976E-07         2.404E-09         2.578         0.42           AWSA 4         2009         0.574         0.018         1.600         0.016         6.323E-08         1.166E-09         2.578         0.42           AWSA 5         2010         0.612         0.023         1.480         0.014         7.69E-08         1.269E-09         2.54         0.32           AWSA 5         2010         0.475         0.018         1.427         0.014         7.69E-08         1.269E-09         2.54         0.32           AWSA 6         2010         0.528         0.023         1.863         0.019         4.65E-08         9.99E-10         2.54         0.224           AWSA 12         2000         0.787         0.024         0.22         0.027         1.947E-07         2.016-09										
AWSA 3         2000         0.830         0.026         0.701         0.007         2.005E-07         2.447E-09         25.84         0.24           AWSA 3         2010         0.856         0.033         0.702         0.007         2.905E-07         2.404E-09         25.73         0.21           AWSA 4         2009         0.574         0.018         1.600         0.016         6.323E-08         1.166E-09         2.578         0.421           AWSA 5         2010         0.612         0.020         1.537         0.016         6.631E-08         1.256E-09         2.524         0.321           AWSA 5         2010         0.475         0.018         1.427         0.014         7.256E-08         7.30E-10         2.650         0.221           AWSA 6         2010         0.475         0.013         1.658         0.39E-10         2.744         0.444           2012         0.566         0.021         1.789         0.017         5.77E-08         6.50E-10         2.662         0.22           AWSA 13         2009         0.767         0.204         0.720         0.66E-09         2.63         0.221           AWSA 13         2010         0.566         0.017         0.99B<	Well	Year	<sup>3</sup> He/ <sup>4</sup> He R <sub>A</sub>	$\Delta^3 He/^4 He \ R_A$	Ne/He	$\Delta$ Ne/He	Terr. <sup>4</sup> He ccSTP/g	$\Delta$ Terr. <sup>4</sup> He ccSTP/g	NGT °C	$\Delta$ NGT °C
AWSA 3         2009         0.836         0.026         0.701         0.007         2.0075         2.244E-09         25.84         0.24           2010         0.856         0.033         0.704         0.007         2.858E-07         2.404E-09         2.67.8         0.21           AWSA 4         2009         0.574         0.016         6.323E-08         1.166E-09         2.57.8         0.42           2010         0.645         0.023         1.480         0.014         7.235E-08         1.295E-09         2.534         0.32           AWSA 5         2010         0.475         0.018         1.427         0.014         7.268E-08         6.730E-10         2.642         0.23           AWSA 6         2010         0.528         0.023         1.863         0.014         7.268E-08         1.298E-09         2.54         0.32           AWSA 6         2010         0.528         0.023         1.863         0.119         5.172E-08         6.500E-10         2.662         0.23           AWSA 12         2010         0.750         0.029         0.819         0.010         1.443E-07         2.16E-09         2.541         0.22           AWSA 13         2010         0.750         0	AWSA well field									
AWSA 420120.08580.0330.7020.0071.976E-072.404E-092.6780.39AWSA 420090.5740.0181.6000.0166.323E-081.166E-092.5780.4220100.6120.0261.5370.0166.323E-081.166E-092.5780.42AWSA 520100.4750.0181.4270.0147.235E-087.997E-102.6090.22AWSA 620100.5330.0201.6740.0165.880E-086.370E-102.6550.23AWSA 620100.5280.0231.8630.0194.655E-089.949E-102.7440.44AWSA 120100.5280.0211.7890.0175.172E-086.050E-102.620.22AWSA 1220090.7870.0240.7220.0071.947E-072.215E-092.5410.22AWSA 1320090.7870.0240.7220.0071.947E-072.165E-092.5330.25AWSA 1320090.5660.0170.9080.0101.641E-072.067E-092.4320.32AWSA 1520100.5500.0210.8290.0091.631E-072.060E-092.4320.33AWSA 1520100.5680.0170.9080.0101.464E-072.067E-092.3220.33AWSA 1520100.5680.0210.3230.3310.2520.330.3530.3530.3530.353	AWSA 3	2009	0.830	0.026	0.701	0.007	2.005E-07	2.247E-09	25.84	0.24
AWSA 420090.5740.0330.7040.0072.868-072.100E-092.6730.21AWSA 420090.6720.0221.5370.0166.6323E-081.166E-092.730.8820120.6450.0231.4800.0147.235E-087.997E-102.6900.22AWSA 520100.4750.0181.4270.0147.696E-081.269E-092.5940.32AWSA 620100.5280.0231.6630.0194.655E-082.949E-102.7.440.4420120.5860.0211.7890.0175.172E-086.050E-102.6620.22AWSA 1220090.7870.0240.7220.0071.947E-072.216E-092.5310.25AWSA 1320090.5660.0170.9080.0101.641E-072.006E-092.4030.25AWSA 1620100.5430.0210.7200.071.976E-072.606E-092.3820.23AWSA 1520100.5430.0210.8290.0031.631E-072.006E-092.4320.23AWSA 1620100.7820.0323.4310.0311.262E-087.829E-102.3040.22AWSA 1620100.7820.0333.4310.0327.569E-092.035E-102.3240.42AWSA 1620100.8890.0333.4310.0327.569E-092.036E-102.3240.32AWSA 162010<		2010	0.856	0.033	0.702	0.007	1.976E-07	2.404E-09	26.78	0.39
AWSA 4         2009         0.574         0.018         1.600         0.016         6.321.808         1.166E-09         2.578         0.42           2010         0.645         0.023         1.480         0.014         7.235.088         7.997E-10         26.90         0.22           AWSA 5         2010         0.475         0.018         1.427         0.014         7.265E-08         1.266E-09         2.53         0.22           AWSA 6         2010         0.528         0.023         1.663         0.019         4.655E-08         9.949E-10         2.744         0.44           AWSA 1         2010         1.129         0.070         3.431         0.029         2.011E-08         7.760E-09         3.840         5.58           AWSA 13         2009         0.576         0.029         0.819         0.009         1.645E-07         2.106E-09         2.531         0.22           2010         0.530         0.012         0.829         0.009         1.641E-07         2.046E-09         2.532         0.232           2010         0.530         0.012         0.829         0.009         1.631E-07         2.040E-09         2.432         0.232           AWSA 15         2010 <t< td=""><td></td><td>2012</td><td>0.858</td><td>0.033</td><td>0.704</td><td>0.007</td><td>2.868E-07</td><td>2.100E-09</td><td>26.73</td><td>0.21</td></t<>		2012	0.858	0.033	0.704	0.007	2.868E-07	2.100E-09	26.73	0.21
111	AWSA 4	2009	0.574	0.018	1.600	0.016	6.323E-08	1.166E-09	25.78	0.42
AWSA 520120.6450.0231.4800.0147.285E-087.997E-102.6900.22AWSA 520100.4750.0181.4617.669E-086.730E-102.6950.23AWSA 620100.5280.0211.7890.0175.172E-086.050E-102.6420.42AWSA 120101.1290.0703.4310.0292.101E-087.760E-093.8305.58AWSA 1220090.7870.0240.7220.0071.947E-072.215E-092.5410.22AWSA 1320090.7500.0290.8190.0091.631E-072.047E-092.8420.28AWSA 1320090.5060.0170.8080.0101.464E-072.047E-092.8420.28AWSA 1520100.5430.0200.7200.0071.970E-072.663E-092.6330.21AWSA 1520100.4330.0161.0660.0111.179E-071.647E-092.3820.33AWSA 1620100.7420.0323.1430.0311.27E-087.829E-102.3440.22AWSA 1820200.9740.0313.7270.0353.533E-096.155E-102.3320.41AWSA 2020090.6730.0212.3540.730.324.750.320.41Farm wells		2010	0.612	0.026	1.537	0.016	6.641E-08	1.253E-09	27.43	0.88
AWSA 5         2010         0.475         0.018         1.427         0.014         7.686         6.7306-10         25.94         0.32           AWSA 6         2010         0.538         0.023         1.863         0.019         4.655E-08         9.949E-10         27.44         0.44           AWSA 1         2010         0.586         0.021         1.789         0.017         5.172E-08         6.056E-10         26.62         0.22           AWSA 11         2010         0.787         0.024         0.722         0.007         1.947E-07         2.105E-09         2.541         0.22           AWSA 13         0.029         0.787         0.024         0.722         0.007         1.947E-07         2.046E-09         2.40         0.28           AWSA 13         0.020         0.566         0.017         0.908         0.010         1.464E-07         2.047E-09         2.402         0.28           AWSA 15         2.010         0.543         0.020         0.270         0.007         1.979E-07         2.663E-09         2.633         0.21           AWSA 15         2.010         0.732         0.031         1.262E-06         7.595E-10         2.324         0.33           AWSA 15		2012	0.645	0.023	1.480	0.014	7.235E-08	7.997E-10	26.90	0.22
AWSA 620120.5330.0201.6740.0165.890E-086.730E-102.6950.23AWSA 620100.5860.0211.7890.0175.172E-086.050E-102.6620.22AWSA 1120101.1290.0703.4310.0292.401E-087.760E-093.8.05.58AWSA 122090.7870.0240.7220.0071.947E-072.215E-092.5410.2220100.7500.0290.8190.0091.464E-072.047E-092.4020.2820100.5300.0210.8290.0091.361E-072.066E-092.6330.21AWSA 1320190.5500.0200.7200.0071.970E-072.061E-092.3820.33AWSA 1520100.4330.0161.0660.0111.179E-071.647E-092.3820.33AWSA 1520100.7820.0323.1430.0311.262E-087.829E-102.3640.22AWSA 1820190.9740.0313.7270.353.338-096.155E-102.320.41AWSA 202090.6730.0212.8350.0281.827E-087.906E-102.3020.22Farm wells	AWSA 5	2010	0.475	0.018	1.427	0.014	7.669E-08	1.269E-09	25.94	0.32
AWSA 620100.5280.0231.8630.0194.655E-089.949E-102.7.440.44AWSA 1120101.1290.0703.4310.0292.401E-087.760E-0938.805.58AWSA 1220090.7870.0240.7220.0071.947E-072.215E-092.5410.22AWSA 1320090.5660.0170.9080.0101.464E-072.047E-092.4320.28AWSA 1320090.5660.0170.9080.0101.464E-072.047E-092.4330.21AWSA 1520100.4330.0200.7200.0071.970E-072.068E-092.6330.21AWSA 1520100.4330.0161.0660.0111.179E-071.647E-092.3820.33AWSA 1620100.7820.0333.4310.0327.569E-092.039E-102.3640.22AWSA 1820090.9740.0313.7270.353.533E-096.155E-102.3320.41AWSA 200.900.9740.0313.7270.362.827E-087.596E-102.3020.22F374120120.4660.0171.5250.1557.707E-087.906E-102.3020.22F374120120.6630.0012.785E-087.906E-102.3020.52F396020120.8690.0372.4580.0362.882E-084.759E-102.0320.52F39602012 <t< td=""><td></td><td>2012</td><td>0.533</td><td>0.020</td><td>1.674</td><td>0.016</td><td>5.890E-08</td><td>6.730E-10</td><td>26.95</td><td>0.23</td></t<>		2012	0.533	0.020	1.674	0.016	5.890E-08	6.730E-10	26.95	0.23
AWSA 1120120.5860.0211.7890.0175.172E-086.650E-102.6.620.22AWSA 1220090.7870.0240.7220.0071.947E-072.215E-092.5.410.22AWSA 1220090.7500.0290.8190.0091.643E-072.106E-092.5.930.25AWSA 1320090.5660.0170.9080.0101.644E-072.047E-092.4.020.2820100.5530.0200.7200.0071.570E-072.206E-092.4.330.25AWSA 1520100.4330.0161.0660.0111.179E-071.647E-092.3.620.33AWSA 1620100.7820.0323.1430.0311.262E-087.829E-102.3.640.22AWSA 1820190.7820.0313.7270.0353.533E-096.155E-102.3.540.73AWSA 2020090.6730.0212.8350.0281.827E-087.595E-102.3.540.73Farm wellsF337520120.4680.0171.5250.0157.076E-087.906E-102.3.020.220.22Farm wellsF337620120.480.0160.9210.0132.825E-084.759E-102.3.020.220.22Farm wells<	AWSA 6	2010	0.528	0.023	1.863	0.019	4.655E-08	9.949E-10	27.44	0.44
AWSA 11         2010         1.129         0.070         3.431         0.029         2.401E-08         7.760E-09         3.8.0         5.58           AWSA 12         2010         0.757         0.024         0.722         0.079         1.447E-07         2.215E-09         2.51         0.22           AWSA 13         2009         0.506         0.017         0.908         0.010         1.464E-07         2.046E-09         2.433         0.25           AWSA 15         2010         0.553         0.020         0.720         0.007         1.476E-07         2.068E-09         2.6.03         0.21           AWSA 15         2010         0.533         0.010         1.404E-07         2.068E-09         2.3.43         0.23           AWSA 15         2010         0.583         0.020         0.720         0.007         1.970E-07         2.63E-09         2.3.44         0.23           AWSA 18         2010         0.783         0.031         1.727E-0.035         3.533E-09         6.155E-10         2.3.2         0.23           AWSA 20         2099         0.673         0.021         2.355         0.028         2.036E-10         2.3.22         0.25           F3741         2012         0.466 <td></td> <td>2012</td> <td>0.586</td> <td>0.021</td> <td>1.789</td> <td>0.017</td> <td>5.172E-08</td> <td>6.050E-10</td> <td>26.62</td> <td>0.22</td>		2012	0.586	0.021	1.789	0.017	5.172E-08	6.050E-10	26.62	0.22
AWSA 12         2009         0.787         0.024         0.722         0.007         1.947E-07         2.215E-09         2.541         0.22           AWSA 13         2009         0.506         0.017         0.908         0.010         1.448E-07         2.016E-09         2.533         0.25           AWSA 13         2009         0.506         0.017         0.908         0.010         1.448E-07         2.047E-09         2.402         0.28           AWSA 15         2010         0.533         0.021         0.829         0.007         1.970E-07         2.068E-09         2.382         0.33           AWSA 15         2010         0.433         0.016         1.066         0.011         1.179E-07         1.647E-09         2.382         0.33           AWSA 15         2010         0.782         0.032         3.143         0.031         1.262E-08         7.829E-10         2.34         0.23           AWSA 18         2009         0.673         0.021         2.353         0.028         1.827E-08         7.595E-10         2.13         0.32           Farm wells	AWSA 11	2010	1.129	0.070	3.431	0.029	2.401E-08	7.760E-09	38.80	5.58
AWSA 1320100.7500.0290.8190.0091.643E-072.106E-092.5.930.25AWSA 1320090.5430.0210.9080.0101.631E-072.080E-0924.020.2820120.5500.0200.7200.0071.970E-072.063E-0924.030.21AWSA 152100.4330.0161.0660.0111.179E-071.647E-092.3.820.33AWSA 1620100.7820.0323.4310.0327.569E-092.039E-102.3.640.22AWSA 1820090.9740.0313.7270.0353.533E-096.155E-102.3.220.41AWSA 2020090.6730.0212.8350.0281.827E-087.598E-102.3.240.73AWSA 2020090.6730.0212.8350.0281.827E-087.598E-102.3.240.73Farm wellsF37412120.2660.0171.5250.0157.076E-087.906E-102.3.220.52F396020120.8690.0372.4580.0362.882E-084.759E-102.0.320.52F396020120.7210.0320.6330.0022.196E-064.089E-0831.160.96DW-7 50m2120.2720.640.0066.826E-071.306E-082.0420.69NDW-7 50m20120.1310.010	AWSA 12	2009	0.787	0.024	0.722	0.007	1.947E-07	2.215E-09	25.41	0.22
AWSA 13         2009         0.506         0.017         0.908         0.010         1.464E-07         2.047E-09         2.402         0.28           2010         0.543         0.021         0.829         0.009         1.631E-07         2.068E-09         2.483         0.25           AWSA 15         2010         0.433         0.016         1.066         0.011         1.779E-07         1.647E-09         2.32         0.33           AWSA 16         2012         0.888         0.033         3.431         0.032         7.569E-09         2.039E-10         2.34         0.23           AWSA 18         2009         0.974         0.031         3.727         0.035         5.53E-09         6.155E-10         2.32         0.41           AWSA 20         2009         0.673         0.021         2.835         0.028         1.827E-08         7.595E-10         2.32         0.73           Farm wells		2010	0.750	0.029	0.819	0.009	1.643E-07	2.106E-09	25.93	0.25
20100.5430.0210.8290.0071.631E-072.080E-092.4.830.25AWSA 1520100.5500.0200.7200.0071.970E-072.063E-092.6.030.21AWSA 1520100.7820.0323.1430.0311.262E-087.829E-1023.040.28AWSA 1620120.8880.0333.4310.0327.569E-092.039E-1023.640.22AWSA 1820100.8890.0313.7270.0353.533E-096.155E-1023.320.41AWSA 200.6730.0212.8350.0281.827E-087.595E-1023.640.73AWSA 200.6730.0212.8350.0281.827E-087.595E-1023.020.22Farm wells	AWSA 13	2009	0.506	0.017	0.908	0.010	1.464E-07	2.047E-09	24.02	0.28
20120.5500.0200.7200.0071.970E-072.063E-092.6.30.21AWSA 1520100.4330.0161.0660.0111.179E-071.647E-0923.820.33AWSA 1620100.7820.0323.1430.0311.262E-087.829E-1023.640.22AWSA 1820090.9740.0313.7270.0353.533E-096.155E-1023.540.73AWSA 2020090.6730.0212.8350.0281.827E-087.595E-1021.320.41Farm wells77.5550.0157.076E-087.905E-1023.020.220.22F374120120.4660.0171.5250.0157.076E-087.906E-1020.320.22F374120120.4660.0110.5630.0662.771E-072.904E-0920.450.25F396020120.8690.0372.4580.0362.882E-084.759E-1020.320.52F396020120.4180.0610.9210.0131.8451E-071.707E-0920.450.52Peep wells77.0140.3880.0094.211E-078.548E-0920.270.64NDW-7 50 m20120.1770.0140.2480.0066.826E-071.305E-0820.220.64NDW-7 50 m20120.1310.0100.1480.0059.400E-071.205E-0819.030.76NDW-7 50 m20120.0		2010	0.543	0.021	0.829	0.009	1.631E-07	2.080E-09	24.83	0.25
AWSA 15         2010         0.433         0.016         1.066         0.011         1.179E-07         1.647E-09         23.82         0.33           AWSA 16         2010         0.782         0.032         3.143         0.031         1.262E-08         7.829E-10         23.04         0.22           AWSA 18         2009         0.974         0.031         3.727         0.035         3.533E-09         6.155E-10         23.32         0.41           AWSA 20         2009         0.673         0.021         2.859         0.028         7.595E-09         2.958E-10         23.54         0.73           AWSA 20         2009         0.673         0.021         2.855         0.028         1.827E-08         7.595E-10         23.02         0.22           Farm wells		2012	0.550	0.020	0.720	0.007	1.970E-07	2.063E-09	26.03	0.21
AWSA 16         2010         0.782         0.032         3.143         0.031         1.262E-08         7.829E-10         23.04         0.28           AWSA 18         2009         0.974         0.031         3.727         0.032         7.569E-09         2.039E-10         23.64         0.22           AWSA 18         2010         0.889         0.033         3.699         0.036         4.052E-09         6.558E-10         23.54         0.73           AWSA 20         2009         0.673         0.021         2.835         0.028         1.827E-08         7.956E-10         23.54         0.73           AWSA 20         2010         0.666         0.017         1.525         0.015         7.076E-08         7.906E-10         23.02         0.22           F3771         2012         0.466         0.017         1.525         0.016         2.771E-07         2.904E-09         20.45         0.25           F3960         2012         0.418         0.016         0.921         0.11         1.451E-07         1.707E-09         19.54         0.37           Deep wells         V         V         V         V         V         0.633         0.002         2.196E-06         4.898E-08         2.027<	AWSA 15	2010	0.433	0.016	1.066	0.011	1.179E-07	1.647E-09	23.82	0.33
20120.8880.0333.4310.0327.569E-092.039E-1023.640.22AWSA 1820090.9740.0313.7270.0353.533E-096.155E-1023.520.41AWSA 2020090.6730.0212.8350.0281.827E-087.595E-1021.730.32Farm wells	AWSA 16	2010	0.782	0.032	3.143	0.031	1.262E-08	7.829E-10	23.04	0.28
AWSA 1820090.9740.0313.7270.0353.533E-096.155E-1023.320.4120100.8890.0333.6990.0364.052E-096.588E-1023.540.73AWSA 2020090.6730.0212.8350.0281.827E-087.595E-1021.730.32Farm wells		2012	0.888	0.033	3.431	0.032	7.569E-09	2.039E-10	23.64	0.22
20100.8890.0333.6990.0364.032E-096.588E-1023.540.73AWSA 2020090.6730.0212.8350.0281.827E-087.595E-1021.730.32Farm wells0.230.220.220.230.220.220.230.220.250.0157.076E-087.906E-102.3.020.220.250.350.362.882E-084.759E-102.0.320.510.510.510.540.540.540.540.5	AWSA 18	2009	0.974	0.031	3.727	0.035	3.533E-09	6.155E-10	23.32	0.41
AWSA 20 Farm wells20090.6730.0212.8350.0281.827E-087.595E-1021.730.32F397520120.4660.0171.5250.0157.076E-087.906E-1023.020.22F374120120.2860.0110.5630.0062.771E-072.904E-0920.450.25F396020120.8690.0372.4580.0362.82E-084.759E-1020.320.52Moh20120.4180.0160.910.0131.451E-071.707E-0919.540.52Deep wells0.0222.196E-064.089E-0831.160.96NDW-7 50 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 150 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 150 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 200 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 250 m20120.0350.0020.0550.0012.857E-065.373E-0815.490.54NDW-7 569 m20120.0350.0020.0550.0012.759E-065.116E-0822.160.54NDW-7 569 m20120.0350.0020.0550.0012.759E-065.116E-082.2160.54 </td <td></td> <td>2010</td> <td>0.889</td> <td>0.033</td> <td>3.699</td> <td>0.036</td> <td>4.052E-09</td> <td>6.588E-10</td> <td>23.54</td> <td>0.73</td>		2010	0.889	0.033	3.699	0.036	4.052E-09	6.588E-10	23.54	0.73
Farm wellsF397520120.4660.0171.5250.0157.076E-087.906E-1023.020.22F374120120.2860.0110.5630.0062.771E-072.904E-0920.450.25F396020120.8690.0372.4580.0362.882E-084.759E-1020.320.52Moh20120.4180.0160.9210.0131.451E-071.707E-0919.540.37Deep wells </td <td>AWSA 20</td> <td>2009</td> <td>0.673</td> <td>0.021</td> <td>2.835</td> <td>0.028</td> <td>1.827E-08</td> <td>7.595E-10</td> <td>21.73</td> <td>0.32</td>	AWSA 20	2009	0.673	0.021	2.835	0.028	1.827E-08	7.595E-10	21.73	0.32
F397520120.4660.0171.5250.0157.076E-087.906E-1023.020.22F374120120.2860.0110.5630.0062.771E-072.904E-0920.450.25F396020120.8690.0372.4580.0362.882E-084.759E-1020.320.52Moh20120.4180.0160.9210.0131.451E-071.707E-0919.540.37Deep wells0.0222.196E-064.089E-0831.160.96NDW-7 50 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 50 m20120.1960.0090.2940.0085.716E-071.252E-0820.490.69NDW-7 100 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 200 m20120.1310.100.1940.0059.400E-072.004E-0819.820.80NDW-7 250 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 500 m20120.0350.0020.0550.0012.857E-065.373E-0816.970.51NDW-7 300 m20120.0350.0020.0550.0012.857E-065.373E-0816.970.51NDW-7 544 m20120.0420.0020.0550.0012.759E-065.373E-0816.970.51 <td>Farm wells</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	Farm wells									
F374120120.2860.0110.5630.0062.771E-072.904E-0920.450.25F396020120.8690.0372.4580.0362.882E-084.759E-1020.320.52Moh20120.4180.0160.9210.0131.451E-071.707E-0919.540.37Deep wells </td <td>F3975</td> <td>2012</td> <td>0.466</td> <td>0.017</td> <td>1.525</td> <td>0.015</td> <td>7.076E-08</td> <td>7.906E-10</td> <td>23.02</td> <td>0.22</td>	F3975	2012	0.466	0.017	1.525	0.015	7.076E-08	7.906E-10	23.02	0.22
F396020120.8690.0372.4580.0362.882E-084.759E-1020.320.52Moh20120.4180.0160.9210.0131.451E-071.707E-0919.540.37Deep wellsNDW-5 684 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 50 m20120.2280.0100.3880.0094.211E-078.548E-0920.270.64NDW-7 100 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 150 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 200 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 250 m20120.0320.0020.0520.0012.857E-065.373E-0815.480.44NDW-7 300 m20120.0320.0020.0520.0012.857E-065.373E-0816.970.51NDW-7 54 m20120.0350.0020.0520.0012.857E-065.373E-0816.970.51NDW-7 569 m20120.0350.0020.0550.0012.857E-065.373E-0816.970.51Northern wells <th< td=""><td>F3741</td><td>2012</td><td>0.286</td><td>0.011</td><td>0.563</td><td>0.006</td><td>2.771E-07</td><td>2.904E-09</td><td>20.45</td><td>0.25</td></th<>	F3741	2012	0.286	0.011	0.563	0.006	2.771E-07	2.904E-09	20.45	0.25
Moh20120.4180.0160.9210.0131.451E-071.707E-0919.540.37Deep wellsNDW-5 684 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 50 m20120.2280.0100.3880.0094.211E-078.548E-0920.270.64NDW-7 100 m20120.1960.0090.2940.0085.716E-071.252E-0820.020.64NDW-7 150 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 200 m20120.0350.0080.1400.0041.293E-062.786E-0819.030.76NDW-7 250 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 300 m20120.0320.0020.0520.0012.759E-065.373E-0815.480.44NDW-7 544 m20120.0420.0020.0550.0012.759E-065.116E-0822.160.51Northern wells0.0313.4940.0336.428E-096.443E-1023.740.21F138120091.0140.0323.7910.0362.086E-096.222E-1026.060.22KM14020090.9790.0313.6360.0343.269E-096.127E-1030.080.23	F3960	2012	0.869	0.037	2.458	0.036	2.882E-08	4.759E-10	20.32	0.52
Deep wellsNDW-5 684 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 50 m20120.2280.0100.3880.0094.211E-078.548E-0920.270.64NDW-7 100 m20120.1760.0090.2940.0085.716E-071.252E-0820.090.69NDW-7 150 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 200 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 250 m20120.0850.0080.1400.0041.293E-062.786E-0819.030.76NDW-7 300 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 300 m20120.0420.0020.0520.0012.857E-065.373E-0816.970.51NDW-7 544 m20120.0350.0020.0550.0012.857E-065.116E-0822.160.51Northern wellsMkeifteh 220091.0170.0313.4940.0336.428E-096.443E-1023.740.21F138120091.0140.0323.7910.0362.086E-096.222E-1026.060.22KM14020090.9790.0313.6360.0343.269E-096.127E-1030.080.23	Moh	2012	0.418	0.016	0.921	0.013	1.451E-07	1.707E-09	19.54	0.37
NDW-5 684 m20120.7210.0320.0630.0022.196E-064.089E-0831.160.96NDW-7 50 m20120.2280.0100.3880.0094.211E-078.548E-0920.270.64NDW-7 100 m20120.1960.0090.2940.0085.716E-071.252E-0820.490.69NDW-7 100 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 200 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 250 m20120.0850.0080.1400.0041.293E-062.786E-0819.030.76NDW-7 300 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 544 m20120.0420.0020.0550.0012.857E-065.373E-0816.970.51NDW-7 569 m20120.0350.0020.0550.0012.857E-065.116E-0822.160.54Northern wellsVVVVVV0.210.230.210.230.210.230.240.02KM14020091.0170.0313.4940.0336.428E-096.443E-1023.740.21F138120091.0140.0323.7910.0362.086E-096.222E-1026.060.22KM14020090.9790.0313.6360.034 </td <td>Deep wells</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	Deep wells									
NDW-7 50 m20120.2280.0100.3880.0094.211E-078.548E-0920.270.64NDW-7 100 m20120.1960.0090.2940.0085.716E-071.252E-0820.490.69NDW-7 100 m20120.1770.0140.2480.0066.826E-071.306E-0820.020.64NDW-7 200 m20120.1310.0100.1940.0059.400E-072.004E-0819.820.80NDW-7 250 m20120.0850.0080.1400.0041.293E-062.786E-0819.030.76NDW-7 300 m20120.0370.0040.0570.0023.029E-066.875E-0815.480.44NDW-7 544 m20120.0420.0020.0550.0012.857E-065.373E-0816.970.51Nothern wellsNottferh wellsF138120091.0170.0313.4940.0362.086E-096.222E-1026.060.22KM14020090.9790.0313.6360.0343.269E-096.127E-1030.080.23	NDW-5 684 m	2012	0.721	0.032	0.063	0.002	2.196E-06	4.089E-08	31.16	0.96
NDW-7 100 m         2012         0.196         0.009         0.294         0.008         5.716E-07         1.252E-08         20.49         0.69           NDW-7 150 m         2012         0.177         0.014         0.248         0.006         6.826E-07         1.306E-08         20.02         0.64           NDW-7 200 m         2012         0.131         0.010         0.194         0.005         9.400E-07         2.004E-08         19.82         0.80           NDW-7 250 m         2012         0.085         0.008         0.140         0.004         1.293E-06         2.786E-08         19.03         0.76           NDW-7 300 m         2012         0.037         0.004         0.057         0.002         3.029E-06         6.875E-08         15.48         0.44           NDW-7 544 m         2012         0.035         0.002         0.055         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 50 m	2012	0.228	0.010	0.388	0.009	4.211E-07	8.548E-09	20.27	0.64
NDW-7         150 m         2012         0.177         0.014         0.248         0.006         6.826E-07         1.306E-08         20.02         0.64           NDW-7 200 m         2012         0.131         0.010         0.194         0.005         9.400E-07         2.004E-08         19.82         0.80           NDW-7 250 m         2012         0.085         0.008         0.140         0.004         1.293E-06         2.786E-08         19.03         0.76           NDW-7 300 m         2012         0.037         0.004         0.057         0.002         3.029E-06         6.875E-08         15.48         0.44           NDW-7 544 m         2012         0.042         0.002         0.055         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 100 m	2012	0.196	0.009	0.294	0.008	5.716E-07	1.252E-08	20.49	0.69
NDW-7 200 m         2012         0.131         0.010         0.194         0.005         9.400E-07         2.004E-08         19.82         0.80           NDW-7 250 m         2012         0.085         0.008         0.140         0.004         1.293E-06         2.786E-08         19.03         0.76           NDW-7 300 m         2012         0.037         0.004         0.057         0.002         3.029E-06         6.875E-08         15.48         0.44           NDW-7 544 m         2012         0.032         0.002         0.052         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 150 m	2012	0.177	0.014	0.248	0.006	6.826E-07	1.306E-08	20.02	0.64
NDW-7         250 m         2012         0.085         0.008         0.140         0.004         1.293E-06         2.786E-08         19.03         0.76           NDW-7 300 m         2012         0.037         0.004         0.057         0.002         3.029E-06         6.875E-08         15.48         0.44           NDW-7 544 m         2012         0.042         0.002         0.052         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 200 m	2012	0.131	0.010	0.194	0.005	9.400E-07	2.004E-08	19.82	0.80
NDW-7 300 m         2012         0.037         0.004         0.057         0.002         3.029E-06         6.875E-08         15.48         0.44           NDW-7 544 m         2012         0.042         0.002         0.052         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 250 m	2012	0.085	0.008	0.140	0.004	1.293E-06	2.786E-08	19.03	0.76
NDW-7 544 m         2012         0.042         0.002         0.052         0.001         2.857E-06         5.373E-08         16.97         0.51           NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells	NDW-7 300 m	2012	0.037	0.004	0.057	0.002	3.029E-06	6.875E-08	15.48	0.44
NDW-7 569 m         2012         0.035         0.002         0.055         0.001         2.759E-06         5.116E-08         22.16         0.54           Northern wells         Mkeifteh 2         2009         1.017         0.031         3.494         0.033         6.428E-09         6.443E-10         23.74         0.21           F1381         2009         1.014         0.032         3.791         0.036         2.086E-09         6.222E-10         26.06         0.22           KM140         2009         0.979         0.031         3.636         0.034         3.269E-09         6.127E-10         30.08         0.23	NDW-7 544 m	2012	0.042	0.002	0.052	0.001	2.857E-06	5.373E-08	16.97	0.51
Northern wells         Mkeifteh 2         2009         1.017         0.031         3.494         0.033         6.428E-09         6.443E-10         23.74         0.21           F1381         2009         1.014         0.032         3.791         0.036         2.086E-09         6.222E-10         26.06         0.22           KM140         2009         0.979         0.031         3.636         0.034         3.269E-09         6.127E-10         30.08         0.23	NDW-7 569 m	2012	0.035	0.002	0.055	0.001	2.759E-06	5.116E-08	22.16	0.54
Mkeifteh 2         2009         1.017         0.031         3.494         0.033         6.428E-09         6.443E-10         23.74         0.21           F1381         2009         1.014         0.032         3.791         0.036         2.086E-09         6.222E-10         26.06         0.22           KM140         2009         0.979         0.031         3.636         0.034         3.269E-09         6.127E-10         30.08         0.23	Northern wells									
F1381         2009         1.014         0.032         3.791         0.036         2.086E-09         6.222E-10         26.06         0.22           KM140         2009         0.979         0.031         3.636         0.034         3.269E-09         6.127E-10         30.08         0.23	Mkeifteh 2	2009	1.017	0.031	3.494	0.033	6.428E-09	6.443E-10	23.74	0.21
KM140 2009 0.979 0.031 3.636 0.034 3.269E-09 6.127E-10 30.08 0.23	F1381	2009	1.014	0.032	3.791	0.036	2.086E-09	6.222E-10	26.06	0.22
	KM140	2009	0.979	0.031	3.636	0.034	3.269E-09	6.127E-10	30.08	0.23

helium, indicating that, under a normal geothermal gradient of 30 K/km, the average abstraction depth of cluster II, III and IV water is about 100 m deeper than that of cluster I water, i. e. they are expected to abstract older water. The low  $O_2$  content of these wells supports the assumption of old water affecting cluster II–IV wells.

The pH values of the year 2010 and 2012 are shown in Fig. 5c. The data of the two years form separate branches, as the 2012 pH values are consistently higher. This offset is most probably owed to bad calibration of the analysis device; a change due to the transient conditions in the system is unlikely to cause such a uniform shift. However, not the absolute pH values, but the differences between the clusters matter in this study. When each sampling year is considered separately, the same feature can be identified: those wells with pronounced <sup>4</sup>He content have a lower pH compared to the wells considered as baseline water (cluster I). This observation indicates that the water affecting the saline wells (cluster III and IV) originates from a different geochemical environment. The basalt part of the shallow aquifer is made up of alkaline magmas (Boom, 1968), suggesting that the cluster I wells with a comparatively high pH have a stronger influence of water from the basaltic, i.e. shallower regime of the upper aquifer than the other wells.

The major ion composition of the samples collected during the 2012 field trip is displayed in the Piper plot in Fig. 6 and listed in Table 2. In addition to the color code used for the AWSA well

clusters the shallow farm wells are given in green, the middle aquifer wells NDW-5 in purple and NDW-7 in different blue tones according to sampling depth (lightest blue represents the 50 m sample).

In the cation triangle the farm wells around the *Sabkha* fall into two distinct groups. All AWSA wells cluster close to each other and between the two groups of farm wells. Compared to the freshwater wells of cluster I and II, the salty cluster III wells locate slightly more towards the group in the Na/K water type corner, while AWSA 15 (cluster IV) is shifted towards the other group of farm wells. This may indicate that all salty AWSA wells are influenced by the saline water body in the central playa, but by different water types present there. The samples from the NDW-7 borehole obviously display a trend, where the deeper samples exhibit a stronger Na/K imprint.

The picture is quite different when the anions are regarded. The AWSA wells scatter widely and the salty wells are clearly shifted from the unaffected wells towards chloride type water and the farm wells, which again indicates an influence of shallow salt water from the central part of the oasis. The farm wells, being much closer together regarding the anions, form again two groups, but their members are different from the groups in the cation triangle. AWSA 15 plays a special role because its sulfate content cannot be explained by admixing of any of the tested farm well waters to either cluster I, II or III type water. All NDW-7 samples plot more or less identical in the anion triangle and are dominated by chloride. The water in NDW-5 is obviously different from all other water types.

#### 5.3. Stable isotopes, carbon isotopes and radon

The stable isotope data, listed in Table 2S (Supporting Material), are displayed in the  $\delta^2 H - \delta^{18}O$  plot in Fig. 7 alongside the local Jordanian meteoric water line (JMWL, Bajjali, 2012) and the global meteoric water line (GMWL, Craig, 1961; Rozanski et al., 1993). Additionally, the rainwater compositions in the Azraq Oasis ( $\delta^{18}O = -5.16\%$ ,  $\delta^2 H = -24.56\%$  (Bajjali, 2012)) and in Suweida at the Syrian part of Jabal ad-Druze ( $\delta^{18}O = -6.87\%$ ,  $\delta^2 H = -32.45\%$  (IAEA/WMO, 2014)) are shown; the latter represents the isotopic rainwater composition in the recharge area of the shallow aquifer in the Azraq Basin.

All sampled waters are shifted from the JMWL towards more enriched  $\delta^{18}$ O values, indicating more or less strong influence of evaporation after the rainwater reached the land surface. Furthermore, the stable isotope data of all wells are very different from local precipitation in Azraq Town, revealing that local precipitation is negligible and all shallow water types present in Azraq originate from the mountain ad-Druze (compare the stable isotope data from Suweida, located on this mountain). Notably, water from the shallow farm wells in the central mud pan has a very different stable isotope composition than local precipitation and is obviously most affected by evaporation. This signals that they discharge water that was transported from the mountain towards the *Sabkha* by surface runoff and recharged locally under significant evaporation of the former pools.

Two of the northern baseline wells (F1381 and especially KM140, grey triangles) have very similar isotopic compositions to the AWSA wells which supports the assumption of this water being the original groundwater flowing to the center of the Azraq Basin.



**Fig. 6.** Piper diagram of the 2012 samples. Samples from different depths of the middle aquifer well NDW-7 are shown in blue shades, starting with light blue at 50 m depth down to 250 m, the darkest blue. Mainly the anion triangle shows that AWSA 15 can hardly be explained by a mixture of *Sabkha* water and water belonging to cluster I, II or III. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The AWSA wells cluster quite close to each other and are shown in more detail in the inset. The wells containing elevated terrigenic helium (cluster II and III, yellow and orange) are slightly depleted in  $\delta^{18}$ O and deuterium compared to the unaffected wells (cluster I, red), which again hints at different water types abstracted by the well field. However, the well containing most salt, AWSA 15 (cluster IV, brown), does not fit into this picture and plots close to cluster I.

The samples from the NDW-7 borehole fit almost perfectly to the GMWL. The trend with depth seen in the cations is also clearly visible in the stable isotopes. NDW-5 penetrates different geologic units because it is situated beyond the Fuluq Fault and has a different isotopic composition than NDW-7.

Although only few wells were tested for  $\delta^{13}$ C, radiocarbon and radon activities, slight support of different water sources of the brackish and the non-affected wells is given by these tracers (see Table 2S (Supporting Material)).  $\delta^{13}$ C values of the brackish wells (clusters III and IV, i. e. AWSA 12, 13 and 15) are less depleted than the freshwater wells of cluster I and II (AWSA 4, 5, 11 and 18). A similar picture is found in the radon activities, where the cluster I well AWSA 16 is characterized by much lower radon content than AWSA 13 and 15 of cluster III and IV, respectively. Although not much statistical consolidation is available, both  $\delta^{13}$ C and radon indicate that the water types of the given clusters originate from different geochemical environments.

Radiocarbon clearly classifies AWSA 4, 5 and 12 (cluster II and III) as old water with almost no <sup>14</sup>C present, whereas AWSA 15 is obviously much younger, or at least incorporates some recently infiltrated water. This finding is in accord with Al-Momani et al. (2006) who found elevated <sup>14</sup>C activities only in AWSA 11 (23 pmC, cluster I) and AWSA 15 (38 pmC).

Summarizing, the stable and radioactive isotope analyses hint at not less than two different groundwater reservoirs contributing to the AWSA discharge.

#### 5.4. Noble gases

The analysis of noble gases in groundwater of the Azraq Oasis reveals further insight into the origins of the water masses contributing to the well field's discharge. The <sup>3</sup>He/<sup>4</sup>He and Ne/<sup>4</sup>He ratios as well as the calculated noble gas temperatures (NGTs) and amounts of terrigenic <sup>4</sup>He are listed in Table 1. The data of all measured noble gas isotopes, which are employed for the determination of NGTs and terrigenic <sup>4</sup>He, along with the fitting results, are given in Tables 4S and 5S (Supporting Material).

The sample of AWSA 11 exhibits very high noble gas contents with a typical excess air pattern, i. e. the relative excess is highest in neon and lowest in xenon. Most likely the pump drew soil air because bubble formation during sampling could not be eliminated. Some other samples have noble gas concentrations below the equilibrium concentration, which indicates degassing (KM140 and NDW-5).

The farm wells mostly have NGTs around 20°C, suggesting local recharge in the *Sabkha* from possibly slightly warmed, shallow pools, as the mean annual air temperature in Azraq Town is 17.5°C. NGTs of cluster II and III wells are significantly higher, mostly between 25 and 27°C, while cluster I and IV wells have NGTs between 22 and 24°C. The generally high NGTs found in the AWSA wells reflect the deep unsaturated zone at Jabal ad-Druze (more than 400 m in northern Jordan (Margane et al., 2002)), where the ambient temperature at the groundwater table (where equilibration between groundwater and soil air determines the equilibrium component of the noble gases) is considerably higher than the mean annual air temperature at the surface due to the local geothermal gradient. AWSA 11 shows an unrealistic high NGT of 39°C which is most likely owed to the large amount of excess air

#### Table 2

Water chemistry data. The ion balance is calculated by ( $\sum$ Cations –  $\sum$ Anions)/ $\sum$ Anions. Some more constituents than listed here were measured and are included in the ion balance calculation (see Table 3S (Supporting Material)).

Well	Ca meq/L	Mg meq/L	K meq/L	Na meq/L	Cl meq/L	SO <sub>4</sub> meq/L	HCO3 meq/L	Ion balance %	Salinity g/kg
AWSA well field									
AWSA 3	2.03	1.70	0.25	9.20	9.59	1.42	2.16	-0.53	0.83
AWSA 4	0.93	0.73	0.22	3.45	2.45	0.84	2.28	-5.53	0.39
AWSA 5	0.90	0.72	0.13	2.98	1.91	0.73	2.11	-1.62	0.34
AWSA 6	0.80	0.61	0.10	2.26	1.12	0.56	2.16	-3.57	0.28
AWSA 13	2.05	1.79	0.46	8.54	8.41	2.00	2.16	1.94	0.81
AWSA 15	7.24	7.57	0.57	17.75	20.68	10.06	2.05	-0.10	2.04
AWSA 16	0.80	0.91	0.13	3.49	2.17	1.62	1.78	-7.51	0.39
Farm wells									
F3731	26.20	17.94	0.38	46.76	71.46	15.33	7.64	-3.29	5.58
F3975	8.81	17.40	4.39	171.81	164.11	34.42	5.02	-0.57	12.31
F3741	10.78	19.26	6.39	138.54	161.36	9.72	3.46	0.25	10.30
F3960	18.76	18.76	1.01	29.84	65.00	1.63	1.32	0.79	3.81
Moh	29.19	54.31	11.34	486.30	527.48	48.44	2.85	0.40	34.12
Deep wells									
NDW-5 250 m	1.06	3.40	0.44	5.70	5.94	3.84	1.13	-3.24	0.68
NDW-7 50 m	8.78	9.87	2.21	48.89	64.73	7.62	0.33	-3.92	4.20
NDW-7 100 m	8.04	8.41	2.14	49.93	63.97	7.30	0.33	-4.23	4.14
NDW-7 150 m	7.47	7.13	2.36	53.15	62.56	6.95	0.33	0.42	4.13
NDW-7 200 m	6.81	6.30	2.50	57.76	66.82	7.12	0.37	-1.20	4.38
NDW-7 250 m	7.14	6.83	2.41	56.72	66.06	7.19	0.33	-0.60	4.34



Fig. 7. Stable isotope plot of the sampled wells in the Azraq basin together with the local Jordan meteoric water line (JMWL) and the global meteoric water line (GMWL). All wells show signals of evaporation, most notable the shallow farm wells. The AWSA well field is zoomed in the inset. The same clusters delineated from the terrigenic He-salinity relation can be distinguished. Samples from different depths of NDW-7 scatter along the GMWL and NDW-5 plots a little bit off the GMWL. The isotope composition of precipitation at Azraq town and at Jabal ad-Druze (Suweida) is added for comparison.

and consequent fitting problems. NGTs obtained from several depths of the deep well NDW-7 range from 21°C in the uppermost 250 m, cooler temperatures of around 16°C at 300 and 544 m and again 22°C at 569 m. The high noble gas temperature calculated for NDW-5 of 31°C may reflect a large unsaturated zone in the area or fitting difficulties due to the degassed condition of this water.

The influence of the three helium reservoirs on Earth – atmosphere, mantle and crust – on the sampled water is visualized in the  ${}^{3}$ He/ ${}^{4}$ He–Ne/ ${}^{4}$ He isotope plot in Fig. 8. The reservoirs are illustrated in the plot as endmembers and labeled AEW (air equilibrated water), Crust and Mantle (outside the plot range). The Ne concentration is included to account for additional atmospheric He from excess air. In this type of plot, recently formed groundwater locates close to the atmospheric endmember. In a pure crustal

environment it evolves along the dashed mixing line towards the crustal endmember due to predominant accumulation of <sup>4</sup>He in the water. Samples that plot above this mixing line may contain either tritiogenic <sup>3</sup>He, which is typically the case for young waters near the AEW endmember, or mantle He, in which case the Ne/<sup>4</sup>He ratio is reduced but the <sup>3</sup>He/<sup>4</sup>He ratio is higher than indicated by the radiogenic mixing line. The distinction between these two sources of elevated <sup>3</sup>He is not always clear-cut, but measured <sup>3</sup>H concentrations and inferred <sup>3</sup>H–<sup>3</sup>He ages can put constraints on the tritiogenic <sup>3</sup>He component.

Tritium values are only available for the AWSA well field samples of 2010 (Table 3). In view of the analytical uncertainty of about 1 TU, the detection limit on a  $2\sigma$ -level is considered to be 2 TU, which is exceeded only by the AWSA 18 sample. Wells 5, 11, 15, and 16 have

tritium concentrations above their  $1\sigma$ -error. Dating by the  ${}^{3}H$ - ${}^{3}He$  method will therefore yield highly uncertain ages, but was nevertheless undertaken to test whether excess  ${}^{3}He$  could be of tritiogenic origin.

The so-called  ${}^{3}\text{H}-{}^{3}\text{He}$  age,  $\tau$ , is calculated after Schlosser et al. (1988) by

$$\tau = \frac{T_{1/2}}{\ln 2} \cdot \ln\left(1 + \frac{[^3\text{He}]}{[^3\text{H}]}\right),\tag{1}$$

where  $T_{1/2} = 12.32$  years is the half-life of tritium and the brackets symbolize the concentration of tritiogenic <sup>3</sup>He and <sup>3</sup>H, respectively. The maximum amount of tritiogenic <sup>3</sup>He is given by the total nonatmoshperic <sup>3</sup>He, i. e. the difference between the measured <sup>3</sup>He and the modeled atmospheric <sup>3</sup>He concentrations. This amount of <sup>3</sup>He is listed in Table 3 along with the resulting maximum <sup>3</sup>H–<sup>3</sup>He ages. These ages can be used to reconstruct the year of recharge, and the initial tritium concentration at that time is given by the sum of tritium and tritiogenic <sup>3</sup>He.

The basic idea of this approach is that this initial tritium should match the meteoric tritium content at the time of recharge calculated from the age, if no mixing occurred and all assumptions were correct. The meteoric tritium activity in precipitation since 1961 is shown in Fig. 9 for Jordan (red, combined from several GNIP stations around Amman) and, due to sparse data from the country of interest, also from the GNIP station in Bet Dagan close to Tel Aviv, Israel, in blue (all data from the Global Network of Isotopes in Precipitation – GNIP (IAEA/WMO, 2014)).

Three of the ten 2010 samples do not vield <sup>3</sup>H-<sup>3</sup>He ages. AWSA 3 and 4 because no tritium was detected and AWSA 18 due to a nonexistent tritiogenic <sup>3</sup>He content. For all other samples, the calculated initial tritium content at the time of recharge is plotted in Fig. 9. The dashed line in Fig. 9 indicates the decay-corrected initial tritium content of a hypothetical sample at the detection limit of 2 TU in 2010. This corresponds to the maximum initial tritium content compatible with the low tritium results of the samples. The intersection of this line with the input curve at the onset of the bomb peak around 1960 shows that the maximum initial tritium content is below 40 TU. Therefore, the higher amounts of nonatmospheric <sup>3</sup>He found in samples AWSA 3, 11, 12, and 13 (Table 3) cannot be solely of tritiogenic origin. Indeed, the calculated years of recharge of AWSA 11, 12 and 13 are before the bomb peak in the 1960s, thus the initial tritium content should be at the natural background of a few TU.

The overall highest non-atmospheric <sup>3</sup>He content (91 TU) of AWSA 3 is furthermore incompatible with the fact that no tritium activity was detected in this sample. An initially high tritium concentration leading to such an amount of tritiogenic <sup>3</sup>He must remain clearly measurable in the sample. So at least for the cluster III samples AWSA 3, 12, and 13, which have no tritium within  $1\sigma$ -errors and are not affected by sampling problems, we can unequivocally conclude that their excess <sup>3</sup>He cannot be explained by tritium decay alone. In fact, given the vanishing tritium content, it is unlikely that tritiogenic <sup>3</sup>He is an important contribution.

More difficult to interpret are the samples of clusters II and IV. AWSA 5 and 15 might have some tritium, thus  ${}^{3}H-{}^{3}He$  ages can be calculated. The extrapolated tritium concentrations in the year of recharge of these wells lie below the input function (see Fig. 9), which could be explained by mixing with tritium-free older water. It is, therefore, possible that these two wells contain a component of water from around 1970, whose tritium has largely decayed to produce the observed  ${}^{3}He$  excess. This explanation, however, is less probable for the other cluster II wells AWSA 4 and 6, for which no meaningful ages can be calculated due to their near-zero measured tritium content. In particular the substantial non-atmospheric  ${}^{3}He$  content of about 14 TU of AWSA 4 should, if tritiogenic, leave a remaining tritium concentration of at least 1 TU, which is barely compatible with the measured value of  $0 \pm 0.9$  TU. More precise tritium measurements would be needed to decide this issue. In view of the clear result that the excess <sup>3</sup>He of the cluster III wells is mainly not tritiogenic and the position of cluster II and IV wells in Fig. 9, it appears probable that these wells are also influenced by another source of <sup>3</sup>He.

Another possible cause of <sup>3</sup>He concentrations exceeding typical values present in a crustal environment is the occurrence of unusually Li-rich minerals, because after neutron capture <sup>6</sup>Li decays to tritium, which eventually produces <sup>3</sup>He. No extraordinary lithium deposit, however, is reported for the Azraq Basin. In general, high lithium contents are typically found in granitic rock types (James and Palmer, 2000), but the shallow aquifer rock is separated from the bedrock by a several kilometer thick sequence of sedimentary rock. Li-rich minerals can therefore not account for the helium isotope pattern found in the saline wells.

Concluding, it is very unlikely that the elevated <sup>3</sup>He contents of the cluster II, III and IV wells originate from decayed bomb tritium or Li-rich minerals alone. Ascending mantle fluids that influence the shallow groundwater are therefore the most probable explanation for the elevated <sup>3</sup>He/<sup>4</sup>He–Ne/<sup>4</sup>He pattern found in Azraq. All AWSA wells belonging to clusters II, III and IV fall in this category, with cluster III (AWSA 3, 12 and 13) having the most pronounced and unequivocal mantle signal. Interestingly, the same groups deduced from Fig. 5a can be recognized in Fig. 8 again, signaling that the distinct clusters are also differently influenced by mantle helium. AWSA 15 has a small mantle component, comparable to the samples of cluster II.

The farm wells seem to exhibit a slight mantle component, too, but a tritiogenic contribution can not be excluded in their case. They vary in their <sup>4</sup>He content, indicating different groundwater ages at shallow depths. Samples from different depths of NDW-7 show a trend where shallower groundwater contains some mantle helium, but the deep samples (more than 300 m below surface) plot nearly identical and are almost purely crustal.

NDW-5, situated east of the Fuluq Fault, has a strong mantle imprint, as it contains a lot <sup>4</sup>He, while at the same time having a <sup>3</sup>He/<sup>4</sup>He ratio way above the crustal endmember ratio. The slightly degassed state of NDW-5 does not alter the <sup>3</sup>He/<sup>4</sup>He ratio significantly, because the solubilities of the two isotopes are very similar (Weiss, 1970). Also the 15% difference in diffusivities of <sup>3</sup>He and <sup>4</sup>He (Jähne et al., 1987) cannot explain the high enrichment of <sup>3</sup>He. Hence, NDW-5 undoubtedly proves that generally mantle helium is present in groundwater in the vicinity of the Azraq Oasis.

## 6. Discussion

#### 6.1. Sampling a standing water column

Four of the studied wells had no pump installed and where sampled without prior purging using a bailer and diffusion samplers. However, open boreholes facilitate vertical exchange of water and tracers (by diffusion or advection) and it is questionable if the samples represent the actual groundwater in the well and especially the groundwater at a specific depth. Indeed, the samples collected from different depths of NDW-7 exhibit a trend in all observed tracers. Especially the systematics of samples from the top 300 m of NDW-7 (where the borehole is not screened) argue for a vertical transport within the water column.

On the other hand, sampling different depths of NDW-7 offers the possibility to assess a potential effect of vertical exchange on the deepest, and therefore most interesting samples. The systematic trend in the cations (Fig. 6) and in the stable isotopes (Fig. 7) is



Fig. 8. The <sup>3</sup>He/<sup>4</sup>He vs. Ne/<sup>4</sup>He plot of the Azraq samples. The three endmembers are shown, AEW represents atmospheric composition in water after equilibration. Again, the four clusters are found. Especially the saline AWSA wells of cluster III exhibit distinct helium isotope signals typical for mantle influence and reveal an intrusion of deep groundwater into the shallow aquifer in Azraq.

#### Table 3

Dating of the 2010 AWSA samples with the <sup>3</sup>H–<sup>3</sup>He method reveals that tritiogenic production is unlikely to solely account for the detected non-atmospheric <sup>3</sup>He component. A detailed discussion is found in the text.

Well	<sup>3</sup> H TU	$\Delta^3$ H TU	non-atm. <sup>3</sup> He TU	$\Delta$ non-atm. <sup>3</sup> He TU	<sup>3</sup> H— <sup>3</sup> He age years	$\Delta^3 H^{-3} He$ age years	year of recharge	Calculated <sup>3</sup> H content at recharge
AWSA 3	0.00	0.94	91.00	4.15	_	_	_	_
AWSA 4	0.00	0.87	13.96	1.30	_	-	-	_
AWSA 5	1.43	0.97	8.20	1.01	33.89	10.43	1977	9.63
AWSA 6	0.20	0.87	3.32	0.94	50.99	73.08	1960	3.52
AWSA 11	0.94	0.90	54.50	19.58	72.47	17.87	1938	55.44
AWSA 12	0.53	0.96	63.07	3.02	85.09	31.94	1926	63.60
AWSA 13	0.62	0.97	38.84	2.20	73.82	27.39	1937	39.46
AWSA 15	1.89	0.97	15.41	1.25	39.36	8.23	1971	17.30
AWSA 16	1.19	0.96	0.37	0.81	4.82	9.85	2006	1.56
AWSA 18	2.05	0.98	-0.16	-	-	-	-	-



**Fig. 9.** Tritium activity in precipitation in Jordan (red) and Israel (blue). The dashed line represents the extrapolated activity of a hypothetical sample having a tritium activity of 2 TU in 2010. The calculated tritium contents at the time of recharge of the AWSA samples are plotted. AWSA 11, 12 and 13 are dated before the rise of the bomb peak. Their high <sup>3</sup>He content cannot be explained by the decay of tritium alone. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

present only in the top 200 m, that of the noble gas isotope ratios only in the top 250 m (Fig. 8). Likewise the absolute <sup>3</sup>He and <sup>4</sup>He concentrations of the 300, 544 and 569 m samples of NDW-7 are very similar (compare Table 4S (Supporting Material)). For these reasons we assume that the noble gas composition from below 300 m and the 250 m data of the other tracers do, indeed, represent the water characteristics of the middle aquifer at NDW-7.

Because both middle aquifer wells are constructed very similarly, it is justifiable to transfer the reasoning above to NDW-5, where the 684 m deep noble gas sample and the 250 m bailer sample represent the conditions in the middle aquifer east of the Fuluq Fault.

The two farming wells without pump (F3960 and Moh), however, are quite shallow and the samples are doubtlessly affected by vertical disturbance. But, because of the shallowness, the question of which depth they represent does not arise at all; therefore, the traditional tracers can be trusted. Noble gases, however, assumingly exchange with the air above the water column to a certain degree and should therefore be interpreted with caution. If diffusion would influence the noble gas concentration in the borehole, the measured  ${}^{3}$ He/ ${}^{4}$ He ratio, however, should be lower than the actual He isotope ratio because the slightly higher diffusivity of  ${}^{3}$ He (Jähne et al., 1987) would cause a depletion of  ${}^{3}$ He.

#### 6.2. Discussion of the previously published salinization scenarios

Following, all three salinization scenarios investigated by Al-Momani et al. (2006) are reviewed in the context of the new data.

The first scenario, the backflow from the *Sabkha* to the AWSA well field in consequence of a reversed hydraulic head gradient, was already rejected by these authors. The helium isotope pattern found in the shallow farm wells supports the rejection of this salinization scheme, because admixing of water from the shallow and saline groundwater body in the *Sabkha* cannot explain the high <sup>3</sup>He and <sup>4</sup>He content of the cluster III wells.

The second proposed scenario of Al-Momani et al. (2006), the development of an altered mineral dissolution pattern, resulting from changed groundwater flow paths in consequence of the intense groundwater abstraction in Azraq, could only explain the observed helium isotope data if minerals affecting the salty AWSA wells would contain high amounts of lithium, which would cause an untypically high <sup>3</sup>He/<sup>4</sup>He ratio of the locally produced radiogenic helium. As stated above, unusually high Li concentration can be ruled out and this scenario, therefore, has to be rejected as well.

The third scenario, the upward leakage from the middle aquifer into the shallow one, – which could not be refuted in the Al-Momani et al. (2006) study – is disproved by the noble gases, too. The absolute amount of <sup>3</sup>He in AWSA 3 and 12 is considerably higher than that found at any depth of NDW-7 and therefore cannot originate from this source. The same picture results from the <sup>3</sup>He/<sup>4</sup>He ratio: a mixture of middle aquifer water, having an almost crustal signature, and baseline water found in the unaffected cluster I wells, plotting close to atmospheric composition, would result in a noble gas signature falling on the radiogenic mixing line in Fig. 8, which is obviously not the case for the cluster II, III and IV wells. Hence, the noble gas composition of these wells cannot be explained by upwards leakage from middle aquifer water into the well field area.

In consequence, a new hypothesis of the hydrological circumstances is proposed in the following which can explain all findings presented above. Two aspects have to be addressed: first, how can the presence of mantle helium in the shallow aquifer be explained, while the underlying formation exhibits a crustal character? Second, why are only a few AWSA wells affected by salt and mantle He, although the well field's extension is rather small and the wells are constructed similarly? Most notably, our explanation introduces a new reservoir of brackish and mantle He influenced water, present at the very bottom of the shallow aquifer, which is responsible for the rising salinity in some AWSA wells. The proposed and in the following justified groundwater flow scheme in Azraq, deduced from noble gas data from the shallow and middle aquifers, is visualized in Fig. 10.

#### 6.3. Mantle helium distribution

Since <sup>3</sup>He arising from meteoric tritium or from <sup>6</sup>Li is unlikely to be responsible for the elevated <sup>3</sup>He/<sup>4</sup>He ratio and because the middle aquifer cannot serve as the source of the high <sup>3</sup>He content, an ascent of mantle fluids from even deeper layers is the only remaining explanation of the observed He isotope patterns within the shallow aquifer. The Azraq Oasis and its surroundings are crossed by many faults (see Fig. 4), of which some are likely to reach deep and be hydraulically conductive. Most notable is the Fuluq Fault, striking about 10 km NE of the AWSA well field in NW–SE direction. There are two reasons that lead us to regard the Fuluq Fault as the most likely source of deep groundwater and mantle He in the Azraq Oasis. First, groundwater flow in the middle aquifer is known to be in eastern to northeastern direction beneath the oasis (Margane et al., 2002), towards the Fuluq Fault. This prevents fluids ascending in the Fuluq Fault to enter the middle aquifer in direction of the AWSA well field. If one of the other main faults, situated west of NDW-7, would be the major upstream pathway, mantle helium would also be found in NDW-7. The second reason is the fact that the Fuluq Fault experienced the strongest tectonic forces of all faults in the Azraq basin over a long period of time (compare Fig. 3), rendering it in all probability a vertically conductive zone. The finding of a clear mantle signal in NDW-5, east of the Fuluq Fault, is in accord with groundwater in the middle aquifer crossing the Fuluq Fault and thereby entraining ascending mantle fluids into the middle aquifer east of the fault.

On the other hand, the presence of mantle fluids beneath the AWSA well field argues for a groundwater flow from the Fuluq Fault towards the central area within the shallow aquifer. This agrees with the groundwater flow pattern of this aquifer being generally towards the central part of the Azraq depression (Margane et al., 2002), where the discharge area is located (spring discharge under undisturbed conditions and today pumped groundwater abstraction).

Because the groundwater table in the shallow aquifer has been lowered by more than 20 m since the early 1980s, the hydrostatic pressure conditions between the shallow and deeper aquifers changed, too. This state favors advection through the Fuluq Fault from the deep parts of the aquifer system into the shallow aquifer, thereby entraining the mantle signal of the helium isotopes upwards. Other means of transport, like diffusion, are therefore thought to play only a nominal role (compare the discussion about advection vs. diffusion in Ballentine et al. (2002)).

#### 6.4. Groundwater mixing pattern in the AWSA well field

Both, the discharge temperatures and the pH values indicate that the saline wells of cluster III and IV abstract water from deeper parts of the shallow aquifer. At first glance, this is surprising as the AWSA wells are constructed very similar. Most of them are drilled to a depth of roughly 200 m into the shallow aquifer, piercing the basalt shield completely (compare the lithologic data in Table 1S (Supporting Material)). Because the boreholes are constructed without casing, water from all parts of the lithologic profile is drawn.

However, the transmissivities of the formations comprising the shallow aquifer vary widely: the hydraulic conductivity of the fractured basalt is much better than in the underlying B4/B5 formation. Hence, the basalt part of the shallow aquifer is the dominant route of fresh groundwater from the recharge area to the *Sabkha*. Mantle fluids, therefore, accumulate mainly in the deeper layers of the shallow aquifer. Moreover, the different permeabilities cause most of the discharged water from the AWSA wells to be abstracted from the basaltic part of the aquifer – as long as there is water in this layer.

As the groundwater table is lowered, the transmissivity of the basalt shield decreases because there are less permeable fractures available for water transport. This effect is enhanced as pumping creates a cone of depression around the boreholes, where the water table can locally be lowered by several meters, depending on the discharge rate and transmissivity of the surrounding rock. In consequence of the reduction of the local groundwater table, the relative share of water from the deeper part of the shallow aquifer increases.

In addition, the transmissivity reduction does not necessarily need to be uniform, it strongly depends on the individual environment of a well. If, for example, the water table falls below a well conductive fracture, the transmissivity steeply drops and the cone of depression gets deeper rather abruptly. This occurs particularly as soon as the local groundwater table falls below the basalt due to



**Fig. 10.** Sketch showing the proposed groundwater flow scheme in the Azraq Oasis. Saltwater bodies are shown in green color, the one below the AWSA well field is newly proposed in this study. Water from the deep aquifer system, loaded with mantle helium (orange arrows), ascends along the Fuluq Fault. Because groundwater flow in the middle aquifer west of the Fuluq Fault is towards it (blue arrows), NDW-7 is not affected by mantle gases, but mantle gases are transported into the aquifers east of the fault and are found in NDW-5. In the shallow aquifer the flow is in the opposite direction, towards the AWSA well field, and mantle helium containing water admixes mainly into the deep part of the shallow aquifer. Beside fresh water from the basalt layer, the saline AWSA wells increasingly abstract brackish water from the bottom of the shallow aquifer, where mantle helium containing, brackish water is present. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the lower transmissivities of the B4/5 unit.

The depth of the bottom of the basalt shield at each AWSA well (see Table 1S (Supporting Material)) determines how deep the water table has to drop to force an enhanced abstraction from deeper layers of the shallow aquifer. The base of the basalt in wells No 12, 13 (cluster III) and 15 (cluster IV) is at around 473 masl, while it is 10–30 m deeper in the cluster II wells AWSA 4, 5 and 6 as well as in AWSA 11 (cluster I). It is, therefore, clear that under otherwise equal conditions the basaltic layer is depleted earlier in the cluster III and IV wells than in the cluster I and II wells. As in 2012 the groundwater table in the (unpumped) observation well AZ-12 (on the margin of the well field, see the map in Fig. 4) was only 17 m above the basalt base at AWSA 12, 13 and 15, it is easily conceivable that the water yield from the basalt aquifer has significantly diminished since the 1980s at those locations (in 1986 the water level in AZ-12 was 17 m higher than in 2012, compare Al-Momani et al. (2006)). In consequence, a substantial amount of water is abstracted from the deeper part of the shallow aquifer system nowadays. Under the assumption that saline groundwater with a mantle imprint exists in the deep part of the shallow aquifer, the proposed scenario can explain the different salinization behavior of the AWSA wells.

However, an exception is AWSA 3, the cluster III well which exhibits the overall highest mantle helium component found in the AWSA well field. At this well the basalt base is considerably lower than at the other brackish wells. The initial transmissivity determined in AWSA 3 was among the highest of all AWSA wells (17,500 m<sup>2</sup>/day according to Ayed (1996)). But this situation may have been owed to a highly permeable fracture in the upper part of the basalt, possibly related to the nearby Al-Bayda Fault. In case this fracture is no longer available for abstraction, the cone of depression would have deepened and significantly more water from the deep part of the shallow aquifer would be abstracted nowadays. This explanation is supported by the fact that the salinity in AWSA 3 started to increase several years later than in wells No 12, 13 and 15

(compare Fig. 1). Therefore, beside the depth of the basalt base, the individual permeability profile of a well determines its salinization behavior. Yet, permeability profiles of the AWSA wells are not available, so a direct confirmation of the observed salinization processes is not possible.

The wells of cluster II (AWSA 4, 5 and 6) are not affected by rising salinity, but show a distinct terrigenic <sup>4</sup>He content as well as a presumed mantle helium influence. The base of the basalt in these wells is comparatively deep (444–464 masl). They are located near each other and in close vicinity of the Al-Bayda Fault, and so they possibly draw groundwater from a deeper reservoir connected by this fault. Their high discharge temperature and the slightly lower pH support this explanation. However, due to the different composition of their discharged water, this would mean that there is an additional water body, which is characterized by an impact of terrigenic helium but at the same time has a low mineralization.

AWSA 15 plays a unique role, as its helium-salinity pattern is different from all other wells. Because of the high mineralization in connection with its rather low terrigenic helium amount and <sup>3</sup>He/<sup>4</sup>He ratio, this well seems to feed from an additional source which is even more saline than the deep part of the shallow aquifer. Although the boundary of the saline water body in the central playa is still far away from the well field and the hydraulic head gradient drives the general groundwater flow towards the farm area (Al-Momani et al., 2006; El-Naqa, 2010), strong pumping in connection with a conductive fracture might lead to a very local flow of salt water from the center of the oasis towards AWSA 15. However, the anion composition of AWSA 15 (compare Fig. 6) shows that its high relative SO<sub>4</sub> content cannot result from Sabkha water mixing into cluster I, II or III water. Therefore, it cannot be ruled out that AWSA 15 taps an unknown additional, highly mineralized and possibly very local water source.

The wells of cluster I, i. e. AWSA 11, 16, 18 and 20, have in common that they are less deep than the other AWSA wells. AWSA 11 is the shallowest one (62 m) and penetrates the B5 unit, right

below the basalt shield, just a few meters. It is, hence, comprehensible that this well does not discharge deep water. AWSA 18 is 171 m deep and the local basalt base is most shallow of all AWSA wells (488masl); it therefore seems to be a good candidate for early salinization. Yet, it still shows no signs of it, which may be due to a well conductive fracture at the bottom of the basalt which still supplies AWSA 18 and prevents it from abstracting a detectable amount of water from the deep part of the shallow aquifer. Another possibility is that the saline regime with the terrigenic helium component is located below the depth of 171 m, but is present at ~200 m. Regarding AWSA 16 (160 m) and AWSA 20 (117 m), no lithologic information could be obtained.

The general presence of different groundwater reservoirs is supported by all other measured tracers. Stable isotopes,  $\delta^{13}$ C as well as <sup>14</sup>C and radon activities suggest the principal existence of more than one groundwater source feeding the AWSA well field. The water chemistry data indicate admixing of different water sources into the salt affected AWSA wells, too. Last but not least, the depleted dissolved oxygen contents of cluster II, III and IV samples signal older and, hence, deeper water.

Verification of the hypothesis of a brackish reservoir at the bottom of the shallow aquifer, spoiling the water quality at some points of the AWSA well field, is difficult. Information published about water in the deep part of the shallow aquifer is very scarce due to the fact that all wells in the area are open boreholes with no specific screen interval in combination with the large variety of hydraulic conductivities at different depths. The sole description of a well discharging only from the lower part of the shallow aquifer is found in Abu-Jaber et al. (1998) (unfortunately, the well's name or ID is not indicated), where a salinity of 2373 mg/L is reported, which is higher than the solute content of the cluster III and IV wells AWSA 3, 13 and 15 (compare Table 2). The water of this well is reported to be rich in magnesium, calcium and chloride, but has a low sodium concentration (though it should be noted that the ion charge balance error of 20% is very high). Because AWSA 3, 13 and 15 contain significantly more Mg and Ca compared to the other wells, these authors might indeed have sampled similar water that influences those AWSA wells.

## 7. Conclusions

A multi-tracer approach including the application of noble gas isotopes, notably <sup>3</sup>He and <sup>4</sup>He, reveals a very complex groundwater mixing scheme in the Azraq Oasis which is not accessible by traditional tracer methods alone. The presence of mantle helium in the upper aquifer, while the underlying middle aquifer is not affected by mantle gases, is a unique feature to our knowledge. Nevertheless, several questions remain unanswered.

The presented data confirms the assumption that a groundwater reservoir below the middle aquifer contributes to the discharge of the AWSA wells. However, without knowledge of the exact He isotope composition of the deep source and the amount of middle aquifer water potentially admixing to it on its way upwards, it is not possible to estimate the total water volume entering the shallow aquifer from below. This information would be an important boundary condition for prospective groundwater flow models. At least, the very different noble gas temperatures of the brackish AWSA wells and of the deep samples of NDW-7 indicate that only a rather small amount of middle aquifer water finds its way into the shallow aquifer. However, no information on the influx rate from the deep aquifer system can be determined by our data.

The origin of the salinization of some AWSA wells cannot ultimately be determined yet. Possibly the groundwater containing the mantle helium and rising through the Fuluq Fault is already brackish, be it because the source water is already brackish or the mantle impacted water is mineralized by addition of some saline middle aquifer water. However, the finding of the highest mantle signal of all sampled wells in Azraq in the deep well NDW-5, together with its rather low salinity argues against a direct relationship of salt content and mantle influence. Also the presence of cluster II water with its low salinity, yet slight mantle helium signature argues against this relationship. Most likely, the brackish water is already present in the lower part of the shallow aquifer and deep water carrying mantle fluids is merely admixed to it.

The discharge temperature of the AWSA wells gives a hint about the absolute mineralization level of the saline water body at the bottom of the shallow aquifer. The fact that groundwater containing additional helium is two to 4 K warmer than the water supposedly abstracted from the basalt suggests that the average abstraction depth of cluster II, III and IV water is about 100 m deeper than that of cluster I water. This means that the first mentioned wells already today abstract mainly groundwater from the deeper part of the shallow aquifer and therefore the salinity of the AWSA wells is not expected to rise significantly above present values. Nevertheless, an investigation targeting particularly the deeper part of the shallow aquifer in Azraq is advised to ensure the potential upper limit of future salinization of the AWSA wells. This is an important assessment of how vulnerable the prospective supply with high quality drinking water from the Azraq Oasis is.

Moreover, past estimates about the total water resources available in Jordan (MWI, 2009) do not consider the brackish regime at the bottom of the shallow aquifer in Azraq and thus presumably overestimate the available freshwater resources in the country. These assessments should be reviewed considering the presented new data. In order to shed light on the discharge rate from the deeper aquifers into the shallow one, deep drillings are recommended to complete the knowledge of the deep groundwater system in Azraq.

### Acknowledgments

We thank Paul Königer of the Federal Institute for Geosciences and Natural Resources (BGR) in Hannover, Germany, for the analysis of the 2012 stable isotopes samples. The project was financially supported by the Federal State of Baden-Württemberg and the Heidelberg University in the framework of the Global Change & Globalization research cluster. Furthermore, we'd like to thank the editor Michael Kersten and two anonymous reviewers for their comments, who helped considerably to improve the manuscript.

### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.apgeochem.2015.12.003.

#### References

- Abdulla, F.A., Al-Khatib, M.A., Al-Ghazzawi, Z.D., 2000. Development of groundwater modeling for the Azraq basin, Jordan. Environ. Geol. 40.
- Abu-El-Sha'r, W.Y., Rihani, J.F., 2007. Application of the high performance computing techniques of parflow simulator to model groundwater flow at Azraq basin. Water Resour. Manag. 21, 409–425.
- Abu-Jaber, N.S., Ali, A.J., Al-Qudah, K., 1998. Use of solute and isotopic composition of ground water to constrain the ground water flow system of the Azraq area, Jordan. Groundwater 36, 361–365.
- Aeschbach-Hertig, W., El-Gamal, H., Wieser, M., Palcsu, L., 2008. Modeling excess air and degassing in groundwater by equilibrium partitioning with a gas phase. Water Resour. Res. 44, W08449.
- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., Kipfer, R., 1999. Interpretation of dissolved atmospheric noble gases in natural waters. Water Resour. Res. 35, 2779–2792.
- Aeschbach-Hertig, W., Peeters, F., Beyerle, U., Kipfer, R., 2000. Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air. Nature 405, 1040–1044.

- Aeschbach-Hertig, W., Solomon, D.K., 2013. Noble gas thermometry in groundwater hydrology. In: Burnard, P. (Ed.), The Noble Gases as Geochemical Tracers. Springer, Berlin, Heidelberg, pp. 81–122. Advances in Isotope Geochemistry.
   Aeschbach-Hertig, W., Stute, M., Clark, J., Reuter, R., Schlosser, P., 2002.
- Aeschbach-Hertig, W., Stute, M., Clark, J., Reuter, R., Schlosser, P., 2002. A paleotemperature record derived from dissolved noble gases in groundwater of the Aquia Aquifer (Maryland, USA). Geochimica Cosmochimica Acta 66, 797–817.
- Al-Kharabsheh, A., 2000. Ground-water modelling and long-term management of the Azraq basin as an example of arid area conditions (Jordan). J. Arid Environ. 44, 143–153.
- Al-Momani, M.R., Amro, H., Kilani, S., El-Naqa, A., Rimawi, O., Katbeh, H., Tuffaha, R., 2006. Isotope response to hydrological systems for long term exploitation, case of Azraq basin, Jordan. In: IAEA TecDoc 1507, pp. 177–211.
- Aljazzar, T.H., 2003. Groundwater Recharge Modeling in the Azraq Basin Considering the Unsaturated Flow Components. Master's Thesis. Jordan University of Science and Technology, Irbid.
- Ayed, R., 1996. Hydrological and Hydrogeological Study of the Azraq Basin, Jordan. PhD Thesis. University of Baghdad, Iraq.
- Bajjali, W., 2012. Spatial variability of environmental isotope and chemical content of precipitation in Jordan and evidence of slight change in climate. Appl. Water Sci. 2, 271–283.
- Ballentine, C.J., Burgess, R., Marty, B., 2002. Tracing fluid origin, transport and interaction in the crust. In: Porcelli, D., Ballentine, C., Wieler, R. (Eds.), Noble Gases in Geochemistry and Cosmochemistry, Rev. Mineral. Geochem., vol. 47. Mineralogical Society of America, Geochemical Society, Washington, DC, pp. 539–614.
- Ballentine, C.J., Hall, C.M., 1999. Determining paleotemperature and other variables by using an error-weighted, nonlinear inversion of noble gas concentrations in water. Geochimica Cosmochimica Acta 63, 2315–2336.
- Beyerle, U., Aeschbach-Hertig, W., Imboden, D.M., Baur, H., Graf, T., Kipfer, R., 2000. A mass spectrometric system for the analysis of noble gases and tritium from water samples. Environ. Sci. Technol. 34, 2042–2050.
- Boom, G., 1968. Zur Petrogenese der Plateaubasalte Nordostjordaniens. In: Geologisches Jahrbuch. Bundesamt für Bodenforschung und Geologische Landesämter der Bundesrepublik Deutschland, vol. 85, pp. 489–496.
- Chang, S.J., van der Lee, S., 2011. Mantle plumes and associated flow beneath Arabia and East Africa. Earth Planet. Sci. Lett. 302, 448–454.
- Clarke, W.B., Jenkins, W.J., Top, Z., 1976. Determination of tritium by mass spectrometric measurement of <sup>3</sup>He. Int. J. Appl. Radiat. Isotopes 27, 515–522.
- Class, C., Goldstein, S.L., 2005. Evolution of helium isotopes in the earth's mantle. Nature 436, 1107–1112.
- Craig, H., 1961. Isotopic variations in meteoric water. Science 133, 1702–1703. El-Naqa, A., 2010. Study of Saltwater Intrusion in the Upper Aquifer in Azraq Basin.
- Technical Report. IUCN.
  El-Waheidi, M.M., Merlanti, F., Pavan, M., 1992. Geoelectrical resistivity survey of the central part of the Azraq basin (Jordan) for identifying saltwater/freshwater interface. J. Appl. Geophys. 29, 125–133.
- Friedrich, R., 2007. Grundwassercharakterisierung mit Umwelttracern: Erkundung des Grundwassers der Odenwald-Region sowie Implementierung eines neuen Edelgas-Massenspektrometersystems. PhD Thesis. Heidelberg University.
- Graham, D.W., 2002. Noble gas isotope geochemistry of mid-ocean ridge and ocean island basalts: characterization of mantle source reservoirs. In: Porcelli, D., Ballentine, C., Wieler, R. (Eds.), Noble Gases in Geochemistry and Cosmochemistry, Rev. Mineral. Geochem., vol. 47. Mineralogical Society of America, Geochemical Society, Washington, DC, pp. 247–317.
- Holden, W., 1998. Modelling and isotope study of the Azraq basin. In: Dutton, R.W., Clarke, J.I., Batticki, A. (Eds.), Arid Land Resources and Their Management:

Jordan's Desert Margin. Kegan Paul International, London, pp. 87-93.

- Humphreys and Sons, 1982. Azraq Well-field Evaluation, Hydrochemistry and Monitoring. Technical Report. Amman Water and Sewerage Authority, Amman, Jordan.
- IAEA/WMO, 2014. Global Network of Isotopes in Precipitation Database. Accessible at. www.iaea.org/water.
- Jähne, B., Heinz, G., Dietrich, W., 1987. Measurement of the diffusion coefficients of sparingly soluble gases in water. J. Geophys. Res. 92 (C10), 10767–10776.
- James, R.H., Palmer, R.P., 2000. The lithium isotope composition of international rock standards. Chem. Geol. 166, 319–326.
- Jung, M., 2014. Noble Gas Thermometry in Groundwater Hydrology: Development of Advanced Evaluation Methods and Review of Data Sets from the Literature. PhD Thesis. Heidelberg University.
- Jung, M., Wieser, M., von Öehsen, A., Aeschbach-Hertig, W., 2013. Properties of the closed-system equilibration model for dissolved noble gases in groundwater. Chem. Geol. 339, 291–300.
- Kaudse, T., 2014. Noble gases in Groundwater of the Azraq Oasis, Jordan, and along the Central Dead Sea Transform – Two Case Studies. PhD Thesis. Heidelberg University.
- Mamyrin, B.A., Tolstikhin, I.N., 1984. Helium Isotopes in Nature. Elsevier, Amsterdam.
- Margane, A., Hobler, M., Al-Momani, M., Subah, A., 2002. Contributions to the hydrogeology of northern and central Jordan. Geol. Jahrb. C 68, 3–52.
- MWI, 2009. National Water Master Plan Vol. 2: Water Resources in Jordan. Technical Report, second ed. Ministry of Water an Irrigation.
- Nelson, J.B., 1985. Azraq a case study. In: Hadidi, A. (Ed.), Studies in the History and Archaeology of Jordan, vol. 2. Routledge, London, pp. 39–44.
- Rozanski, K., Araguás-Araguás, L., Gonfiantini, R., 1993. Isotopic patterns in modern global precipitation. Geophys. Monogr. 78, 1–36.
- Sanford, W.E., Shropshire, R.G., Solomon, D.K., 1996. Dissolved gas tracers in groundwater: simplified injection, sampling, and analysis. Water Resour. Res. 32, 1635–1642.
- Schlosser, P., Stute, M., Dörr, C., Sonntag, C., Münnich, K.O., 1988. Tritium/f <sup>3</sup>Hedating of shallow groundwater. Earth Planet. Sci. Lett. 89, 353–362.
- Schmidt, G., Subah, A., Khalif, N., 2008. Model investigations on the groundwater system in Jordan – a contribution to the resources management (National Water Master Plan). In: Zereini, F., Hötzl, H. (Eds.), Climatic Changes and Water Resources in the Middle East and North Africa. Springer, Berlin, Heidelberg.
- Sheldon, A.L., 2002. Diffusion of Radiogenic Helium in Shallow Groundwater: Implications for Crustal Degassing. PhD Thesis. University of Utah.
- Solomon, D.K., 2000. <sup>4</sup>He in groundwater. In: Cook, P., Herczeg, A.L. (Eds.), Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publisher, Boston, pp. 425–439.
- Torfstein, A., Hammerschmidt, K., Friedrichsen, H., Starinsky, A., Garfunkel, Z., Kolodny, Y., 2013. Helium isotopes in dead sea transform waters. Chem. Geol. 352, 188–201.
- Weiss, R.F., 1970. Helium isotope effect in solution in water and seawater. Science 168, 247–248.
- Wieser, M., 2006. Entwicklung und Anwendung von Diffusionssamplern zur Beprobung gelöster Edelgase in Wasser. Diploma Thesis. Heidelberg University.
- Wieser, M., 2011. Imprints of Climatic and Environmental Change in a Regional Aquifer System in an Arid Part of India Using Noble Gases and Other Environmental Tracers. PhD Thesis. Heidelberg University.
- Yogeshwar, P., Tezkan, B., Haroon, A., 2013. Investigation of the Azraq sedimentary basin, Jordan using integrated geoelectrical and electromagnetic techniques. Near Surf. Geophys. 11, 283–291.