Natural radioactivity in groundwaters around a fertilizer factory complex in South of Spain

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Abstract

A study of the concentration of the U isotopes, [226]Ra and [230]Th in a groundwater system has been carried out. This aquifer, located in the provinces of Sevilla and Huelva, is the most important in the south of Spain having a surface area of 2500 km^2. The proximity of a fertilizer factory complex to this aquifer system is of particular concern given that it releases a significant part of its waste directly into the estuary of the Odiel and Tinto rivers, also storing a further part on the right bank of the Tinto river. Investigation has been made of the environmental impact of the fertilizer factory, either as a result of leaching of radionuclides from the phosphogypsum piles or otherwise as a result of intrusion of the Odiel and Tinto waters, both of which are in close contact with the aquifer. Results show U concentration in waters of this system around the phosphogypsum piles to be significantly higher than those in other areas of the same aquifer. The low [226]Ra concentrations found in the same locations add support to the origin of part of the U in these samples.

Keywords: Natural radioactivity; Fertilizer plant; Groundwater; Spain

1. Introduction

In southwest Spain, the presence of elevated levels of U, Th and [226]Ra in rivers around a fertilizer factory complex has been established in several previous studies (Martínez-Aguirre and García-León, 1991; Martínez-Aguirre et al., 1994). In particular, elevated concentrations of several natural radionuclides were found in water, suspended particles and sediments collected along the course of the Odiel and Tinto rivers. Contamination along the Odiel river was mainly attributed to solid and liquid waste discharges which were made directly into the course of this river at its estuary. This area is highly affected by tidal movement, with contamination migrating both up- and downstream. Tidal movements of the waters also lead to contamination of the Tinto river in areas close to the Odiel, these rivers having a common

confluence into the Atlantic ocean. A smaller degree of contamination of the Tinto river has been observed to be due to storage of solid wastes (phosphogypsum piles). Concentrations as high as 950 and 2000 mBq/g of U and [226]Ra were obtained in samples of phosphogypsum collected in 1988 (Martínez-Aguirre, 1991). These waste piles, connected by several small tributaries to the Tinto river, allow for the possibility of leachate entering the riverine system. However, the phosphogypsum piles are mainly calcium suphates and, complexed in this form, Ra is insoluble.

The groundwater system of interest is the most important in southwestern Spain, covering a surface area of 2500 km^2. This aquifer system, used both for consumption and irrigation water, may be affected either through intrusion by the elevated concentration levels of contaminants in the Odiel and Tinto rivers or by leachate from the phosphogypsum piles. Consequently, contamination of this aquifer system would affect a large region of Spain. Investigating the possible influence of the fertilizer manufacture, either by direct leaching of

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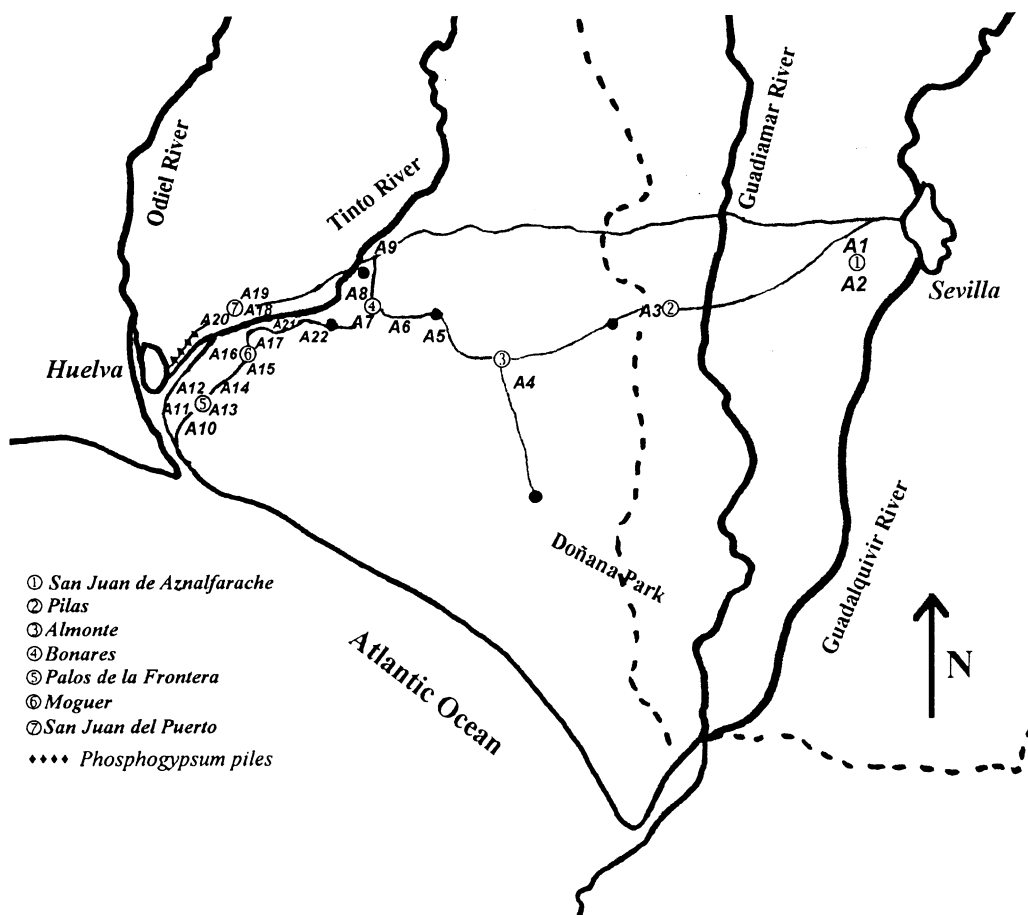*E-mail address:* arancha@cica.es (A. Martínez-Aguirre).

Fig. 1. Map of Almonte-Marismas groundwater system. In the figure the locations of the sampling stations are shown.

radionuclides from the phosphogypsum piles or intrusion of Odiel and Tinto river waters, is the main objective of this paper.

2. Samples and experimental methods

Twenty-two monitoring stations (see Fig. 1) have been selected across the Almonte-Marismas groundwater system in order to determine what influence the contamination produced by the fertilizer factory located in the Huelva estuary may have on the system. Some of the samples have been collected near the city of Sevilla in order to compare these with water samples collected around the fertilizer complex. Activity concentrations of the U-isotopes, ^{230}Th and ^{226}Ra have been measured in the samples.

In January 1997, a 5 liter quantity of water was sampled at each monitoring station, pH and temperature being measured at the time of sampling. Suspended matter was separated as soon as possible by filtration through 0.45 μm pore size Millipore filters and the solution acidified to pH $\sim$ 2 with HNO$_3$ to avoid the growth of microorganisms and to minimize water–wall interactions before the analysis.

From the original sample, 1–3 liters of each of these aqueous media was spiked with known activities of ^{232}U and ^{229}Th for U and Th determinations, respectively. After homogenization, the solution was evaporated to approximately 1 liter and iron hydroxides precipitation with concentrated ammonia was carried out. The anion-exchange resin method has been used for U and Th separation and purification (Martínez-Aguirre, 1991). Final solutions were electroplated onto stainless-steel planchets and U and Th activities measured by α-spectrometry with surface barrier or ion-implantated Si detectors.

^{226}Ra activity concentrations were measured in most water samples by using an LB770 α counter. Samples, each of 1 liter, were first neutralized, followed by addition of 5 mg of Ba carrier. Precipitation of Ra–BaSO$_4$, by adding H$_2$SO$_4$ 1 M, was then carried out

Table 1

U-isotopes, [226]Ra and [230]Th activity concentrations (mBq/l) in water samples collected across the Almonte-Marismas groundwater system[a]

Sample code	pH	T (°C)	[238]U	[234]U	[226]Ra	[230]Th
A1	7.7	16.7	7.93 ± 0.70	13.0 ± 1.0	NM	ND
A2	7.7	17.2	82.0 ± 4.7	120.3 ± 6.3	9.76 ± 0.29	0.32 ± 0.06
A3	7.6	16.1	6.58 ± 0.50	7.07 ± 0.52	6.94 ± 0.17	2.38 ± 0.17
A4	7.6	13.9	10.6 ± 0.6	12.0 ± 0.7	NM	2.01 ± 0.21
A5	7.6	12.8	90.7 ± 5.3	103.7 ± 6.0	8.30 ± 0.18	ND
A6	7.3	15.2	44.3 ± 3.7	46.3 ± 3.7	NM	0.23 ± 0.06
A7	6.7	12.8	3.41 ± 0.28	3.55 ± 0.28	NM	4.0 ± 0.3
A8	7.8	16.7	208 ± 10	181 ± 9	4.91 ± 0.14	ND
A9	7.7	11.7	43.0 ± 2.7	44.7 ± 2.7	NM	0.14 ± 0.04
A10	7.1	13.7	13.4 ± 0.7	13.2 ± 0.7	NM	0.70 ± 0.09
A11	8.8	13.5	34.6 ± 1.6	38.9 ± 1.8	NM	0.17 ± 0.04
A12	7.3	17.8	93.6 ± 3.8	119.3 ± 4.8	5.49 ± 0.15	0.10 ± 0.03
A13	7.3	15.9	91.8 ± 4.5	91.2 ± 4.4	14.3 ± 0.3	0.04 ± 0.02
A14	8.5	13.8	0.35 ± 0.08	0.22 ± 0.06	ND	0.04 ± 0.02
A15	7.5	16.2	16.8 ± 0.9	18.7 ± 1.0	2.15 ± 0.10	ND
A16	7.3	15.4	17.4 ± 0.9	23.1 ± 1.1	2.62 ± 0.09	0.12 ± 0.04
A17	7.5	16.7	30.3 ± 1.6	27.3 ± 1.4	1.80 ± 0.07	0.11 ± 0.04
A18	7.7	14.2	90.3 ± 3.8	109 ± 4.5	1.93 ± 0.08	0.17 ± 0.05
A19	7.5	15.6	93 ± 4	120 ± 5	2.65 ± 0.11	NM
A20	7.9	16.7	71 ± 3	112 ± 4	1.89 ± 0.08	NM
A21	8.0	15.6	90.3 ± 4.5	93.7 ± 4.7	2.84 ± 0.10	0.10 ± 0.03
A22	7.2	15.8	45.7 ± 2.1	53.0 ± 2.5	12.6 ± 0.2	NM

[a] The pH and temperature of the waters at the time of sampling are also given. ND means not detected and NM not measured.

and collected following filtration using 0.45 μm pore size Millipore filters. After 20 days (to allow secular equilibrium of [226]Ra daughters) the ingrown alpha activity of the samples was counted (Martínez-Aguirre and Periañez, 1998).

3. Results and discussion

In Table 1, activity concentrations for U-isotopes, [226]Ra and [230]Th are presented together with the pH and temperature of the waters at the time of sampling. As seen, most samples have close to neutral pH, in the range 6.7–8. Exceptions are samples A11 and A14, with pHs of 8.8 and 8.5, respectively. The water temperatures ranged from 12°C to 18°C with no apparent trend between stations. Samples 7–22 were collected around the Tinto river channel and the phosphogypsum piles (see Fig. 1).

U-isotope activity concentrations ranged from 0.35 to 208 mBq/l for [238]U and 0.22 to 181 mBq/l for [234]U, revealing two orders of magnitude difference between samples. The samples can be grouped in three different sets of concentration, low, medium and high. In the first set, [238]U concentration ranged from 0.35 to 17.4 mBq/l, in the second 30.3 to 45.7 mBq/l and in the third 71 to 93 mBq/l (also including one outlier with 208 mBq/l in sample A8).

From data in Table 1 and Fig. 1, most samples with U concentrations within the third set (71–208 mBq/l) have been found in areas close to the course of the Tinto river, particularly around *San Juan del Puerto* village and the upper part of the Tinto river channel. An exception is sample A2 collected close to the city of Sevilla, with a concentration well above those in the same area (A1 and A3). The maximun U concentration has been found in sample A8, collected upstream of the phosphogypsum piles and close to *Bonares* village. Two samples, A12 and A13, located close to *Palos de la Frontera* village, at the right bank of the Tinto river, have U concentrations in the high range. However, samples collected in *Moguer* village, close to *Palos de la Frontera* have much lower U concentrations than samples A12 and A13. In particular, sample A14 yields a minimum concentration, 0.35 mBq/l of [238]U. It is well known that precipitation of iron oxyhydroxides takes place at pH ~ 8, resulting in a decrease of activity concentration in the aqueous phase. The high pH of sample A14 is strongly supportive of a low U concentration. The same reasoning can be applied to sample A11, with high pH and U concentration lower than that of samples A12 and A13.

Table 2
U concentrations and associated activity ratios in water samples collected from the Almonte-Marismas groundwater system

Sample code	[U] (μg/l)	$^{234}U/^{238}U$	$^{226}Ra/^{234}U$	$^{230}Th/^{234}U$
A1	0.642 ± 0.057	1.64 ± 0.16		
A2	6.60 ± 0.38	1.47 ± 0.11	0.081 ± 0.005	$\leqslant 0.003$
A3	0.53 ± 0.04	1.08 ± 0.09	0.986 ± 0.076	0.337 ± 0.034
A4	0.85 ± 0.05	1.14 ± 0.06		0.166 ± 0.019
A5	7.30 ± 0.43	1.14 ± 0.09	0.080 ± 0.005	
A6	3.56 ± 0.30	1.05 ± 0.12		$\leqslant 0.005$
A7	0.27 ± 0.02	1.04 ± 0.11		1.127 ± 0.123
A8	16.6 ± 0.8	0.87 ± 0.02	0.027 ± 0.002	
A9	3.4 ± 0.2	1.07 ± 0.05		$\leqslant 0.003$
A10	1.08 ± 0.06	0.98 ± 0.05		0.053 ± 0.007
A11	2.78 ± 0.13	1.13 ± 0.04		$\leqslant 0.004$
A12	7.53 ± 0.31	1.28 ± 0.02	0.046 ± 0.002	$\leqslant 0.001$
A13	7.39 ± 0.36	0.99 ± 0.03	0.157 ± 0.008	$\leqslant 0.001$
A14	0.018 ± 0.005	1.58 ± 0.58		0.182 ± 0.104
A15	1.36 ± 0.08	1.12 ± 0.06	0.115 ± 0.008	
A16	1.40 ± 0.07	1.33 ± 0.06	0.113 ± 0.007	$\leqslant 0.005$
A17	2.44 ± 0.13	1.11 ± 0.05	0.066 ± 0.004	$\leqslant 0.004$
A18	7.26 ± 0.31	1.21 ± 0.03	0.018 ± 0.001	$\leqslant 0.002$
A19	7.48 ± 0.32	1.29 ± 0.03	0.022 ± 0.001	
A20	5.71 ± 0.24	1.58 ± 0.03	0.017 ± 0.001	
A21	7.32 ± 0.37	1.04 ± 0.03	0.030 ± 0.002	$\leqslant 0.001$
A22	3.77 ± 0.17	1.16 ± 0.04	0.238 ± 0.012	

The presently reported U concentrations ranging between 0.02 and 16.6 μg/l (see Table 2) are generally higher than those obtained by Andrews and Kay, 1982; Kronfeld, 1974; Kraemer, 1981 for other aquifers but are in good agreement with those obtained by Osmond and Cowart, 1976, for some aquifers in the USA. It is possible that some of the water samples and thus, some locations in the aquifer may be affected by releases from the fertilizer factories.

$^{234}U/^{238}U$ activity ratios are shown in Table 2. As observed in most samples, these isotopes are in approximate secular equilibrium, ^{234}U being slightly in excess of ^{238}U. Only one sample, A8, shows a slightly lower value of ^{234}U than ^{238}U. No relationships have been found between the activity ratio, U concentration and/or sample location. All activity ratios are in agreement with other results found in the current literature for groundwaters (Osmond and Cowart, 1976).

The activity concentration of ^{226}Ra in water samples ranges from 1.8 to 14.3 mBq/l (Table 1). As for U isotopes three sets of activity concentration range may be suggested: the first showing concentrations ranging from 1 to 3 mBq/l which are located around *San Juan del Puerto* (samples A15–A21), while the second set which ranges from 5 to 10 mBq/l, were obtained in samples collected far from the Tinto river (A2, A3,

A5 and A8) an exception being sample A12. The highest ^{226}Ra concentrations were found in samples A13 and A22.

In contrast to the case for U, the lowest ^{226}Ra concentrations were found in the area around the phosphogypsum piles. If we consider that phosphogypsum is composed of calcium sulfate a highly insoluble complex, this result is to be expected.

In all cases, other than sample A3, the ^{226}Ra activity concentration is much lower than the activity of U isotopes, with the $^{226}Ra/^{234}U$ activity ratios being below 0.2. In sample A3, both radionuclides are practically in secular equilibrium. The difference in comparison with other samples cannot be explained at this time, although the relatively low U concentration for the particular area is noted.

^{230}Th has been also measured in the samples. Generally, the activity concentrations are much lower than U and ^{226}Ra, ranging from 0.04 to 4 mBq/l, being for most samples in a range below 0.3 mBq/l. Exceptions are sample A10 with 0.7 mBq/l and samples A3, A4 and A7 with concentrations above 1 mBq/l. The higher ^{230}Th activity concentrations are not related with the vicinity of the samples to the phosphogypsum piles, the concentration in this area being in fact very low.

The $^{230}Th/^{234}U$ activity ratio is well below unity, reflecting the higher solubility of ^{234}U relative to ^{230}Th.

Contamination from the fertilizer production would probably also give activity ratios below unity, albeit higher than the normal values as found in the Odiel and Tinto river waters (Martínez-Aguirre and García-León, 1991, Martínez-Aguirre et al., 1994).

4. Conclusion

U concentration in samples of water from the Almonte-Marismas groundwater system, collected in the vicinity of solid waste (phosphogypsum) piles of the Huelva fertilizer factory, are significantly higher than those in other areas of the same aquifer. This could either result from U leaching from the phosphogypsum piles or intrusion of Odiel and Tinto river waters into the aquifer system. The low ^{226}Ra concentrations found in the same locations are related to the high insolubility of calcium sulfates.

Acknowledgements

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