Distinguishing seawater from geologic brine in saline coastal groundwater using radium-226; an example from the Sabkha of the UAE

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ABSTRACT

Sabkhat (Salt flats) are common geographic features of low-lying marine coastal areas that develop under hyper-arid climatic conditions. They are characterized by the presence of highly concentrated saline solutions and evaporitic minerals, and have been cited in the geologic literature as present-day representations of hyper-arid regional paleohydrogeology, paleoclimatology, coastal processes, and sedimentation in the geologic record. It is therefore important that a correct understanding of the origin and development of these features be achieved. Knowledge of the source of solutes is an important first step in understanding these features. Historically, two theories have been advanced as to the main source of solutes in sabkha brines: an early concept entailing seawater as the obvious source, and a more recent and dynamic theory involving ascending geologic brine forced upward into the base of the sabkha by a regional hydraulic gradient in the underlying formations. Ra-226 could uniquely distinguish between these sources under certain circumstances, as it is typically present at elevated activity of hundreds to thousands of Bq/m^3 (Becquerels per cubic meter) in subsurface formation brines; at exceedingly low activities in open ocean and coastal water; and not significantly supplied to water from recently formed marine sedimentary framework material. The coastal marine sabkha of the Emirate of Abu Dhabi was used to test this hypothesis. The distribution of Ra-226 in 70 samples of sabkha brine (mean: 700 Bq/m^3), 7 samples of underlying deeper formation brine (mean: 3416 Bq/m^3), the estimated value of seawater (<16 Bq/m^3) and an estimate of supply from sabkha sedimentary framework grains (<~6 Bq/m^3) provide the first direct evidence that ascending geologic brine contributes significantly to the solutes of this sabkha system.

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1. Introduction

Sabkhat (salt flats) are extensive geographic features in many arid and hyper-arid coastal environments of the world and are typically associated with highly concentrated brines occurring in the shallow surficial aquifers beneath the surface. As a result, contemporary sabkha environments have become geological analogs for evaporitic environments in the sedimentary record and therefore it is important to identify and correctly understand the processes responsible for accumulation of solutes in these systems.

Early models of sabkha brine formation assumed that the solutes were concentrated by evaporation of seawater (Kinsman, 1969; Butler, 1969; Patterson and Kinsman, 1977, 1981, 1982) or seawater and shallow groundwater (Hsü and Siegenthaler, 1969; Hsü and Schneider, 1973; McKenzie et al., 1980; Müller et al., 1990).

Later, a fundamentally different model was presented whereby the majority of the water making up these brines was supplied by local rainfall, but solutes originated to a large extent from upward migration of geologic brine from deeper formations, with seawater contributing only initially and in a minor way to the composition (Sanford and Wood, 2001; Wood and Sanford, 2002; Wood et al., 2002; Wood et al., 2005; Wood and Sanford, 2007; van Dam et al., 2009).

This ascending brine model (ABM) overcame difficulties inherent in sea water-based models, and was in agreement with solute mass balance, water isotope data, solute ratios and positive hydraulic head in the underlying formations. However, clear direct evidence that the model functioned as described, and is currently active, was lacking. Here we use the presence of Ra-226 to provide such primary evidence based on 1) its elevated activity of several hundred to thousands of Bq/m^3 (Becquerels per cubic meter) in subsurface brines (Kraemer and Reid, 1984; Vengosh et al., 2009), 2) near absence in open ocean and coastal seawater (<16 Bq/m^3, Okubo et al., 1979; Moore et al., 1985; Liu et al., 2010; Su et al., 2010; Ohta et al., 2011; Charette et al., 2013), and 3) lack of supply in significant amounts (as compared to formation brines) by sedimentary grains (<~6 Bq/m^3).

The presence of radium in significant amounts (greater than a few hundred Bq/m^3) in the sabkha brine would therefore be strong evidence for the ultimate source of solutes being from geologic brines, whose accumulation in the sabkha brine, additionally, would have to be recent owing to the geologically short half-life of Ra-226 ($t_{1/2} = 1601$ y).

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2. Site description

Our study area is in the coastal region of the Arab Gulf, southwest of Abu Dhabi City in the United Arab Emirates, the classic site where most studies relating to development of sabkha-hosted hyper-saline brines has taken place. The area (Fig. 1) is a flat, low-lying region approximately 300 km long by 10 km wide. The surficial formation (Abu Dhabi formation, Wood et al., 2002) upon which the sabkha has developed has been inferred by sedimentalogical and ^{14}C methods at 7000 y or older (Evans, 1995) and by the optically stimulated luminescence method at 8000 ± 800 y (Wood et al., 2002), and overlies local cemented Pleistocene age dunes and more regional carbonate deposits of the Middle to Upper Miocene age Gachsaran Fm. (Peebles, 1999).

The wedge-shaped sabkha formation averages 10 m in thickness (thickest toward the Gulf) and is composed of un-cemented, reworked sand dune deposits of uniform grain size (98% of its mass is between 0.16 and 0.22 mm) exhibiting a porosity of approximately 0.38 (+/− 5%), spatially uniform hydraulic conductivity of approximately 1 m/d (+/− 25%), low hydraulic gradient (0.00014) and seepage velocity of approximately 0.15 m/y. Annual rainfall, associated with Shamal (north) winds in January through March, averages 60 mm over the study area. Annual potential evaporation exceeds 3800 mm (all values from the work of Wood and others, see references cited).

Authigenic mineral precipitation is common and largely limited to the surface and capillary zone below the sabkha surface as water is drawn upward in response to intensive evaporation and regional hydraulic head. Retrograde soluble calcite, dolomite, gypsum, and anhydrite precipitate within the capillary zone, while halite, carnallite, sylvite, and niter precipitate on the sabkha surface.

3. Methods

Three different drilling techniques were used in installing the wells and piezometers from which the samples were taken. The shallow RP-series ("R" designations on Fig. 1) piezometer nests were drilled using mud-rotary equipment in a profile perpendicular to the Gulf shoreline approximately 60 km west of Abu Dhabi City. All piezometer nests, except those at site RP-5, are completed at various depths in the Abu Dhabi formation. Five-centimeter diameter PVC pipe, slotted by a hacksaw on the bottom 0.5 m and fitted with end cap, identification collar, and cap, was installed into the holes immediately after drilling. Water samples from the RP piezometers were collected by peristaltic pump. Pump tubing was rinsed both inside and out in distilled water prior to sampling, and several liters of brine were pumped to waste before installing an in-line filter for sample collection. Three well volumes were discharged before sampling all wells.

The deep GWP-series of wells ("G" designation on Fig. 1) were drilled parallel to the coast using reverse air rotary equipment and penetrated into the underlying bedrock of Miocene age. These wells were finished with approximately 40 m of steel surface casing, with open hole for the remainder of their total depth. All of the GWP wells flowed
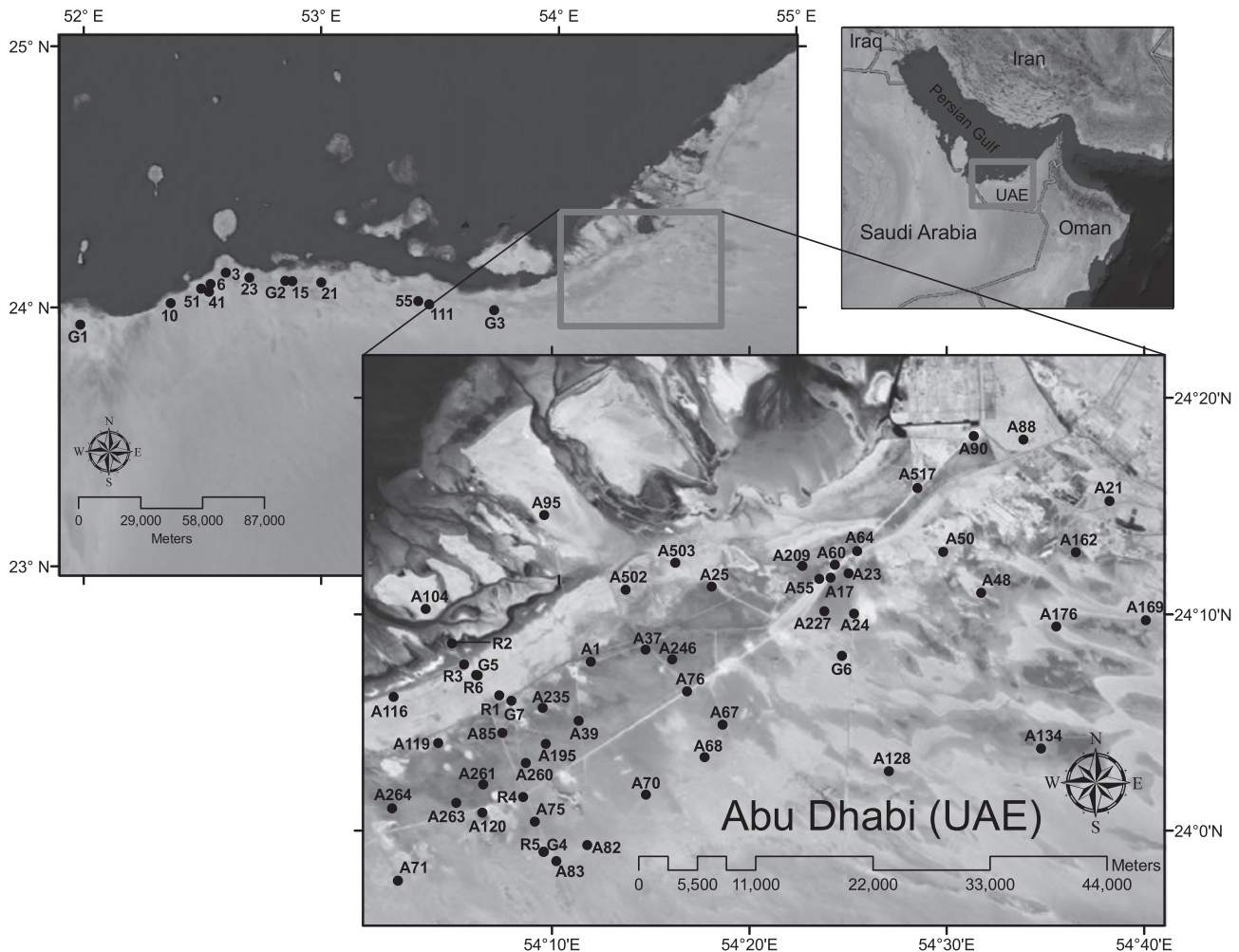

Fig. 1. Location map of study area. Sample designations are described in the text and Table 1. Abu Dhabi City is located just to the north of the expanded box.

Table 1
Location and Ra-226 activity of samples analyzed.

Field identification	Latitude N	Longitude E	Map	^{226}Ra Bq/m^3
Sabkha				
ABU 001	24.1303	54.1992	A1	338
ABU 017	24.1943	54.3923	A17	1333
ABU 021	24.2543	54.6372	A21	302
ABU 023	24.1985	54.4170	A23	3750
ABU 024	24.1673	54.4217	A24	7050
ABU 025	24.1881	54.3012	A25	117
ABU 037	24.1396	54.2455	A37	352
ABU 039	24.0848	54.1890	A39	680
ABU 048	24.1834	54.5291	A48	2217
ABU 050	24.2149	54.4967	A50	2637
ABU 055	24.2049	54.4054	A55	537
ABU 060	24.1953	54.4018	A60	1017
ABU 064	24.2156	54.4243	A64	540
ABU 067	24.0819	54.3107	A67	457
ABU 068	24.0569	54.2953	A68	193
ABU 070	24.0278	54.2458	A70	325
ABU 071	23.9615	54.0365	A71	168
ABU 075	24.0071	54.1520	A75	525
ABU 076	24.1075	54.2805	A76	400
ABU 082	23.9889	54.1965	A82	468
ABU 083	23.9766	54.1703	A83	235
ABU 085	24.0755	54.1246	A85	322
ABU 088	24.3015	54.5646	A88	230
ABU 090	24.3042	54.5227	A90	307
ABU 095	24.2433	54.1601	A95	475
ABU 104	24.1709	54.0601	A104	118
ABU 116	24.1031	54.0330	A116	257
ABU 119	24.0676	54.0705	A119	692
ABU 120	24.0138	54.1079	A120	937
ABU 128	24.0460	54.4511	A128	202
ABU 134	24.0633	54.5793	A134	42
ABU 162	24.2146	54.6088	A162	178
ABU 169	24.1624	54.6679	A169	383
ABU 176	24.1574	54.5924	A176	2033
ABU 195	24.0670	54.1613	A195	2033
ABU 209	24.2041	54.3780	A209	277
ABU 227	24.1693	54.3966	A227	1268
ABU 235	24.0947	54.1585	A235	278
ABU 246	24.1322	54.2681	A246	937
ABU 260	24.0521	54.1445	A260	650
ABU 261	24.0356	54.1085	A261	783
ABU 263	24.0215	54.0856	A263	1043
ABU 264	24.0172	54.0315	A264	1200
ABU 502	24.1858	54.2286	A502	533
ABU 503	24.2067	54.2708	A503	1083
ABU 517	24.2641	54.4752	A517	1210
RUW 003	24.1323	52.5980	3	180
RUW 006	24.0897	52.5337	6	103
RUW 010	24.0163	52.3666	10	863
RUW 015	24.1003	52.8785	15	540
RUW 021	24.0958	53.0003	21	2497
RUW 023	24.1129	52.6971	23	372
RUW 041	24.0599	52.5271	41	58
RUW 051	24.0713	52.4941	51	53
TAR 055	24.0233	53.4090	55	28
TAR 111	24.0112	53.4550	111	12
RP 1–2.5	24.1043	54.1219	R1	152
RP 1–10.0	24.1041	54.1219		355
RP 1–36.0	24.1043	54.1220		330
RP 2–4.5	24.1444	54.0820		33
RP 2–12.0	24.1445	54.0820	R2	15
RP 2–21.0	24.1445	54.0821		28
RP 3–3.0	24.1281	54.0922	R3	10
RP 3–10.0	24.1281	54.0922		23
RP 4–3.0	24.0260	54.1421	R4	390
RP 5–16	23.9839	54.1593	R5	543
RP 5–35	23.9840	54.1593		533
RP 6–10.0	24.1198	54.1040	R6	313
RP 6–16.0	24.1199	54.1036		428
RP 6–35.0	24.1198	54.1040		617
Miocene bedrock				
GWP 289 (119 m)	23.9891	53.7282	G3	745

Table 1 (*continued*)

Field identification	Latitude N	Longitude E	Map	^{226}Ra Bq/m^3
GWP 290 (88 m)	23.9839	54.1596	G4	910
GWP 288 (89 m)	24.1010	52.8476	G2	2333
GWP 306A (137 m)	24.1003	54.1323	G7	3662
GWP 292 (119 m)	24.1347	54.4112	G6	4000
GWP 291 (142 m)	24.1201	54.1025	G5	4560
GWP 287A (121 m)	23.9333	51.9859	G1	7688

Bq/m^3 (Becquerels per cubic meter).
m (meters below land surface).
Map: location in Fig. 1.

and were fitted with a watertight cap, small diameter-sampling pipe, shut-off valve, and pressure gage.

Shallow piezometers (designated "ABU", "TAR", and "RUW" in Table 1 and as alpha-numerics in Fig. 1) were drilled to a depth of between 1 and 2 m below the water table using a portable, auger-type drill. Five-centimeter diameter PVC pipe, slotted by a hacksaw on the bottom 0.5 m and equipped with a wooden-drive point, identification collar, and cap, was installed into the holes immediately after drilling.

Chemical analyses of the brines were performed using techniques and methods as reported by Wood et al., 2002. Results of some of the chemical analyses have been reported previously in the publications referenced above describing the ascending brine model (the RP series samples).

Radium analyses were carried out on clear or filtered samples (generally 100 ml or less for shallow sabkha samples, up to 1000 ml for GWP and some RP samples) by adding 6 ml of saturated $Ba(NO_3)_2$ solution. Normally there was enough natural sulfate present in the sample to precipitate sufficient $Ba(Ra)SO_4$ for analysis. However, in a majority of cases H_2SO_4 was added to ensure conditions for complete precipitation of barite. The precipitate was collected, washed, dried and placed in a polyethylene vial for counting in a 25% relative efficiency, well-type HPGe detector. Aliquots of NBS 4539 radium standard were processed in the same manner as the samples to calibrate the efficiency of the processing and counting procedures.

To determine uranium concentration an aliquot of sample was diluted several-hundred fold with 0.1 N HCl and analyzed by using the EPA method 200.8 (EPA, 1994) on an Elan 9000 ICP/MS. After uranium concentrations were determined, a suitable volume of sample was processed for U-234/U-238 activity ratio according to the method of Kraemer et al. (2002), using an Elan 9000 ICP/MS with ultrasonic nebulizer.

4. Results

77 samples, collected from the entire length of the sabkha, were analyzed for Ra-226 (Table 1) and many also for major ions (Table 2, most from previously unpublished sources). The most intensive sampling was done south of the city of Abu Dhabi, where the sabkha has its maximum width (Fig. 1), and in the area where most of the previous work published in the literature has taken place.

Total dissolved solids of the brines were in general very high, mostly above 200,000 mg/l, similar to results found by others working in the region (Butler, 1969; Patterson and Kinsman, 1981; Kinsman, 1969; McKenzie et al., 1980) and consist of sodium/chloride brines with high concentrations of calcium and magnesium and a Mg/Ca ratio (on a mass basis) over a range from 0.5 to 2, but which in some cases approach 10 (e. g. RP3-3.0), presumably representing areas where gypsum or anhydrite precipitation is occurring. Sulfate is common at nearly all sabkha sites, as well, although in many instances is less concentrated than other, more conservative, ions suggesting removal by sulfate mineral precipitation during the brine formation process. Sulfide was not

Table 2
Chemical and uranium isotopic composition of some Abu Dhabi sabkha samples.

ID number	Na	Ca	Mg	K	Cl	SO4	Br	Ba	TDS	pH	U-234/U-238	Error	U	Ra-228/Ra-226
ABU001	105,000	3500	1500	1200	164,300	3750	10	160	282,751	7.6				
ABU017	40,300	40,000	31,000	13,600	240,000	200	50	2300	374,570	5.6				
ABU021	92,500	4200	10,800	4100	190,000	1300	25	300	304,734	6.7				
ABU023	41,000	25,000	18,300	7650	171,500	700	35	600	268,347	6.2				
ABU024	71,500	15,800	17,900	7100	197,000	650	15	480	314,658	6.0				
ABU025	93,100	3700	7600	4250	178,000	1900	60	140	289,735	6.9				
ABU037	85,000	8600	11,700	6200	190,500	850	25	320	307,577	6.3				
ABU039	78,500	10,500	13,900	7350	186,500	850	25	780	303,208	6.4				
ABU048	59,000	28,000	19,000	4850	198,500	6050	37		319,485	6.0				
ABU050	80,600	6600	3700	1900	140,700	2400	20	700	236,591	7.4				
ABU055	29,000	50,000	37,000	7500	247,300	6000	33		384,577	5.4				
ABU060	70,000	24,000	18,000	5600	208,000	5900	5		335,931	6.0				
ABU064	50,000	35,000	25,000	6100	208,700	5900	32		335,291	5.8				
ABU075	100,400	5800	6000	3600	182,000	2000	33	80	302,168	6.8				
ABU076	98,000	6200	6800	3300	188,000	1500	17	260	306,927	6.9				
ABU085	7200	17,500	14,500	5800	186,400	900	20		302,436	6.4				
ABU090	90,000	8500	7500	3700	176,000	1300	340		287,717	6.7				
ABU104	87,000	3400	6500	4400	155,000	3100	335		259,924	6.7				
ABU116	83,100	5700	8500	4300	161,400	2200	315		265,776	6.6				
ABU120	67,200	12,500	8500	3300	155,800	1150	10		253,367	6.7				
ABU134	83,000	13,000	13,000	4000	184,000	950	80	180	299,700	6.6				
ABU162	89,000	8900	9600	3000	177,500	1300	62	100	290,775	6.7				
ABU169	87,000	4300	7200	2750	158,600	2200	21	80	262,503	6.8				
ABU176	114,000	3050	4100	2350	183,000	2600	11	370	309,929	7.4				
ABU195	79,000	19,000	15,000	7000	194,000	950	33	1500	320,969	6.5				
ABU209	82,000	13,700	9700	4850	177,500	7100	11	325	298,019	7.2				
ABU227	84,000	14,500	12,900	5400	180,000	7400	12		308,319	6.2				
ABU235	89,000	11,900	10,000	4600	177,500	7200	45	550	303,272	6.7				
ABU246	86,000	15,000	13,300	6100	184,000	7200	6		317,910	6.5				
ABU260	79,600	11,500	10,000	5300	176,500	7200	10	800	295,947	6.7				
ABU261	79,500	14,400	13,700	7950	180,000	7200	9	1200	307,346	6.6				
ABU263	96,900	8100	7100	4800	173,000	8100	8	500	303,011	7.0				
ABU264	103,800	4200	4100	4000	171,000	8100	9	250	298,587	6.7				
ABU502	93,200	8000	10,900	5100	194,500	3400	355		322,887	6.2				
ABU503	102,000	6000	8400	4600	202,000	4600	250		328,209	6.4				
ABU517	82,500	13,600	18,000	6200	200,000	5100	285		326,533	5.6				
RUW003	78,000	6000	6200	2500	152,000	1500	230		247,019	6.2				
RUW006	100,000	1500	2600	1900	172,000	4700	30		284,261	6.7				
RUW010	84,000	11,300	12,500	4200	196,000	1000	60		313,371	6.3				
RUW015	98,500	3100	5800	2430	182,000	2000	45		295,702	6.7				
RUW021	97,500	7800	8200	5000	193,000	900	25		318,374	6.5				
RUW023	104,000	3600	4400	2600	180,000	1600	30		298,858	6.8				
RUW041	70,800	950	1700	1400	111,000	10,700	50	40	197,002	7.5				
RUW051	119,000	3000	4600	3000	196,400	3000	36	20	330,243	6.8				
TAR055	40,000	1000	1800	1100	60,500	14,000	60	20	118,602	7.6				
TAR111	112,000	750	1000	4000	164,000	19,500	67	40	302,210	7.3				
RP1–2.5	86,500	4650	9400	3700	166,000	3800	41		274,646	6.8				
RP1–10.0	85,500	4600	10,000	4000	178,000	4000				6.5			0.5	
RP1–36.0	87,000	4550	9850	3900	174,000	4000			283,454	6.8			0.5	
RP2–4.5	31,000	1400	3500	1100	57,000	10,000			104,136	7.3	1.144	0.010	9.7	
RP2–12.0	60,000	1100	6700	2050	112,000	12,000			197,000	7.0	1.102	0.006	5.5	
RP2–21.0	71,000	1450	6850	2550	123,000	8800			213,806	6.9	1.144	0.004	16.1	
RP3–3.0	97,000	975	9550	3875	167,000	10,000			288,554	6.9	1.155	0.005	2.8	
RP3–10.0	87,000	1650	6700	3150	151,500	8400			258,566	7.2	1.155	0.007	0.6	
RP4–3.0	91,500	5800	6500	3200	172,000	1600			280,786	6.7			0.2	
RP5–16	34,000	2000	2000	550	60,000	7000			105,657	7.4				
RP5–35	34,000	2200	2000	600										
RP6–10.0	91,000	3750	4300	2700	151,000	5250			258,111	7.0			0.1	
RP6–16.0	91,000	3750	4300	2700	151,000	5250			258,111	7.0				
RP6–35.0	92,000	4100	4650	2650	153,000	5200			261,727	6.8			0.6	
GWP287	35,000	4800	2600	1300	69,500	2850	140		118,039					0.05
GWP288	10,500	1450	950	300	19,700	4050	11		37,109	8.0				0.07
GWP289	5600	1150	675	120	10,300	4000	5		21,922	7.8				0.11
GWP290	15,500	1500	950	450	25,000	6750	15		50,251	7.4				0.07
GWP291	31,500	2200	1350	950	55,100	4650	20		95,867	7.8				0.04
GWP292	48,000	3600	2400	1500	87,300	3300	6		146,239	7.4				0.15
GWP306	34,500	2750	1250	1100	62,500	4800	12		107,056					0.01
Arab Gulf	13,000	625	1750	625	24,000	3450	72		43,563	7.6	1.16[a]	0.03[a]	4.1	
Sabkha material carbonate														
Random selection 1											1.138	0.004		
Random selection 2											1.150	0.004		
Random selection 3											1.157	0.006		

analyzed in any of these samples, but no H_2S odor or black precipitate was noticed during the preparation of samples in the field or laboratory.

Varying Ra-226 activity is found in the brine along the extent of the sabkha, including several occurrences greater than 1000 Bq/m³. A two dimensional picture of greater areal resolution is possible in the area just to the south of the city (Fig. 2), where values reach as high as 7050 Bq/m³. The lowest-radium areas occur along irregular seaward and landward edges of the sabkha.

Owing to the nature of the gamma spectroscopic method used in this study, Ra-228 as well as Ra-226 can be quantified from the same spectrum, if it is present in sufficient activity. The nature of the sabkha samples is such, however, that due to the generally small sample size available, the activity of Ra-228 present in the sabkha sample aliquots is unquantifiable or undetectable. The GWP-series sample analyses were of sufficient quality that it can be determined that the Ra-228/Ra-226 activity ratio of all samples is less than or equal to 0.15.

5. Discussion of sources of radium

A. Seawater

The Ra-226 in the sabkha brines could originate from a number of different sources, many of which are difficult to quantify due to a lack of knowledge of the detailed compositions of these possible sources. It is important, however, to reasonably estimate or evaluate their potential magnitudes.

The first possibility to be considered is whether seawater could be a viable source of the Ra-226 by itself. Studies of radium in seawater clearly demonstrate that Ra-226 occurs in quantities less than 1 or 2 Bq/m³, even in coastal regions receiving riverine supplies of water and sediment (Moore, 1976; Okubo et al., 1979; Moore, 1981; Moore et al., 1985; Liu et al., 2010; Su et al., 2010; Ohta et al., 2011). The coastal Arab Gulf itself has been found to contain low values of Ra-226 of no higher than 5 Bq/m³ (Fadlelmawla et al., 2013). One sample of Arab Gulf seawater taken from a beach area during our study, in the approximate mid-point of the sabkha study area length, although of small volume, was found to contain no activity of Ra-226 above blank amounts, and is therefore conservatively interpreted to contain Ra-226 activity less than 30 Bq/m³. It is therefore unlikely that seawater could be the major source of the highest radium activities found in the sabkha brines. It could, however account for the Ra-226 found around the RP2 (within 10 m of high tide) and RP3 (also close to the coast) piezometer nests. Here, the Ra-226 values range between 10 and 33 Bq/m³. Assuming a 7-fold evaporation based on the dissolved chloride ratio between RP3-3 (167,000) and Arab Gulf water (24,000 mg/l), the Ra-226 activity of seawater would be between 1.4 and 4.7 Bq/l, consistent with reported values. In like manner, the lowest values found in sabkha brine along the rest of the sabkha could also be attributed to a seawater source.

B. Matrix

The other source of radium that needs to be considered is the sedimentary framework material itself. All Earth surface material contains some U and Th, and therefore, radium that could potentially be supplied to the brine, either by chemical or physical (alpha-recoil) processes.

Two chemical processes could contribute radium to the brine. One is dissolution of mineral grains containing radium, the other is desorption of radium from surface locations on matrix grains.

Evaporated seawater is a poor solvent for the majority of matrix, which is composed of seawater-precipitated carbonate grains and detrital quartz and clay silicate grains blown or washed in from surrounding areas, as seawater is saturated with respect to carbonate minerals (Chave and Suess, 1970) and simple evaporation of seawater does not increase carbonate solubility, but rather can cause precipitation to occur (McCaffrey et al., 1987).

Secondly, for the majority of the sediment grains (carbonate), their age is too young (Pleistocene to Holocene) to have had the ability to generate Ra-226 from the uranium contained within them, so that even if dissolution were occurring, there would be little radium to supply to the brine. The young age of the carbonate grains is proven by the U-234/U-238 ratio of several samples of carbonate material, which averages 1.15 (modern seawater) (Table 2). Due to the fact that production of Ra-226 is governed by the in-growth of the 76,000 y half-life nuclide Th-230 in the uranium-series decay chain, and as carbonate minerals precipitating from seawater contain little to no initial Th-230 due to its near absence in seawater (Robinson et al., 2004), insufficient time would have elapsed between time of incorporation of uranium (without Th-230) within the grain and any dissolution process, if active, presently removing the Ra-226.

Quartz and other silicate mineral grains have even lower solubility, and are less likely candidates to supply radium during dissolution, even though they may contain several parts per million of uranium and an equilibrium activity of daughter Th-230.

To further emphasize the shear inability of dissolution to contribute any measurable amount of radium to the sabkha solution, consider that calcite has a solubility in fresh water of about 15 mg/l and commonly contains 3 ppm U if precipitated in a marine environment (Osmond et al., 1965; Robinson et al., 2004). Therefore about 5×10^{-8} g (or about 0.0006 μBq) of uranium would be released during dissolution of calcite in 1 l of water, an insignificant amount, resulting in a negligible contribution of Ra-226 even if it were in equilibrium with the uranium.

Adsorption/desorption processes are likewise thought to be of limited effect in determining the Ra-226 activity in the brine. In order for high values of Ra-226 to be found in the brine from desorption from matrix grains, a large percentage of the aquifer material would have to be composed of clay-sized material, contain a large amount of Ra-226 (or Th-230 or U-234), or both. The actual composition of the aquifer material as described by Wood and coworkers states that 98% of the matrix mass is between 0.16 and 0.22 mm in diameter and composed of mostly carbonate and quartz grains. Typically, this type of material would have low exchange capacity, and not be expected to supply adsorbed Ra-226 to solution even as salinities increased due to evaporative concentration.

Most of the remaining 2% of mass is either fine-grain gypsum or anhydrite (authigenic precipitates) or, depending on location, palygorskite, another authigenic material, as revealed by X-ray analysis. Only traces of additional aluminosilicate clay minerals are found. This would make it unlikely that radium brought into the sabkha adsorbed onto fine-grained material would be desorbed. Although unquantifiable, it is difficult to envision exchangeable material added during deposition of the sabkha as adding more than a trace of Ra-226 to the sabkha brine.

The final means of supplying radium from the solid matrix to brine phase is the physical process of alpha-particle recoil, whereby an atom of a decay product in a decay chain is ejected across a phase boundary by the process of alpha decay (Kigoshi, 1971). In this situation, Ra-226 could be ejected from a sabkha grain into pore-water brine as a result of the decay of its parent, Th-230. In fact, there
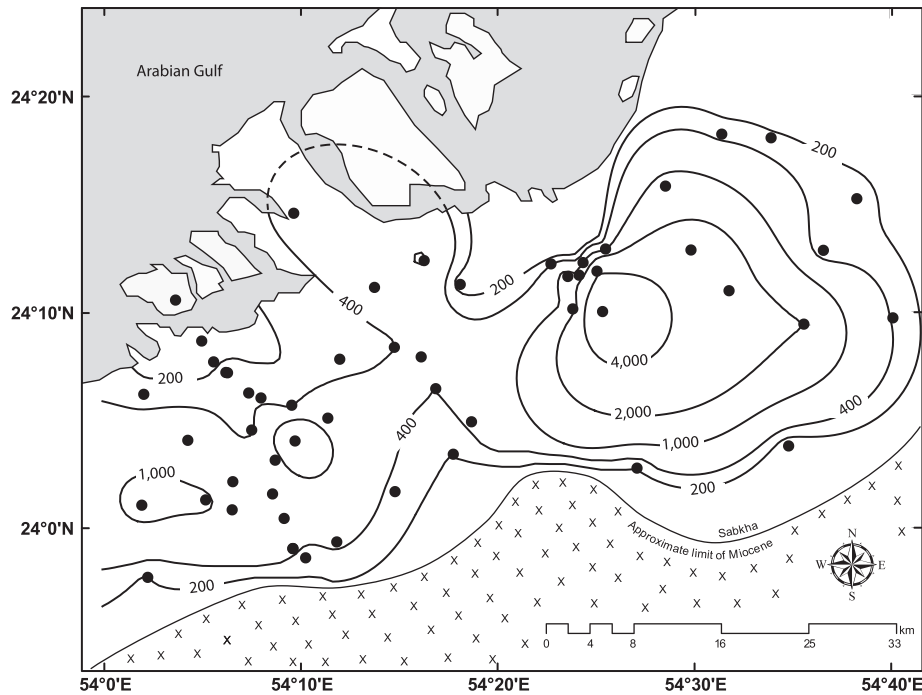
Fig. 2. Contour map of Ra-226 activity in sabkha brine in the area south-west of the city of Abu Dhabi, UAE. Note that to improve clarity the contour intervals do not increase in a constant manner.

would be three opportunities for Ra-226 to ultimately enter solution as a result of alpha-particle decay, since there are three such decay modes in the uranium decay series before Ra-226 is formed (the decay of U-238 to Th-234, the decay of U-234 to Th-230, and the decay of Th-230 to Ra-226). Any of these decays could eject a nuclide that would eventually result in Ra-226 occurring in solution. Kraemer (1981) estimated the equilibrium amount of U-234 recoiled into brine from a sand-grained matrix via alpha-particle recoil using the formula:

$$U\text{-}234_{recoil} = 3LU_{ppm}\rho(1-\phi)C/4r\phi \tag{1}$$

where $U\text{-}234_{recoil}$ is the amount of U-234 that is supplied to a saturating solution occupying the porous space of a rock, L is the recoil length that the decaying atom of U-234 travels as a result of alpha particle emission from the nucleus during decay of U-238, U_{ppm} is the uranium concentration of the matrix grains, ρ is the density of the mineral grains, ϕ is the porosity of the rock, r is the radius of a spherical matrix grain, and C is a proportionality constant. This equation is based on the fact that U-238 will decay to Th-234 and may be transported across a grain/brine interface during this process of decay. The Th-234 then decay into U-234. A modification is needed for the present application to take into consideration that the decay of U-238 to Ra-226 involves three alpha decays (U-238 to Th-234, U-234 to Th-230, and Th-230 to Ra-226), thus giving the atom three chances to enter solution by the physical process of alpha particle recoil. We will neglect considering the chemistry of the products and the possibility of their adsorption once in solution to demonstrate the maximum supply.

Using the modified equation we have:

$$Ra\text{-}226_{recoil} = 3NLU_{ppm}\rho(1-\phi)C/4r\phi \tag{2}$$

where N is the number of alpha decays between the decay of U-238 and the formation of Ra-226. The other symbols are as before. Using $N = 3$, $L = 2 \times 10^{-8}$ m, $U_{ppm} = 3$ μg/g, $\rho = 2.6 \times 10^{6}$ g/m³, $\phi = .38$, r $= 8 \times 10^{-5}$ m and $C = 0.0125$ Bq/μg U-238, the activity present in

the pore water brine at secular equilibrium will be no greater than 90 Bq/m³. This, however, is a maximum value that will only occur after a period of several hundred thousand years, when the system approaches or achieves secular equilibrium. The Abu Dhabi formation, however, is only about 7000 to 8000 years old, so the Ra-226 could only have been accumulating in the pore space for this length of time. If the conditions for the above calculation were operating over 8000 years, the accumulated amount of Ra-226 would be approximately:

$$Ra\text{-}226_{recoil} = Ra\text{-}226_{equil}(1 - \exp(-\lambda_{230}t)) \tag{3}$$

where $Ra\text{-}226_{recoil}$ is the activity of recoil accumulated Ra-226 in the brine after time t, $Ra\text{-}226_{equil}$ is the activity of Ra-226 in the brine when secular equilibrium has been established, and λ_{230} is the decay constant of Th-230, the immediate parent of Ra-226. Therefore, after 8000 years the Ra-226 activity in the sabkha brine as a result of alpha-particle recoil of Ra-226 would be about 6.3 Bq/m³. Even this is a maximum value, since many of the grains making up the matrix are Pleistocene carbonate grains which initially inherit little to no Th-230 during formation, and thus are incapable of supplying Ra-226 in the amount calculated in Eq. (3).

This calculation, while approximate, is intended to show the generally low transfer efficiency of alpha-particle recoiled nuclides from sand-sized particles that make up the vast majority of sabkha material. It is also not likely that the sabkha matrix contains particles with significantly higher uranium concentrations than we have assumed, in that other than marine carbonates the only other sources for sediment in the region are basic to ultrabasic rocks that occur in, for example, the Oman Mountains to the east. This type of rock typically contains less uranium than marine limestones (Larsen and Gottfried, 1960).

Based on the above discussion of chemical and physical process that may supply Ra-226 to brine pore water we conclude that a significant amount of Ra-226 is unlikely to accumulate as a result of their operation. A final question to be resolved is to what extent does the evaporation process itself increase in activity of Ra-226 that may be supplied to the brine by these means?

Typically, if seawater or ascending brine containing radium were continuously supplying the sabkha, the water would evaporate, concentrating the solutes, including radium, in the remaining brine, and the evaporated volume of water would be replaced by new inflowing brine. This is obviously because there is a flow of solutes into the system without subsequent flow out. However, in the case where a component is being supplied by a process independent of what is being brought in by the external source, this concentration mechanism does not apply. Thus, the activity of Ra-226 in solution from the matrix sources would be independent of any solvent evaporation taking place as long as the pore space remains saturated with inflowing brine. To a large degree, therefore, any radium being supplied by processes acting upon the sediment matrix will not be concentrated in the brine as a result of evaporation.

C. Brine

All of the previous discussion has been to illustrate that seawater and matrix material of the sabkha are poor suppliers of radium to the brine. However, based on the data presented in Table 1, activities of Ra-226 are commonly high, and in fact many greatly exceed the estimated supply from matrix material, lending support to the proposal that some other mechanism is responsible for these values.

According to the model of Sanford and Wood (2001), ascending brine enters the Abu Dhabi formation vertically and from inflow from the proximal edge (the contact with the Miocene formations, Fig. 2), where solutes (including radium) then undergo a concentration process as a result of evaporation. To date, according to their analysis, about a seven-fold increase in conservative solutes in the brine should have occurred during the time the sabkha has been developing (about 8000 y), a number that is supported by the approximate seven-fold increase they found in the most conservative element, Mg, in the sabkha brine as compared to the average geologic brine composition (Wood et al., 2002).

Ra-226, like many other non-conservative components, does not show activity increases as high as the more conservative elements like Cl and Mg as compared to the ascending brine in most cases, but does show considerably higher activity than could be accounted for by simple concentration of sea water or likely supply from matrix grains by dissolution, adsorption/desorption or alpha recoil effects.

Further, the distribution of the Ra-226 under the sabkha is suggestive of the source of supply being from ascending brines as well. Fig. 2 shows the distribution of Ra-226 in the region just to the south of the city of Abu Dhabi. It is seen that the highest values of Ra-226 occupy the central portion of the sabkha, with activities decreasing generally toward the open Gulf, consistent with only the distal margin brine being formed from evaporation of seawater whose Ra-226 activity is low.

Vertical variability in radium activity is also shown by the data from the research piezometer nests. The two piezometer nests closest to the Arab Gulf (RP 2 and RP 3) show low Ra-226 activities to a depth of 4.5 m, while the piezometer nests within the main part of the sabkha (RP1, RP5 and RP6) produce brine considerably enriched in Ra-226. Piezometer nests RP2 and RP3 represent the minor area of the sabkha where seawater is important as a contributor of brine in general for this area.

The central area of the sabkha represents an area of generally high but variable activity of Ra-226, from about 300 to over 4000 Bq/m³. The large variation in Ra-226 activity within the main body of the sabkha could be due to two factors. First, the flux of up-flow of the geologic brine is likely highly variable regionally, with fractures or areas of variable hydraulic conductivity controlling flow into the aquifer. Second, the Ra-226 activity in the up-flowing brine (as represented by the GWP wells) may not be uniform over a large area. The fact that the activity at Abu 024 (7050 Bq/m³) is higher than any of the deep wells which are likely supplying the sabkha, except for G1 (7688 Bq/m³) to the extreme west of the study area, suggests that there is considerable variation of Ra-226 activity in the geologic brine.

D. The model

To determine whether the radium activities found in the sabkha brines are within the range expected for supply from geologic brine, the model of Sanford and Wood (2001) was applied for calculating the expected concentrations of solutes in the sabkha brines based on hydrologic parameters develop by them. The model was modified to correct for radioactive decay of Ra-226 that would occur during the accumulation period in the sabkha aquifer. The modified equation is thus:

$$A_{pw} = (A_i Q / b\lambda)(1 - \exp(-\lambda t)) \qquad (4)$$

where A_{pw} is the Ra-226 activity of the pore water (Bq/m³), A_i is the Ra-226 activity in the ascending brine (Bq/m³), Q is the flux of water through the base of the aquifer from below (m³/m²/y), b is the aquifer thickness (m), λ is the decay constant for Ra-226 (1/y), and t is the time (y) that the sabkha aquifer has been accumulating the ascending brine. Using values for A_i of 3416 Bq/m³ (the mean of the GWP samples, Table 1), Q of 0.0025 m³/m²/y, b of 10 m, λ of 0.000433 y⁻¹, and a solute accumulation time of 8000 y (all values from Sanford and Wood, 2001), the model predicts that the present day Ra-226 activity in the sabkha aquifer brine would be 710 Bq/m³, taking into account both evaporation concentration effects and radioactive decay. This value is within the range of measured values found for the sabkha samples, is well above what could likely be expected from seawater and matrix supply, and is therefore consistent with the ascending brine model, considering the many field variables that are not well constrained, as discussed below.

Reasons for variation in radium activity found in the sabkha aquifer brine, in addition to those already mentioned, could be the result, at least in part, of differences in brine upwelling rate over geographic area due to variation in hydrologic properties of the rock through which the ascending brine must flow, and a slow horizontal mixing along the axis of the sabkha aquifer.

Additionally, as the ascending brine is transported to the Abu Dhabi formation from deeper it must transit through up to 100 m of intervening formation between these deep aquifers and the base of the Abu Dhabi formation. The transit time through these formations to the base of the Abu Dhabi formation could allow for significant decay of the Ra-226 depending upon the length of time it takes the solutions to cover these distances, assuming no additional sources of radium to (or removal from) the solution from the passed-through formations themselves.

Another cause of radium variation in sabkha pore-water solution after delivery is co-precipitation with barium sulfate (barite), a process that is well known to remove radium from solution (Doerner and Hoskins, 1925; Zhu, 2004). The fact that sabkha samples contain appreciable activities of radium is a strong indication, however, that barite precipitation does not occur extensively from the sabkha brine, since even a small degree of barite precipitation would likely quantitatively remove a majority of radium from solution. However, there are processes and conditions that can occur in aquifers that could allow for the presence of radium in barite-saturated water, under certain situations (such as if the radium entered the pore space after barite precipitation).

6. Summary and conclusions

Wood et al. (2002) proposed an explanation for the origin of hypersaline brine of the sabkhat of coastal Abu Dhabi that addressed shortcomings in previous seawater based models and incorporated known hydrologic facts concerning flow rates and head properties of fluids in the deeper aquifer. Although the ascending brine model (ABM) was an improvement over previous models in its compatibility with existing information, the present-day functioning of such a model could not at the time be conclusively demonstrated. Analysis of Ra-226 in sabkha

brines has shown that contribution of deep geologic brines is the only reasonable source of the radium, and, therefore, other solutes.

The 1601 y half-life of Ra-226 and the abundance of this nuclide in the ascending deep basin brine allowed for an evaluation of the ABM model. Results of model calculations are within the range of actual measurements of radium in sabkha brines and show that the ABM can explain existing radium occurrence in modern sabkha brines, and that the processes described by the model are operating currently and/or in the recent past. We therefore conclude that the ABM is valid and currently active and responsible for the solutes found in the brines of the Abu Dhabi sabkhat. As a result we have 1) confirmed a general model for the possible origin of solute sources in coastal environments, and 2) resolved a classic question on the origin of solutes in the Abu Dhabi coastal sabkha that has been the subject of interest and debate in the literature for over 50 years. This knowledge could be important in managing the resources of low lying sabkha environments worldwide in response to future human efforts of development and mitigating effects of climate-induced sea level rise. It may also necessitate a re-evaluation of the interpretation of sabkha sediments in the geologic record.

Acknowledgments

References

Butler, G.P., 1969. Modern evaporite deposition and geochemistry of coexisting brines, the sabkha, Trucial Coast, Arabian Gulf. J. Sediment. Petrol. 39, 70–81.

Charette, M., Breier, C., Henderson, P., Pike, S., Rypina, I., Jayne, S., Buesseler, K., 2013. Radium-based estimates of cesium isotope transport and total direct ocean discharges from the Fukushima nuclear power plant accident. Biogeosciences 10, 2159–2167.

Chave, K., Suess, E., 1970. Calcium carbonate saturation in seawater: effects of dissolved organic matter. Limnol. Oceanogr. 15 (4), 633–637.

Doerner, H.A., Hoskins, W.M., 1925. Co-precipitation of radium and barium sulfates. J. Am. Chem. Soc. 47 (3), 662–675. http://dx.doi.org/10.1021/ja01680a010.

EPA, 1994. Methods for determination of metals in environmental samples–Supplement 1, U.S. Environmental Protection Agency,. EPA-600/R-94-111.

Evans, G., 1995. The Arabian Gulf: A modern carbonate-evaporite factory; a review, in Cuadernos de Geologica Iberica: Madrid,. Servicio de Publicaciones, Universidad Complutense 19, 61–95.

Fadlelmawla, A., Al-Senafy, M., Charette, M.A., 2013. Anthropogenic and natural controls on coastal groundwater exchange in an arid region (Kuwait) (written communication).

Hsü, K.J., Schneider, J., 1973. Progress Report on Dolomitization — Hydrology of Abu Dhabi Sabkhas, Arabian Gulf. In: Purser, B.H. (Ed.), The Persian Gulf. Springer-Verlag, New York (471 pp.).

Hsü, K.J., Siegenthaler, C., 1969. Preliminary experiments on hydrodynamic movement induced by evaporation and their bearing on the dolomite problem. Sedimentology 12, 11–25.

Kigoshi, K., 1971. Alpha-recoil thorium [234]Th: dissolution into water and the uranium-234/uranium 238 disequilibrium in nature. Science 173, 47–48.

Kinsman, D.J.J., 1969. Modes of formation, sedimentary associations, and diagnostic features of shallow-water and supratidal evaporates. Am. Assoc. Pet. Geol. Bull. 53, 830–840.

Kraemer, T., 1981. [234]U and [238]U concentration in brine from geopressured aquifers of the northern Gulf of Mexico basin. Earth Planet. Sci. Lett. 56, 210–216.

Kraemer, T.F., Reid, D.F., 1984. The occurrence and behavior of radium in saline formation water of the U.S. Gulf coast region. Chem. Geol. 46 (2), 153–174.

Kraemer, T., Doughten, M., Bullen, T., 2002. Use of ICP/MS with ultrasonic nebulizer for routine determination of uranium activity ratios in natural water. Environ. Sci. Technol. 36, 4899–4904.

Larsen, E.S., Gottfried, D., 1960. Uranium and thorium in selected suites of igneous rocks. Am. J. Sci. 258-A, 151–169.

Liu, G., Men, W., Ji, L., 2010. Calculation of vertical mixing rate based on radium isotope distributions in the Yellow Sea and East China Sea. Chin. J. Geophys. 53, 862–871.

McCaffrey, M.A., Lazar, B., Holland, H.D., 1987. The evaporation path of seawater and the coprecipitation of Br and K with halite. J. Sed. Petrol. 57 (5), 928–937.

McKenzie, J.A., Hsü, K.J., Schneider, J.F., 1980. Movement of subsurface waters under the sabkha, Abu Dhabi, UAE, and its relation to evaporative dolomite genesis. SEPM Special Publication No. 28, pp. 11–30.

Moore, W.S., 1976. Sampling 226Ra in the deep ocean. Deep-Sea Res. 23, 647–651.

Moore, W.S., 1981. Radium isotopes in the Chesapeake Bay. Estuar. Coast. Shelf Sci. 12, 713–723.

Moore, W., Key, R., Sarmeinto, J., 1985. Technique for precise mapping of 226Ra and 228Ra in the ocean. J. Geophys. Res. 90, 6983–6994.

Müller, D.W., McKenzie, J.A., Mueller, P.A., 1990. Abu Dhabi sabkha, Persian Gulf, revisited: application of strontium isotopes to test an early dolomitization model. Geology 18, 618–621.

Ohta, T., Mahara, Y., Kubota, T., Sato, J., Gamo, T., 2011. Concentrations and activity ratios of 228Ra and 226Ra in surface seawater along the Pacific Coast of Japan. Proc. Radiochim. Acta 1, 183–188.

Okubo, T., Furuyama, K., Sakanoue, M., 1979. Distribution of 228Ra in surface sea water of the East Indian Ocean. Geochem. J. 13, 201–208.

Osmond, J.K., Carpenter, J.R., Windom, H.L., 1965. Th-230/U-234 age of the Pleistocene corals and oolites of Florida. J. Geophys. Res. 70 (8), 1843–1847.

Patterson, R.J., Kinsman, D.J.J., 1977. Marine and continental groundwater sources in a Persian Gulf coastal sabkha. Stud. Geol. 4, 381–397.

Patterson, R.J., Kinsman, D.J.J., 1981. Hydrologic framework of a sabkha along Arabian Gulf. Am. Assoc. Pet. Geol. Bull. 65, 1457–1475.

Patterson, R.J., Kinsman, D.J.J., 1982. Formation of diagenetic dolomite in coastal sabkha along Arabian (Persian) Gulf. Am. Assoc. Pet. Geol. Bull. 66, 28–43.

Peebles, R.G., 1999. Stable Isotope Analyses and Dating of the Miocene of the Emirate of Abu Dhabi, United Arab Emirates. In: Whybrow, P.J., Hill, A. (Eds.), Fossil Vertebrates of Arabia. Yale University Press, New London, pp. 88–105.

Robinson, L, Belshaw, N.S., Henderson, G.M., 2004. U and Th concentrations and isotope ratios in modern carbonates and waters from the Bahamas. Geochim. Cosmochim. Acta 68 (8), 1777–1789. http://dx.doi.org/10.1016/jgca.2003.10.005.

Sanford, W.E., Wood, W.W., 2001. Hydrology of the coastal sabkhas of Abu Dhabi, United Arab Emirates. Hydrogeol. J. 9 (4), 358–366.

Su, N., Du, J., Ji, T., Zhang, J., 2010. 226Ra and 228Ra tracer study on nutrient transport in east coastal waters of Hainan Island, China. Water Sci. Eng. 4 (2), 157–169.

Van Dam, R., Simmons, C., Hyndman, D., Wood, W., 2009. Natural free convection in porous media: first field documentation in groundwater. Geophys. Res. Lett. 36, L11403. http://dx.doi.org/10.1029/2008GL036906.

Vengosh, A., Hirschfeld, D., Vinson, D.S., Dwyer, G.S., Raanan, H., Rimawi, O., Al-Zoubi, A., Akkawi, E., Marie, A., Haquin, G., Zaarur, S., Ganor, J., 2009. High naturally occurring radioactivity in fossil groundwater in the Middle East. Environ. Sci. Technol. 43 (6), 1769–1775. http://dx.doi.org/10.1021/es802969r.

Wood, W.W., Sanford, W.E., 2002. Hydrogeology and Solute Chemistry of the Coastal-Sabkha Aquifer in the Emirate of Abu Dhabi. In: Barth, Hans-Joerg, Boer, Benno (Eds.), Sabkha Ecosystem, v. 1 — The Sabkhas of the Arabian Peninsula and Adjacent Countries, 173–185. Kluwer Academic Publishers, Dordrecht (354 pp.).

Wood, W.W., Sanford, W.E., 2007. Atmospheric bromine flux from the coastal Abu Dhabi Sabkhat: a ground-water mass-balance investigation. Geophys. Res. Lett. 34, 14. http://dx.doi.org/10.1029/2007GL029922.

Wood, W.W., Sanford, W.E., Al Habschi, A.R.S., 2002. The source of solutes in the coastal Sabkha of Abu Dhabi. Bull. Geol. Soc. Am. 114 (3), 59–268.

Wood, W.W., Sanford, W.E., Frape, S., 2005. Chemical openness and potential for misinterpretation of the solute environment of coastal sabkhat. Chem. Geol. 215 (1–4), 361–372.

Zhu, C., 2004. Coprecipitation in the barite isostructural family: 1. binary mixing properties. Geochim. Cosmochim. Acta 68, 3327–3337.