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The age and origin of groundwater in the Great Western Erg sub-basin of the North-Western Sahara aquifer system: Insights from Krechba, central Algeria



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ARTICLE INFO

Editorial handling by Philippe Negrel Keywords: Continental Intercalaire aquifer Stable isotopes Radiocarbon Noble gases Palaeo-recharge

ABSTRACT

The North-Western Sahara aquifer system (NWSAS) forms an important transboundary groundwater resource whose properties remain to be fully understood across its whole extent. For example, groundwater flow in the Cretaceous Continental Intercalaire (CI) unit of the NWSAS is well-characterised in the northern part of its range around the Algeria/Tunisia/Libya borders and in the Great Eastern Erg sub-basin immediately to the south. To the southwest, however, the CI of the Great Western Erg sub-basin has been much less studied. The present paper reports hydrogeochemical data from a wellfield in central Algeria which will contribute to a better understanding of this sector of the NWSAS in terms of the age and origin of groundwater within it.

Groundwater pumped from five deep boreholes in the CI aquifer overlying the Krechba gas field has been studied using a variety of environmental tracers including hydrochemistry, environmental isotopes, and reactive and noble gases (the latter being reported for the first time for this sub-basin). All the waters were dilute (SEC 460–600 μ S/cm), contained detectable O₂ (6.3–7.5 mg/L), showed evidence of evaporation (relative enrichment in δ^{18} O), gave late-Pleistocene ¹⁴C model ages (13.5–19.3 ka), and yielded lower than present-day noble gas recharge temperatures (14.3–17.6 °C). Various lines of evidence suggest that these waters are the product of mixing between water recharged direct to the CI and leakage from the Neogene–Quaternary Erg aquifer. The results support the long-held concept of regional flow from a palaeo-recharge area to the northwest. Finally, while the Krechba gas field (Carboniferous) has been since 2004 the site of a pilot carbon capture and storage (CCS) project, the data revealed no evidence for leakage of fluids (gas or brines) into the overlying CI aquifer at the time of sampling (October 2014).

1. Introduction

The North-Western Sahara aquifer system (NWSAS) is one of the largest in the world and includes two main aquifers, the Continental Intercalaire (CI) and the overlying Complexe Terminal (CT), shared between Algeria, Tunisia and Libya. At about 700,000 km², Algeria has approximately 60% of the surface area of the NWSAS (Fig. 1). The CI is the thicker of the two aquifers and has the greater areal extent. However, being the shallower aquifer, the CT is currently the more exploited of the two. There is limited interaction between the aquifers, with most of this occurring in the Ouargla area (Edmunds et al., 2003).

The current abstraction rate of 2.2 billion m³/yr from the NWSAS (60% of this from Algeria) demonstrates the importance of this aquifer system. It remains however to be fully characterised in some areas, particularly the CI in the southwest of the region, where it underlies a

part of the Sahara Desert known as the Great Western Erg (Fig. 1), or GWE.

The CI and the CT have been the subject of several published hydrogeochemical studies during the past half-century. Early isotope-based studies in the CI are summarised by Gonfiantini et al. (1974). These found isotope methods (stable and radioactive) to be important in verifying the concept of flows in the CI derived from necessarily sparse physical measurements. The majority of the data were from the Great Eastern Erg (GEE) sub-basin, but the GWE sub-basin received some coverage, including importantly the role played by the Neogene–Quaternary Erg aquifer in locally recharging the CI. The work of Guendouz et al. (1998) was the first to apply isotopes and noble gases to extract palaeoclimatic information from the CI and CT of the GEE. This was followed by the study of Edmunds et al. (2003) which followed a presumed flow line in the CI across the northern part of the GEE from

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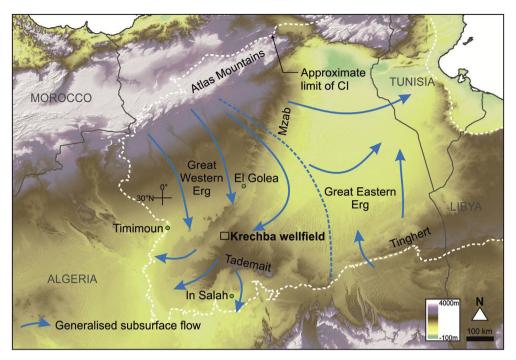


Fig. 1. The area covered by the north west Sahara aquifer system (NWSAS), showing the eastern and western Erg sub-basins and concept of groundwater flow directions based on Castany (1981). Also shown is the location of the Krechba wellfield.

recharge in the Atlas Mountains to discharge in the low-lying Tunisian Chotts area adjacent to the Gulf of Gabes (Fig. 1), and was largely devoted to the evolution of groundwater quality along the flowpath, though isotopic aspects were also considered. Simultaneously, Guendouz et al. (2003) published on the CT aquifer, which is only present in the GEE. Other more specialised papers dealt with subjects such as ³⁶Cl dating in the CI (Guendouz and Michelot, 2006), and uranium series geochemistry of the CI and CT (Elliot et al., 2014). However, none of these papers considered the aquifers of the GWE, principally the CI but also the Erg. This was to be partially addressed by the paper of Moulla et al. (2012) which released a sizeable geochemical and isotopic database for the CI in the GWE sub-basin, but only provided a 'broad brush' picture of the hydrogeochemistry of the aquifer in this sub-basin. Their study could not consider palaeo-climatic information in any detail owing to a lack of radiocarbon or noble gas data.

The work described here contrasts with previous studies in that it focuses on a small area of the GWE, where the existence of the Krechba gas field has given rise to some well-constrained sampling opportunities in the CI in connection with the development of a large-scale carbon capture and storage (CCS) project utilising the underlying Carboniferous gas reservoir. The study reviews a comprehensive set of hydrochemical, isotope and dissolved gas data from the CI at Krechba and relates it to the findings of other relevant studies of the CI within the GWE and beyond. It also briefly considers whether CCS operations have had any effect on the water quality of the CI at Krechba.

2. Background

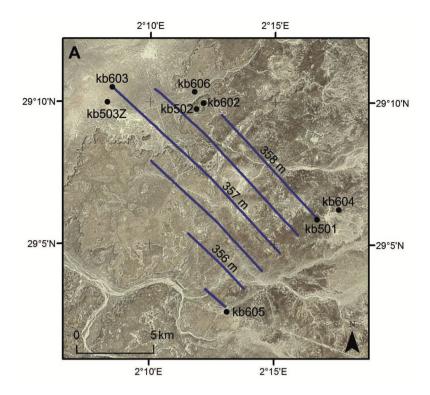
The CI is a formation of Lower Cretaceous age, consisting mainly of detrital sediments separated by intermittent layers or lenses (i.e. 'intercalations') of clay-rich material, which give rise to locally-variable aquifer properties (Edmunds et al., 2003). Equally, large-scale regional water flow directions in the CI vary as a consequence of the underlying geology and topography. Fig. 1 shows the current understanding of conditions in the CI of Algeria (OSS, 2003): (i) Elevated recharge areas in the northwest, south and southeast (Atlas Mountains, Tademait and Tinghert plateaux respectively); (ii) a groundwater divide in the basin centre unrelated to the topographic divide formed by the Mzab N–S

ridge; and (iii) the existence of discharge areas in the Chotts area of Tunisia and at the southwestern end of the GWE by way of the 'foggara' system of the Adrar region. While the combination of the Tademait and the Mzab topographically separates the two Erg (dune) areas, for the purposes of this study the groundwater divide will be taken as the subbasin boundary, which also marks the southwestern limit of the CT as a significant aquifer. On this basis, the CI and CT beneath the GEE discharge to the northeast, while the CI of the GWE discharges to the southwest (Fig. 1).

One part of the GWE with little borehole information until recent times is the Krechba area, situated roughly equidistant from the regionally important settlements of El Golea, Timimoun and In Salah (Fig. 1). The drilling of CI monitoring wells in connection with the development of the Krechba gas field (Fig. 2a) has led to the availability of five deep ($\sim 400 \, \text{mbgl}$) boreholes (kb602–kb606) screened over the approximate depth range of 250–350 mbgl (Fig. 2b) within a block some 250 km² in area. The CI is confined in this area by Cenomanian mudstones (Fig. 2b); piezometric measurements suggest that flow across the wellfield is from NE to SW (Fig. 2a), but the estimated 1:3000 the gradient is extremely low so the precise direction remains uncertain.

At Krechba, the CI is divided into an upper 500 m of largely sandy sediments (the Krechba Formation), and a lower 200 m of much more heterogeneous material (the In Salah Formation). The geology of these formations is described in detail in Newell et al. (2015).

In addition to the five monitoring boreholes kb602–606, three long-reach CO_2 injection boreholes kb501, kb502 and kb503Z (locations in Fig. 2a) penetrate to the Carboniferous gas reservoir, whose storage performance since injection of CO_2 during 2004–2011 has been monitored (e.g. Oye et al., 2013; Ringrose et al., 2013; White et al., 2014). These injection boreholes are necessarily cased off from the CI. While these were not sampled, drill cuttings from one of them (kb502) were examined for information about the mineralogy of the CI by Newell et al. (2015).



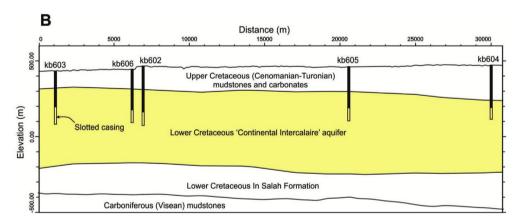


Fig. 2. (a) Krechba wellfield map with estimated groundwater head contours in metres above sea level, (b) simplified geological cross-section showing borehole screen intervals.

3. Methods

3.1. Sampling

Waters were sampled in October 2014 from kb602–606 following a minimum of 7 h test pumping and therefore the abstraction of approximately nine well-volumes before sampling. Following the collection of data for field parameters (temperature, pH, specific electrical conductivity, dissolved O_2 and alkalinity), samples were collected after filtration (0.45 μm) for hydrochemistry (major, minor and trace species) and isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C_{DIC}$ and $^{14}C_{DIC}$) in PTFE bottles, for dissolved reactive gases (N_2 , CO_2 and CH_4) in 50 mL double-ended stainless steel cylinders, and for dissolved noble gases in copper tubes of ~ 7 mL capacity.

3.2. Analysis

All non-field measurements were carried out in the laboratories of ANRH and BGS Keyworth (hydrochemistry), BGS Keyworth (stable O, H

and C isotopes) and BGS Wallingford (reactive and noble gases), except for radiocarbon (1⁴C) which was analysed by RCD Radiocarbon Dating of Wantage, UK. Techniques used included ICP-MS and ion chromatography (hydrochemistry), isotope ratio mass spectrometry (stable isotopes), accelerator mass spectrometry (radiocarbon), and gas chromatography and quadrupole mass spectrometry (gases).

A subset of drill cuttings from the CI in borehole kb502 was obtained for the purposes of whole-rock $\delta^{13}C_{carb}$ analysis. Samples were ground to $<355\,\mu m$ grain size and dissolved in anhydrous phosphoric acid, with the resulting CO_2 being measured for $\delta^{13}C$ at BGS Wallingford by isotope ratio mass spectrometry.

4. Results

4.1. Hydrochemistry

The data in Table 1 reveal well-oxygenated Ca-Na-HCO $_3$ -Cl waters of low salinity, with SEC (specific electrical conductivity) values lying in the range 458–602 μ S/cm. This is consistent with the very clean

Hydrochemical data from CI aquifer of the Krechba wellfield.

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Site ID	Date	Temp °C	Hd	SEC µS/cm	SEC μS/cm DO mg/L Ca m	Ca mg/L	Mg mg/L	Na mg/L	Na mg/L K mg/L	HCO3 mg/L	Cl mg/L	SO4 mg/L	NO3-N mg/L	Si mg/L	NPOC mg/L	F mg/L
kb602	07-0ct-14	33.7	7.96	534	8.9	43.0	14.4	39.0	7.05	88.7	63.8	58.2	4.85	6.84	2.15	0.27
kb603	05-Oct-14	33.2	8.02	602	7.7	38.8	17.5	50.8	96.9	91.7	81.7	62.4	5.38	6.95	4.41	0.30
kb604	05-Oct-14	35.6	7.85	458	6.1	34.2	12.5	30.7	5.66	84.8	46.3	50.0	4.26	7.57	0.72	0.24
kb605	11-Oct-14	34.9	7.90	477	6.5	36.9	13.5	33.4	00.9	88.3	49.4	53.1	4.21	7.76	1.54	0.24
kb606	11-0ct-14	33.7	7.96	533	8.9	39.0	13.6	37.1	6.38	8.98	0.99	58.8	4.94	5.91	0.65	0.28
Site ID	Date	В µg/L	Br µg/L	Ва µg/L	Sr µg/L	Mn μg/L	Fetot µg/L	As µg/L	Se µg/L	Cd μg/L	Cr µg/L	Ni μg/L	Cu µg/L	РЬ µg/L	Zn µg/L	U µg/L
kb602	07-0ct-14	61	79.3	62.5	411	10.7	36.0	1.21	1.0	0.05	10.2	0.4	10.2	0.21	10.9	0.44
kb603	05-Oct-14	70	87.5	63.8	531	8.5	11.0	1.23	1.0	0.02	13.6	9.0	1.8	< 0.02	3.1	0.51
kb604	05-Oct-14	54	62.1	64.1	375	16.2	182	1.44	1.0	0.03	11.0	6.0	4.1	0.13	0.9	0.42
kp605	11-Oct-14	26	65.8	76.0	411	8.3	32.0	1.73	1.0	< 0.01	16.3	< 0.1	8.0	0.04	1.1	0.42
kb606	11-Oct-14	63	6.08	65.8	390	16.8	421	1.35	8.0	0.02	15.3	0.2	5.2	0.22	8.5	0.44

quartz sands noted in the CI drill cuttings from kb502 by Newell et al. (2015).

The inorganic water quality is good, with all relevant species (NO_3 -N, As, B, Ba, Cd, Cu, Cr, F, Ni, Pb, Se and U) being present at significantly below WHO recommended limits. The persistence of nitrate, presumably derived from natural processes rather than of anthropogenic origin (Stone and Edmunds, 2014 and references therein), can be attributed to oxidising conditions enduring in this part of the CI.

A multi-plot of selected species versus chloride (Fig. 3) shows minor but often consistent variations across the wellfield. There are examples of apparent binary mixing (e.g. Na, SO₄, NO₃-N, temperature) but also some instances where this is less apparent. (e.g. Ca, Ba and Si). The reason for this is presumably solubility control: a table of saturation indices (Table 2) shows that the waters are all at or near saturation with respect to calcite, SiO_2 and barite, while they are well below this level for gypsum, anhydrite and halite. Clearly ions such as Na, SO_4 and NO_3 -N are, like Cl, behaving as conservative tracers. The implications of this are considered in 5.1 below.

4.2. Isotopes

O, H and C stable isotope values are reported together with radiocarbon (¹⁴C) activities in Table 3. The O and H stable isotopic compositions of the borehole waters lie far from the composition of presentday rainfall in the region and cannot be derived from it by any likely process of modification (Fig. 4). They also plot well below the Global Meteoric Water Line (GMWL – Craig, 1961) and so must be assumed to contain water which has undergone evaporative fractionation (Clark and Fritz, 1997). The O and H stable isotopes confirm the indications based on hydrochemistry that binary mixing is taking place within the wellfield (Fig. 3), which is also suggested by ¹⁴C.

By contrast, carbon stable isotopes (Table 3) show less consistent variation across the wellfield (Fig. 3). This is presumably the result of the $\delta^{13}C_{DIC}$ values being linked to the carbonate system which, as demonstrated in 4.1, behaves less conservatively than $\delta^{18}O$ or tracer ions like Na and Cl.

Drill cuttings from kb502 gave whole-rock $\delta^{13}C_{carb}$ values ranging from +0.3 to -8.6% (Fig. 5). Somewhat counter-intuitively, the least variation was seen in the In Salah Formation which, as stated earlier, is much more heterogeneous than the overlying Krechba Formation. The implications of these $\delta^{13}C_{carb}$ results for radiocarbon age correction are discussed in 5.1 below.

4.3. Dissolved gases

Table 4 gives results for the major dissolved gases N_2 , O_2 and CO_2 , plus CH_4 . The dominant dissolved gas is N_2 , which is presumably derived entirely from the atmosphere since redox conditions do not favour denitrification (4.1. above). Concentrations of O_2 represent ~110% saturation for the present-day mean annual air temperature (MAAT) of ~24 °C at Krechba. At ~2 mg/L, CO_2 is low in concentration compared to many oxidising groundwaters (e.g. Hem, 1985), implying a soil zone poor in respiratory activity. Methane concentrations are at or below the detection limit of $0.2\,\mu\text{g/L}$.

Concentrations of the noble gases He, Ne, Ar, Kr and Xe are reported in Table 5. In groundwaters, He can vary considerably in concentration due to accumulation over time from in situ production from U-series decay and/or leakage from adjacent formations. In the case of the Krechba wells, however, the He concentrations averaging 1.1×10^{-7} cm³STP/g are only slightly above those expected from simple equilibrium with the atmosphere ($\sim4.6\times10^{-8}$ cm³STP/g), and therefore show evidence of only minor He addition. This is consistent with low concentrations of uranium and the clean quartz sand lithology already noted in connection with the water quality (4.1 above).

The remaining noble gases Ne, Ar, Kr and Xe have solubilities that are strongly dependent on recharge temperature (RT). Using the CE

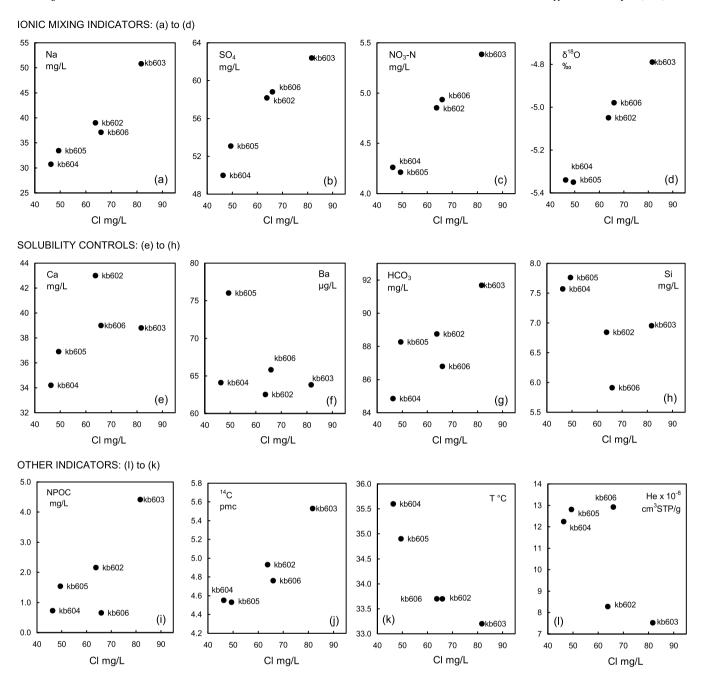


Fig. 3. Multiplot of selected determinands versus Cl for the Krechba boreholes kb602–kb606. Plots are divided into indicators of simple mixing, solubility-control, and selected other indicators.

(closed-system equilibration) approach of Aeschbach-Hertig et al. (2000) via the iterative spreadsheet calculator of Matsumoto (2015), an RT range of 14.3–17.6 °C is indicated (Table 6).

5. Discussion

5.1. Age and origin of the groundwater in the Krechba wellfield

The correction of groundwater radiocarbon activities to allow for dilution by 'dead' mineral carbon in order to obtain an indication of mean residence time is a well-established practice (Clark and Fritz, 1997, and references therein). For this study, the most consistent results were obtained using the approach of Han and Plummer (2013), based on the following assumptions: firstly, soil CO_2 with a $\delta^{13}C$ value of -20% (typical semi-arid to arid value: Clark and Fritz, 1997), and

secondly aquifer matrix carbonate values of 0%, -4% or -5.0%0 respectively. The latter values are based on three different scenarios for the source of dead carbon, (i) the conventional assumption in groundwater dating that the carbonate is marine-derived, (ii) the mean of carbonate in kb502 over the approximate screened depth range of 250–350 mbgl in kb602–606, (iii) the mean from the whole depth of the Krechba Formation in kb502 (Fig. 5). Table 7 shows the results of these assumptions. The fact that much of the Krechba sequence of the CI appears to be of terrestrial origin (Newell et al., 2015) makes option (i) look the least likely to be valid. The difference in ages between options (ii) and (iii) averages 1.1 ka and therefore is of little significance to any palaeo-environmental interpretations.

It is estimated from the pumping test and recovery water level data that groundwater flow velocity across the wellfield lies in the range 4–20 m/a. Over the model age range of ~ 13.5 –19.3 ka indicated by

Table 2
Saturation indices for groundwaters from the CI aquifer of the Krechba well-field.

Mineral	Formula	kb602	kb603	kb604	kb605	kb606
		Saturatio	n indices			
Calcite	CaCO ₃	0.19	0.20	0.00	0.09	0.14
Aragonite	CaCO ₃	0.05	0.06	-0.14	-0.05	0.00
Dolomite	$CaMg(CO_3)_2$	0.33	0.48	0.01	0.17	0.25
Quartz	SiO_2	-0.10	-0.08	-0.08	-0.06	-0.0
Chalcedony	SiO ₃	-0.50	-0.49	-0.47	-0.46	-0.50
Gypsum	CaSO ₄ ·2H2O	-2.01	-2.04	-2.14	-2.09	-2.04
Anhydrite	CaSO ₄	-2.19	-2.22	-2.31	-2.28	-2.2
Halite	NaCl	-7.19	-6.97	-7.43	-7.37	-7.20
Strontianite	$SrCO_3$	-1.42	-1.24	-1.55	-1.46	-1.45
Celestite	SrSO ₄	-2.29	-2.17	-2.36	-2.31	-2.30
Barite	BaSO ₄	-0.14	-0.11	-0.19	-0.09	-0.1
Witherite	BaCO ₃	-3.18	-3.12	-3.27	-3.14	-3.1°

Table 3 Stable isotope (δ^{18} O, δ^2 H and δ^{13} C_{DIC}) and radiocarbon (14 C) data from the CI aquifer of the Krechba wellfield.

Site ID	$\delta^{18}O$	$\delta^2 H$	$\delta^{13}C_{\rm DIC}$	$^{14}\mathrm{C}_{\mathrm{DIC}}$	
	% VSMOW	‰ VSMOW	‰ VPDB	pmc ^a	±
kb602	-5.05	-51.0	-5.66	4.93	0.07
kb603	-4.79	-48.4	-5.40	5.53	0.06
kb604	-5.34	-50.3	-6.41	4.55	0.07
kb605	-5.35	-50.5	-7.25	4.53	0.07
kb606	-4.98	-50.4	-5.35	4.76	0.07

^a Percent modern carbon.

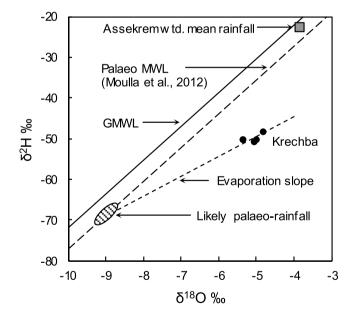


Fig. 4. Plot of $\delta^{18}O$ vs $\delta^{2}H$ for waters from the Krechba boreholes kb602–kb606, showing the relationship to the GMWL, palaeo-MWL and modern rainfall in Algeria (Assekrem station of the GNIP network: https://nucleus.iaea.org/wiser).

Table 7, this would equate to a mean flowpath length of 60–400 km, assuming conditions remained constant over time and space. The upper figure of 400 km fits better with the overall dimensions of the GWE subbasin (Fig. 1); the lower figure of 60 km would imply that water presently arriving at Krechba should be ¹⁴C-dead. Therefore flow velocity across the wellfield seems likely to lie in the upper part of the estimated

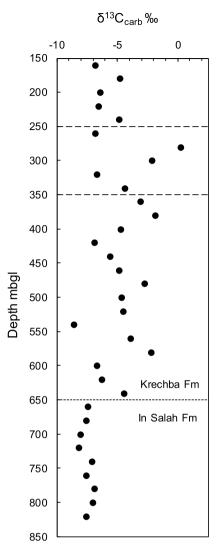


Fig. 5. Plot of $\delta^{13}C_{carb}$ vs depth in metres below ground level for drill cuttings from the kb502 injector borehole. Dashed lines indicate the approximate screen depth interval in boreholes kb602–kb606.

Table 4
Reactive gas data from the CI aquifer of the Krechba wellfield.

Site ID	$N_2 \text{ mg/L}$	${\rm O_2}$ mg/L	${\rm CO_2}$ mg/L	CH ₄ μg/L
kb602	19.4	6.8	1.8	< 0.2
kb603	16.9	7.5	2.1	0.2
kb604	17.5	6.3	2.0	< 0.2
kb605	17.2	6.2	1.8	< 0.2
kb606	18.3	6.5	2.0	< 0.2

range.

The calculated noble gas RT values of 14.3–17.6 °C (Table 6) are significantly below the present-day MAAT in the Krechba area of ~ 24 °C. There are minor differences in RT depending on notional mean recharge elevation, assumed here to lie between 500 and 800 m above sea level (Krechba is at ~ 450 m asl). There is evidence for a limited contribution of 'excess air' (EA), incorporated mainly due to fluctuations in the water table at the time of recharge, from ~ 1 to 6 ccSTP/kg. This is well within the range of EA values noted for sandstone aquifers (Wilson and McNeill, 1997; Aeschbach-Hertig et al., 2002) and does not appear to indicate recharge under conditions favouring high EA, such as large annual water table fluctuations.

Table 5Noble gas data from the CI aquifer of the Krechba wellfield.

Site ID	Не	±	Ne	±	Ar	±	Kr	±	Xe	±
	cm ³ STP/g	× 10 ⁻⁸	cm ³ STP/g	× 10 ⁻⁸	cm ³ STP/g	× 10 ⁻⁵	cm ³ STP/g	× 10 ⁻⁸	cm ³ STP/g	× 10 ⁻⁹
kb602	8.284	0.126	21.27	0.421	32.87	0.399	7.832	0.141	9.556	1.913
kb603	7.521	0.103	19.64	0.354	32.89	0.428	7.145	0.232	9.990	0.329
kb604	12.24	0.183	19.85	0.325	32.91	0.388	7.245	0.133	8.968	1.824
kb605	12.80	0.169	22.30	0.309	33.13	0.430	7.160	0.234	9.913	0.327
kb606	12.92	0.216	28.07	0.452	34.80	1.405	7.741	0.276	10.25	0.445

Table 6
Groundwater recharge temperatures and excess air calculated from noble gas data.

Site ID	Recharge T °C	±	Excess air cm ³ STP/kg	±
Recharge a	t 500 m asl			
kb602	15.6	0.16	1.63	0.04
kb603	16.2	0.16	1.15	0.05
kb604	16.3	0.19	1.22	0.04
kb605	17.6	0.18	2.51	0.04
kb606	17.5	0.22	5.65	0.16
Recharge a	t 800 m asl			
kb602	14.3	0.15	1.89	0.05
kb603	15.0	0.22	1.82	0.05
kb604	15.0	0.18	1.92	0.04
kb605	16.4	0.18	3.23	0.08
kb606	16.3	0.19	5.91	0.13

Table 7 Groundwater model ages (uncalibrated) calculated from carbon isotope data (Table 3) for different rock matrix $\delta^{13}C_{carb}$ values (see text). Percentage error based on ^{14}C measurement precision alone.

Site ID	Correcte	d ¹⁴ C age	Correcte	Corrected ¹⁴ C age		ed ¹⁴ C age
	δ ¹³ Ccarb	0 = 0%	δ ¹³ Ccarb	= -4‰	δ ¹³ Ccarl	o = -5%
	ka	± %	ka	± %	ka	± %
kb602 kb603 kb604 kb605	19.0 17.7 20.6 21.5	0.62 0.58 0.62 0.59	16.3 14.8 18.3 19.3	0.72 0.64 0.70 0.66	15.1 13.5 17.4 18.6	0.81 0.67 0.76 0.70
kb606	19.0	0.64	16.1	0.76	14.8	0.87

The existence of significant concentrations of dissolved O_2 in the CI at Krechba has been noted (4.3). However, assuming the noble gas RTs in Table 6 to be reasonably accurate, the water drops from being apparently oversaturated in O_2 to $\sim 66\%$ saturation. It seems feasible that O_2 concentrations could have fallen by one-third for waters of this apparent age (Table 7), even in a 'clean' aquifer like this part of the CI. Indeed, in the confined conditions under the edge of the Tademait Plateau where the wellfield is situated, it is perhaps surprising that dissolved O_2 concentrations have not declined further.

The indications from the ^{14}C data for mean residence times of the order of 13–19 ka (Table 7) places recharge in the late Pleistocene. This would imply wetter and cooler conditions than at present, the latter consistent with the $\sim 8\,^{\circ}\text{C}$ drop in recharge temperature suggested by the noble gases. As mentioned, the $\delta^{18}\text{O}$ and $\delta^{2}\text{H}$ values of the borehole waters do not appear to be related to modern recharge (Fig. 4), which in any case would be extremely low or absent in the Krechba region (mean rainfall ~ 30 mm/a, potential evaporation > 4000 mm/a). The water must therefore have been recharged under a different climate, which would be consistent with the information provided by radiocarbon and the noble gases.

The plots of ions and other determinands versus Cl in Fig. 3 indicate that simple binary mixing is taking place across the wellfield. Some

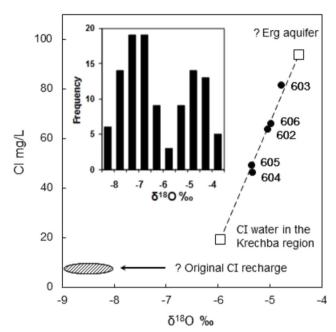


Fig. 6. Plot of δ^{18} O versus Cl showing the Krechba borehole waters lying on a mixing line between notional Cl and Erg aquifer end members. Inset: histogram of δ^{18} O values in the GWE sub-basin based on the data of Moulla et al. (2012).

information about the end-member compositions can be obtained from a plot of δ^{18} O vs Cl (Fig. 6). This suggests that for a Cl concentration of ~ 20 mg/L, among the lowest recorded from the CI of the GWE (Moulla et al., 2012), the corresponding δ^{18} O value would be $\sim -6\%$. The other end-member would necessarily have an enriched isotope composition, the source of which seems most likely to be leakage from the Erg aquifer. This is not well characterised hydrogeochemically, with $\delta^{18}O$ estimates ranging from $\sim -4.5\%$ (Conrad and Fontes, 1970) to $\sim -2\%$ (Moulla et al., 2012). These values would equate to Cl concentrations in the range 95-240 mg/L. A reported mean Cl value for the Erg aquifer of 90 mg/L (Merzougui et al., 2007) suggests the -4.5\% figure is more generally applicable. This is also supported by a histogram of GWE-wide CI δ^{18} O values based on data in Moulla et al. (2012) which shows a markedly bimodal distribution, with the less negative peak between -4 and -4.9% presumably representing leakage from the Erg aquifer into the CI (inset, Fig. 6).

Given the evidence for evaporation provided by stable isotopes, suggestive of recharge to the Erg aquifer from surface water flow via ponding, it seems likely that the Erg water would be more mineralised than the CI water.

5.2. The Krechba wellfield results in the context of previous studies of the Great Western Erg

5.2.1. Groundwater evolution and mixing

The mixing discussed in 5.1 above means that, in contrast to what was inferred for the northern GEE sub-basin by the study of Edmunds

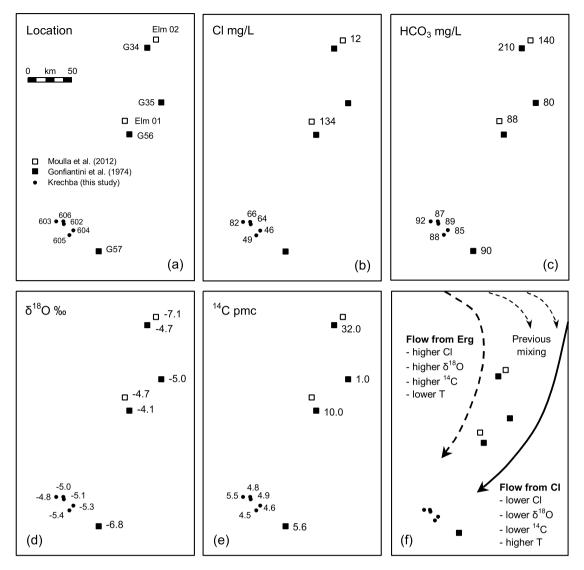


Fig. 7. Maps showing location (a) of the Krechba boreholes in relation to other boreholes upflow of the wellfield, including values (where known) of (b) Cl, (c) HCO_3 , (d) $\delta^{18}O$ and (e) ^{14}C . A schematic of mixing between water from the Continental Intercalaire (CI) and leakage from the Erg aquifer is shown in (f). Data from this study, Gonfiantini et al. (1974) and Moulla et al. (2012) as shown in (a).

et al. (2003), the hydrochemistry of the Krechba waters cannot be interpreted in terms of sites lying on a single evolutionary flowline. Nevertheless, some general points relating to the Krechba water quality can be made. The mineralisation of the waters is significantly lower than found by Edmunds et al. (2003) only a few tens of km away from their assumed recharge area, presumably due to the presence of more halite, gypsum and other minerals in the CI of the GEE. One of the few species present at Krechba in comparable concentrations to the GEE is Si, presumably related to solubility controls. The mean Si concentration at Krechba of 7 mg/L is not reached in the GEE until a distance of 250-300 km down the flowline (Edmunds et al., 2003). All things being equal, this implies that the Krechba waters could have travelled a comparable distance, which given the size of the GWE sub-basin (Fig. 1) is certainly possible. Concentrations of NO₃-N at Krechba are comparable to those in the oxidising portion of the GEE flowline, but this most likely reflects a soil-zone vegetation-related origin in both cases. No dissolved O2 measurements are available from the wider GWE, but the persistence of NO₃ in all the CI waters reported by Moulla et al. (2012) suggests the existence of oxidising conditions throughout the sub-basin. This would be in contrast to the GEE, where the onset of reducing conditions occurs some 350 km down the flowline (Edmunds et al.,

2003).

Assuming the piezometric contouring shown in Fig. 2 is broadly correct, flow in the CI is entering the Krechba wellfield from the NE. This is presumably the consequence of an initially southeasterly flow from the foothills of the Atlas Mountains being diverted by the shape of the sub-basin, resulting in the curved flowpath depicted in Castany (1981) and on Fig. 1. The mixing across the wellfield described in 5.1 above must therefore result from a combination of water recharged directly to the CI, with leakage from the overlying Erg aquifer arriving from a broadly similar direction. The fairly steep mixing gradient across the relatively small area of the wellfield suggests a relatively sharp boundary between Erg and CI water bodies. This may well be a regional rather than local phenomenon, as there is no evidence from the kb borehole logs for preferential flow pathways such as river palaeochannels in the Krechba Formation (Newell et al., 2015).

There are rather few boreholes with any recorded hydrogeochemical data situated in the vicinity of, or upflow from, the well-field. Where data exist, they are shown on Fig. 7. Stable isotope values are generally similar to those in the wellfield, but two sites give $\delta^{18}O$ results closer to -7% (Fig. 7d). These would not fit the wellfield mixing line which predicts a minimum $\delta^{18}O$ value of -6%; indeed it is

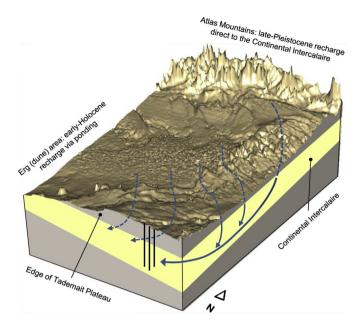


Fig. 8. Conceptual diagram of flow to the Krechba wellfield. Vertical exaggeration $\times 100$.

known that CI waters in the GWE have values as low as -9% (Gonfiantini et al., 1974; Moulla et al., 2012) reflecting their origin as recharge on the slopes of the Atlas Mountains. This implies that even before the CI flow component enters the wider Krechba area, it has already mixed with isotopically heavier water leaking from the Erg aquifer, implying a form of exponential mixing of Erg water with CI water (Fig. 7f).

This mixing may have a three-dimensional aspect: for example, the neighbouring boreholes Elm 02 and G34 in the vicinity of El Golea have contrasting HCO $_3$ and δ^{18} O values (Fig. 7c and d). However, without details of screen depths in those boreholes it is not possible to be more specific about this in terms of flow horizons.

5.2.2. Recharge age

It is apparent from Fig. 6 and Table 7 that the higher TDS, isotopically heavier water derived from the Erg aquifer must be younger than the directly-recharged CI component, which would be consistent with the shorter flowpath of leakage from the Erg aquifer. If the representation of mixing in Fig. 6 is combined with the 14 C ages of Table 7, then end-member ages might be of the order of 12 ka for the Erg recharge and ≥ 22 ka for the CI. While there are clearly considerable uncertainties over these ages, they would broadly fit with available evidence for pluvial periods in and around the Atlas Mountains (Fontes et al., 1985; Rhoujjati et al., 2010; Youcef and Hamdi-Aïssa, 2014).

Dissolved He is sometimes used as a semi-quantitative long-term age indicator on the assumption that concentrations increase linearly with age owing to gradual escape of He produced by decay of U and Th in aguifer minerals (Andrews and Lee, 1979). While there are no previous He data from the CI of the GWE, a comparison with the dataset of Guendouz et al. (1998) for the GEE reveals that concentrations are significantly lower at Krechba. This presumably reflects U concentrations being an order of magnitude below those from the oxidising part of the CI in the GEE (Edmunds et al., 2003; Elliot et al., 2014). Consideration of the plots of ¹⁴C and He vs Cl in Fig. 3 suggests a negative correlation between He and 14C, indicative of He accumulation over time. More He and radiocarbon data might enable a simple ¹⁴C-He age calibration to extend He dating back beyond the limit of groundwater radiocarbon dating (\sim 30 ka). However, the available 14 C data from the wider GWE do not fall below 1 pmc (Gonfiantini et al., 1974), so it may be that the GWE sub-basin does not store water much more than 30 ka in age (or that mixing with younger water is concealing the true age of the old component).

5.2.3. Recharge temperature

There are no noble gas data from the wider GWE, but a limited dataset is available from both the CI and CT in the GEE sub-basin (Guendouz et al., 1998). Excluding outliers and sites on the S–N flow-line from the Tinghert plateau (Fig. 1), an RT range of 14.3–17.8 °C is reported, very close to the range from Krechba (Table 6). While this is doubtless partly coincidental, it will be recalled from Fig. 1 that recharge to both the GWE and northern GEE is derived from the foothills of the Atlas Mountains, so similar RTs would be expected. (By contrast, the CI and CT sites on the Tinghert flowline give higher RTs because of recharge on the Plateau at lower elevation and latitude.)

5.3. The lack of evidence for leakage into the CI aquifer from the underlying gas field

Studies of carbon capture and storage (CCS) projects typically look for evidence for leakage of gases into the overlying aquifer(s) in order to demonstrate the degree of integrity of the reservoir into which the CO₂ is injected (e.g. Smyth et al., 2009; Rostron and Whittaker, 2011; Jenkins et al., 2012). Krechba has been the site of one of the largest CCS projects yet carried out (White et al., 2014). The low concentrations of CO_{2.} CH₄ and He measured in waters from the kb monitoring boreholes (see 4.3) suggest that any leakage from the Carboniferous reservoir into the CI was either not present at all at the time of sampling (October 2014), or at least had not reached the 250-350 mbgl level tapped by boreholes kb602-606. This is supported to some extent by the lack of evidence for the mobilisation of the organic carbon or heavy metal-rich brines (see 4.1) likely to be present in the reservoir (e.g. Kharaka et al., 2006; Stenhouse et al., 2009), though these would be expected to lag behind the gases in terms of diffusion and advection rates. However, possible point-source leakage from the reservoir might not be detected in any of the kb borehole waters if the resulting plume were deflected away from the existing boreholes by the regional flow gradient. An improved knowledge of hydrogeological conditions across the wellfield is required to constrain this possibility further.

6. Summary and conclusions

The existence of a wellfield at Krechba has provided a window into groundwater conditions in the transboundary Continental Intercalaire (CI) aquifer in an area of central Algeria with otherwise sparse data. A comprehensive hydrogeochemical dataset including chemistry, gas and isotopic data has allowed a number of conclusions to be drawn regarding not only the wellfield, but also its context within the wider Great Western Erg (GWE) sub-basin of the NWSAS:

- Water quality (inorganic) is good, meeting the relevant WHO guidelines.
- Binary mixing between CI and Erg aquifer waters takes place across the wellfield.
- A significant proportion of the wellfield water has been recharged from surface ponding at some point in the past.
- Mean residence times based on radiocarbon lie in the range 13.5–19.3 ka, though it is probable they reflect mixing of late-Pleistocene (CI) and earliest-Holocene (Erg) waters.
- Noble gas thermometry on the waters indicates recharge temperatures in the range 14.3–17.6 °C, consistent with a proportion of pluvial-epoch recharge.
- There was no geochemical evidence at the time of sampling (October 2014) for fluid contamination from the underlying Krechba CO₂ storage reservoir.

A summary diagram for groundwater flow in the GWE is presented

in Fig. 8, based on the present focused research and earlier basin-wide studies. Fig. 8 in general supports the concept of flow developed more than 50 years ago, but is able to add some detail unknown at that time. Inevitably there is a degree of speculation involved; it is recommended in particular that much more radiocarbon and screen depth data should be gathered from boreholes and wells across the GWE in order to gain a better understanding of 3-D groundwater flowpaths through the basin.

Acknowledgments

This paper is dedicated to the memory of Mike Edmunds, whose career-long enthusiasm for investigating the groundwater resources of Africa's drylands provided inspiration to many researchers. Members of the In Salah $\rm CO_2$ Storage Project (a joint venture between BP, Sonatrach and Statoil) are thanked for providing the opportunity and facilities to carry out this work, and for consenting to publication. The BGS authors publish with the permission of the Executive Director, British Geological Survey (NERC).

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