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Dissolved uranium, radium and radon evolution in the Continental Intercalaire aquifer, Algeria and Tunisia

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ABSTRACT

Natural, dissolved ^{238}U-series radionuclides (U, ^{226}Ra, ^{222}Rn) and activity ratios (A.R.s: ^{234}U/^{238}U; ^{228}Ra/^{226}Ra) in Continental Intercalaire (CI) groundwaters and limited samples from the overlying Complexe Terminal (CT) aquifers of Algeria and Tunisia are discussed alongside core measurements for U/Th (and K) in the contexts of radiological water quality, geochemical controls in the aquifer, and water residence times. A redox barrier is characterised downgradient in the Algerian CI for which a trend of increasing ^{234}U/^{238}U A.R.s with decreasing U-contents due to recoil-dominated ^{234}U solution under reducing conditions allows residence time modelling ~500 ka for the highest enhanced A.R. = 3.17. Geochemical modelling therefore identifies waters towards the centre of the Grand Erg Oriental basin as palaeowaters in line with reported ^{14}C and ^{36}Cl ages. A similar ^{234}U/^{238}U trend is evidenced in a few of the Tunisian CI waters. The paleoage status of these waters is affirmed by both noble gas recharge temperatures and simple modelling of dissolved, radiogenic ^{4}He-contents both for sampled Algerian and Tunisian CI and CT waters. For the regions studied these waters therefore should be regarded as "*fossil*" waters and treated effectively as a non-renewable resource.

1. Introduction

Low-level activity, naturally-occurring uranium- and thorium-series radionuclides and their isotopes in groundwaters can give insight into reduction–oxidation (redox) and geochemical controls, water–rock interactions, aquifer mixing, and subsurface residence times of sampled waters in aquifer systems (Andrews, 1991; Bonotto, 2004; Porcelli, 2008). They also have significance for health in terms of their alpha (α-)radioactivity, and many countries have adopted regulatory standards for water use (cf. Chau et al., 2011).

In semi-arid and arid zones in Algeria, groundwater is the principal source of drinking water; and in Tunisia in 2010 the Ministry of Agriculture developed a strategic survey for sustainable water usage by 2050 which could include the use of non-traditional sources of water like desalination of seawater or salty groundwater. In Algeria, Amrani (2002) has measured bottled mineral waters (for 8 samples: 2.6–14 Bq/l ^{222}Rn; 12–37 mBq/l ^{226}Ra; 15–39 mBq/l ^{232}Th; 0.4–1.6 Bq/l ^{40}K). Amrani et al. (2000) have published ^{222}Rn measurements as 0.5–19.37 Bq/l (15 samples, only one sample > 11 Bq/l) in groundwater from springs and deep wells of the Tassili N'Ajer high sandstone plateau in southeast Algeria. Most recently, Aït-Ziane et al. (2012) have reported groundwater ^{222}Rn data (21 samples: 0.1–34.4 Bq/l, mean = 11.5 Bq/l) and ^{226}Ra (11 samples: 0.25–5 Bq/l) for the Chott El Hodna (Algeria) region. Much higher concentrations of ^{222}Rn may be associated with oil and gas production (Hamlat et al., 2003) as radon is also a noble gas which naturally and preferentially partitions to non-aqueous liquid and gas phases. High natural radium concentrations also have been reported associated also with palaeowaters, e.g. in the Disi sandstone aquifer in Jordan (Vengosh et al., 2009).

The Continental Intercalaire (CI) formation in North Africa hosts an extensive, regional, internally-drained (endorheic), sedimentary aquifer which underlies Algeria, Tunisia, and Libya. Castany (1981) originally emphasised the deep-basin nature of this aquifer system of the northern Sahara such that "development and management of water stored in aquifer … … [is] 'groundwater mining'". Puri et al. (2006), Mamou et al. (2006) and Edmunds (2012) have asserted

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that in the Saharan basins the water resource often can be shown to be '*fossil*' or palaeowater, almost entirely non-renewable in terms of both their water resources management and in International Law (Eckstein and Eckstein, 2003, 2005). Semi-arid/arid regions like Libya and Algeria are heavily dependent on groundwater as their only water resource; coordinated management of this trans-boundary, shared water resource led to the creation of a Consultation Mechanism Unit for the North Sahara Aquifer System – SASS (Système Aquifere du Sahara Septentrional) in July 1999 (UNESCO, 2010).

Previous attempts to date the geochemical residence times of the Algerian CI waters using ^{14}C ($\tau_{1/2} = 5730$ a: Gonfiantini et al., 1974; Sonntag et al., 1978; Guendouz, 1985; Elliot, 1990; Guendouz et al., 1997; Edmunds et al., 2003) identified that, apart from aquifer margins, the sampled CI waters all have low radiocarbon activities (<5 per cent modern carbon, pmc). Towards the centre of the basin, waters are very close to the limit of age discrimination by the radiocarbon method (~25–30 ka). This along with past climatic signatures archived in the waters through their stable isotopes of water signatures (δ^2H, δ^{18}O) and dissolved noble gas contents (Elliot, 1990; Guendouz et al., 1997) appear to confirm their palaeowater status. Moreover, Guendouz and Michelot (2006) report ^{36}Cl ($\tau_{1/2} = 3 \times 10^5$ a) dates for CI waters suggesting minimum model groundwater ages of 0–134 ka and maximum ages 49–223 ka for relevant samples on the M'Zab ridge (Berriane, Metlili) and ages > 100 ka (Zelfana, El-Hadjira), although initial ^{36}Cl/Cl data are being revised (Petersen et al., 2014a, in press).

Recent literature however has queried the significance and presumption of the paleowater/*fossil* water status (and by implication a stagnant/null recharge or disconnected flow system) particularly for the North-Western Sahara Aquifer System. Al-Gamal (2011) invokes stratification and regional mixing of modern and palaeowaters generally in the system on the basis of moderately-depleted δ^2H, δ^{18}O signatures seen in recharge zones, and states particularly that tritium (^{3}H; $\tau_{1/2} = 12.32$ a) is widespread – although few data are presented and even the presence of ^{14}C signatures > 2 pmc would translate to significant geochemical residence times (Annexe 8, OSS, 2003). From piezometric modelling of the CI aquifer Ould Baba Sy (2005), suggests that a null recharge presumption for the Tademait and Tinrhert plateaux of southern Algeria is reasonable, however he queries null recharge in the Algerian Saharan Atlas and the Dahar Hills (Tunisia) and also the Algerian M'zab (at least for the CT aquifer). Gonçalvès et al. (2013) deploy a regional water balance approach to assess natural recharge, although since all aquifers are distributed flow systems water recharging at any location then is flowing somewhere specific and for water resources management and sustainability of any aquifer equating safe aquifer yield to its natural recharge can be problematic (e.g. Elliot et al., 1998, 2001; Sophocleous, 1997).

Radioactive ^{3}H, ^{14}C and ^{36}Cl dating methods are all based on a 'decay clock' of atmospheric inputs at recharge (albeit with various correction mechanisms for mixing sources and dilution within an aquifer). Natural ^{238}U ($\tau_{1/2} = 4.5 \times 10^9$ a)- and ^{232}Th ($\tau_{1/2} = 1.405 \times 10^{10}$ a) decay is internal to the system, which can provide an 'accumulation clock' for their products – including other U- and Th-isotopes, Ra, Rn (all radioactive) and also (stable) dissolved ^{4}He (since the U- and Th-series decay mechanism is predominantly by α-emission). Whilst natural dissolved U distributions and ^{234}U/^{238}U activity ratios (A.R.s) in Continental Intercalaire (CI) waters have been reported (Edmunds et al., 2003; Chkir et al., 2009), the radiogenic and radioactive daughters ^{226}Ra and ^{222}Rn have not been reported previously. Moreover, ^{234}U/^{238}U disequilibria modelling for these deep basin waters in terms of groundwater dating and as a comparative check for consistency of groundwater ages by other methods in the Algerian aquifer has not been attempted to date. Preliminary results for CI waters in the Tunisian aquifer by Petersen et al. (2013) and Fröhlich (2013) suggest residence times ~500 ka based on an apparent decreasing trend of ^{234}U/^{238}U activity ratios (^{234}U $\tau_{1/2} = 244.5 \times 10^3$ a) with increasing U-contents (see also Bonotto, 2006). In the current study, the evolution of U, ^{234}U/^{238}U A.R., ^{226}Ra (including ^{228}Ra/^{226}Ra A.R.), and ^{222}Rn systematics particularly along a flow line in the Algerian CI are discussed in terms of ^{238}U-series systematics and groundwater dating (including also ^{4}He ages).

2. Study area

The Continental Intercalaire (CI) aquifer underlies continuously an area ~600,000 km^2 in Algeria and Tunisia (Castany, 1982) and ~100,000 km^2 overall (including Libya). In Algeria, the M'Zab Ridge running N–S (Fig. 1) structurally provides a watershed divide between (to the west) the Grand Erg Occidental and (to the east) the Grand Erg Oriental hydrogeological basins. The shallower, overlying Complexe Terminal (CT) aquifer covers ~35,000 km^2. In the Grand Erg Occidental the two aquifers are hydraulically connected (cf. Moulla et al., 2012), whereas in the Grand Erg Oriental the two aquifers are separated by semi-permeable/impermeable layers and confined, artesian conditions exist for the CI aquifer towards the centre of this basin.

The CI formation comprises permeable continental detrital deposits of sand-sandstone and argillaceous sands with intercalations of marine clays and arenaceous clays of Lower Cretaceous (Albian) age (Furon, 1963). Except at its borders and in the western and Djeffara sub-basins, the CI aquifer is confined over the major part by a series of Upper Cretaceous (predominantly Cenomanian) transgressive clays with evaporites. Underlying the whole of the central region from Hassi Messaoud to the great salt-lake Chotts in the N is the confining basal Upper Jurassic Malm. The CT aquifer groups under the same name several very heterogeneous formations: permeable beds of (Upper Cretaceous) Senonian limestones, with Turonian dolomites on the borders (Dahar, M'Zab), and (Tertiary) Mio-Pliocene sands (the CT proper). Guendouz (1985) includes within this CT unit the phreatic aquifer system of the Quaternary aeolian dunes.

The recharge area for the CI aquifer in the Algerian study area is in the Atlas Mountains ~400 km to the NW (Gonçalvès et al., 2013; Fig. 1). The aquifer is hydraulically continuous from here to the Chotts of Tunisia where it discharges. Groundwater samples for radioelements and their isotopes have been taken (Fig. 1) from 12 wells in the Eastern Great Erg (Grand Erg Oriental) basin of Algeria, samples A1–A10 follow a NW–SE radial flow direction identified originally by Guendouz (1985, his Fig. 3) from piezometric data for the CI aquifer and confirmed from the latest piezometric map (OSS, 2003, Planches 10–13). Two samples (A12, A13) were taken from the overlying, shallower CT aquifer, and a further CI sample from a new well (A14) to the North.

A dozen groundwater samples from Tunisia are also reported here: 7 in the CI proper, 2 in the CT, and 3 associated with both aquifers (CI/CT). Major flow directions in the extensive CI aquifer system (Fig. 1) appear broadly to converge on the major Chotts west of Gabès in Tunisia: W–E from the Saharan Atlas to Chott Djerid and the Gulf of Gabès; SW–NE from the M'zab ridge region of southwestern Algeria and the Tademait Plateau and/or the Tinrhert Plateau (S–N) towards Chott Fedjej/Gulf of Gabès; S–N from local recharge in the Dahar uplands in southern Tunisia. The Tunisian CI samples presented here generally are located to the East of the horst structure identified around the region of Tozeur (T9; cf. Edmunds et al., 2003, their Fig. 13) and likely therefore the flow direction is oriented predominantly S–N from the Tinrhert plateau of southern Algeria or the Tunisian Dahar Hills as the possible