

# Low-level radioactivity studies in the marine environment of the South of Spain \*

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In this paper preliminary levels of natural and man-made radionuclides in the South Spanish marine environment are presented. Local man-made sources are found to be the main contributors to the natural environmental radioactivity in such areas while fallout is mainly responsible for the occurrence of artificial radioactivity in our zone.

## 1. Introduction

So far, the presence of environmental radioactivity in Andalucía (South of Spain) had not been studied. Thus, since 1988 a large project for the determination of natural and man-made radionuclides in this region was started.

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Andalucía (see fig. 1) occupies the whole South of Spain and the majority of the South of the Iberian peninsula. The research programme consists of the measurement of  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$ , U-, Ra- and Th-isotopes and  $^{210}\text{Po}$  in a large group of samples, such as seaweed, riverwaters, rainwaters, sediments, etc. (see fig. 1).

We present here some results obtained for the marine side of the environment studied. We will describe in the next sections, levels of  $^{99}\text{Tc}$  and  $^{137}\text{Cs}$  in seaweed samples. U-isotopes and  $^{210}\text{Po}$  in riverwater and sediment samples will also be given.

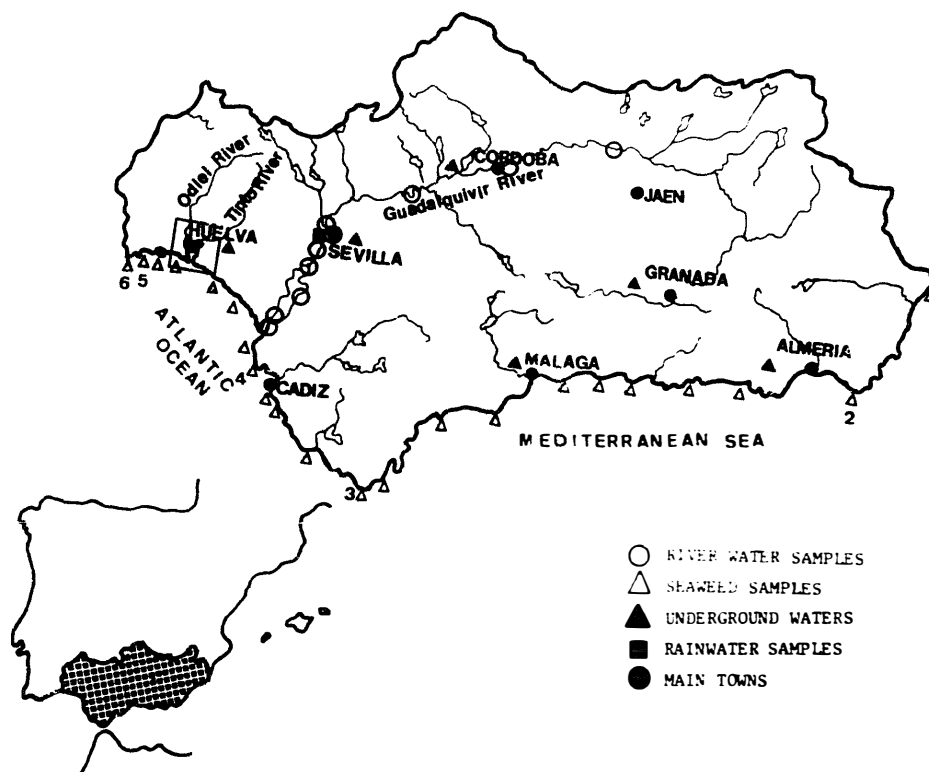


Fig. 1. Map of Andalucía (South of Spain) showing the type of samples and sampling stations included in the research project.

The methods for determination of the above-mentioned isotopes and the results obtained are outlined in the following sections.

## 2. Experimental

Low-background GM gas-flow  $\beta$ -counting,  $\gamma$ - and  $\alpha$ -spectrometry have been used for  $^{99}\text{Tc}$ ,  $^{137}\text{Cs}$  and  $\alpha$ -emitter measurements, respectively. A brief account of the individual methods is given in the following paragraphs.

### 2.1. $^{99}\text{Tc}$

A solvent extraction technique is used for  $^{99}\text{Tc}$  determination. First, some 15–30 g of dried and powdered seaweed are spiked with a known  $^{99\text{m}}\text{Tc}$  activity. The sample is then calcinated at 600 °C. The ashes are dissolved with 2% HCl, and technetium is extracted with tributylphosphate (TBP). Subsequently, Tc is back-extracted from the organic phase with 2M NaOH. This solution is electroplated at 0.35 A for 2 h and technetium is deposited onto a stainless steel planchet [1,2]. Due to the relatively soft  $^{99}\text{Tc}$   $\beta$ -spectrum ( $E_{\text{max}} = 292.3$  keV) an electrodeposition technique for the preparation of the final source is more adequate than a simple evaporation of the 2M NaOH solution, since in this way self-absorption effects are minimized.

The radiochemical yield  $Y$  of the process is calculated by measuring the  $^{99\text{m}}\text{Tc}$  activity recovered. This is accomplished with a 76 mm  $\times$  76 mm NaI(Tl)  $\gamma$ -spectrometer, taking advantage of the 140-keV photon emitted by this radionuclide.

After five or six days, when all the  $^{99\text{m}}\text{Tc}$  ( $T_{1/2} = 6.02$  h) has decayed, the  $^{99}\text{Tc}$   $\beta$ -activity from the sample is measured. Due to the very low  $^{99}\text{Tc}$  concentration in nature, a low-level counting technique has to be ap-

plied. Thus, a low-background (0.2 cpm) gas-flow GM counter is used for  $^{99}\text{Tc}$  measurements. The efficiency of the detector reaches a value of 37%. It was calculated with  $^{99}\text{Tc}$  standard samples of well-known activities.

### 2.2. $^{137}\text{Cs}$

$^{137}\text{Cs}$  is directly determined by HPGe  $\gamma$ -spectrometry. For that, a given mass of dried and powdered seaweed is placed in a standard geometry and counted with the spectrometer [3]. The detector background is reduced by using a passive lead shielding 10 cm thick, internally covered with a few mm of copper.

The counting efficiency was obtained by counting algae material, in the standard geometry, homogeneously spiked with known  $^{137}\text{Cs}$  and  $^{152}\text{Eu}$  activities.

### 2.3. U-isotopes and $^{210}\text{Po}$

The  $\alpha$ -activity from  $^{238}\text{U}$ ,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{210}\text{Po}$  was measured by Si surface barrier or ion implanted  $\alpha$ -spectrometry [4,5]. For that, some few grams of dried and powdered sediment are spiked with known  $^{232}\text{U}$  and  $^{208}\text{Po}$  activities. Then the sample is digested with  $\text{HNO}_3$  and aqua regia. The residue is dissolved in 8M  $\text{HNO}_3$  and the solution filtered into a decantation funnel which contains TBP. After shaking, U and Th pass to the organic phase while Po and Ra remain in the aqueous phase. Both phases are separated.

The aqueous phase is evaporated to near dryness and the residue dissolved with concentrated HCl. After that, Po is self-deposited onto Ni planchets at 60 °C, according to the method of Flynn et al. [6]. It is important to note that some mg of ascorbic acid are added to the electrolyte to avoid the deposition of Fe.

The organic phase is dissolved with xylene and Th is back-extracted from it with 1.5M HCl. The remaining organic phase is mixed with distilled  $\text{H}_2\text{O}$  to back-ex-

Table 1  
 $^{137}\text{Cs}$  levels in seaweed samples collected along the coasts of Andalucía region (South of Spain) during 1988 and 1989

Type of alga	Species	Number of data	Activity (dry weight) [mBq/g]		
			minimum	maximum	average
Brown	halopteris scoparia	10	0.7 $\pm$ 0.2	2.9 $\pm$ 0.3	1.4 $\pm$ 0.7
Green	ulva rigida	7	0.6 $\pm$ 0.5	2.3 $\pm$ 0.3	1.4 $\pm$ 0.6
Green	codium	7	0.7 $\pm$ 0.3	3.8 $\pm$ 1.7	2.2 $\pm$ 1.1
Brown	fucus	6	0.6 $\pm$ 0.2	1.5 $\pm$ 0.3	1.2 $\pm$ 0.3
Green	sargassum vulgare	6	0.7 $\pm$ 0.4	2.8 $\pm$ 0.6	1.3 $\pm$ 0.8
Brown	dyctiota dichotoma	2	0.6 $\pm$ 0.4	1.4 $\pm$ 0.6	1.0 $\pm$ 0.6
Brown	cystoseira ericoides	2	0.3 $\pm$ 0.7	0.8 $\pm$ 0.3	0.6 $\pm$ 0.3
Brown	corallina mediteranea	1	–	–	1.6 $\pm$ 0.6
Brown	cimodocea modosa	1	–	–	1.2 $\pm$ 0.4
Red	holopitis incunous	1	–	–	0.8 $\pm$ 0.3

tract U. The final solution is dried and U is electroplated onto stainless steel planchets by the method of refs. [7] and [8]. As for water samples, some 1 to 5 l are spiked with a known  $^{232}\text{U}$  activity and evaporated. The residue is treated as a sediment sample for U extraction.

### 3. Results

#### 3.1. Levels in seaweed

$^{137}\text{Cs}$  and  $^{99}\text{Tc}$  activities have been studied in a wide number of seaweed species. In table 1 the  $^{137}\text{Cs}$  minimum, maximum and average activity values for some of such species are presented. Very similar, and low,  $^{137}\text{Cs}$  specific activities, roughly 1.3 mBq/g dry weight, are obtained either for the red, brown or green alga species. Such low values do not allow to determine the best bioindicator for our zone. On the other hand, since there is no local source of radioactivity for our region, the levels obtained seem to be representative of the worldwide fallout background in the South of Spain. This idea can be confirmed when our results and the very scarce previous data existing in the current literature are compared.

Table 2

$^{137}\text{Cs}$  and  $^{99}\text{Tc}$  levels found in fucus spiralis and vesiculosus samples collected along the South Spanish coasts during 1988 and 1989. The site number corresponds to the sampling site shown in the map of fig. 1. Mean values for the Mediterranean and Atlantic coasts are also given.

Sampling site (date)	Activity (dry weight) [mBq/g]	
	$^{137}\text{Cs}$ activity	$^{99}\text{Tc}$ activity
Palomares (1988) [1]	$0.6 \pm 0.2$	$0.25 \pm 0.04$
Palomares (1989) [1]	$1.3 \pm 0.5$	$0.31 \pm 0.03$
Cabo de Gata (1988) [2]	$1.6 \pm 0.3$	$0.15 \pm 0.04$
Punta Palomas (1988) [3]	$1.1 \pm 0.4$	$0.43 \pm 0.06$
Rota (1989) [4]	n.m. <sup>a</sup>	$0.1 \pm 0.2$
Isla Cristina (1989) [5]	$1.2 \pm 0.5$	$0.30 \pm 0.03$
Ayamonte (1988) [6]	$1.5 \pm 0.4$	$0.14 \pm 0.03$
Mediterranean coasts	$1.1 \pm 0.4$	$0.25 \pm 0.13$
Atlantic coasts	$1.3 \pm 0.2$	$0.22 \pm 0.11$

<sup>a</sup> n.m. = not measured

Thus, levels of 0.8 mBq/g were found in Galicia, North-West of Spain, during 1984 [9] and of about 0.9 mBq/g in the coasts of Portugal during 1985 [10], both for Fucus species. They were attributed essentially to fallout, which supports our previous comment.

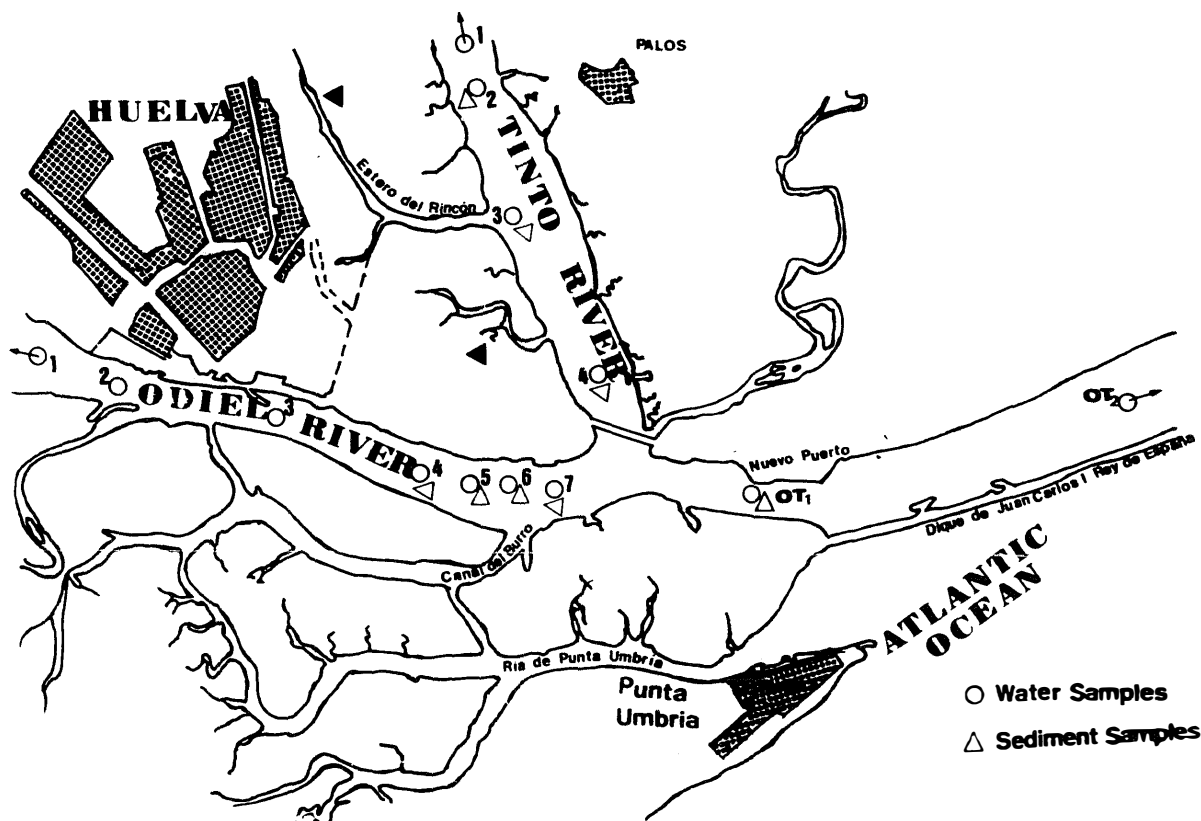


Fig. 2. Map corresponding to the sampling stations of Tinto and Odiel rivers around the town of Huelva (see also fig. 1).

Table 3

U-isotopes activity concentration, together with the  $^{234}\text{U}/^{238}\text{U}$  activity ratio for riverwater samples taken at the Odiel (O) and Tinto (T) rivers. Samples OT were taken at the confluence of both rivers. The pH of the waters are also given. See fig. 2. for an easier comprehension of the table.

Sample	pH	Activity concentration [mBq/l]		Activity ratio
		$^{238}\text{U}$	$^{234}\text{U}$	$^{234}\text{U}/^{238}\text{U}$
T1	2.0	170.0 ± 11.0	350.0 ± 20.2	2.02 ± 0.06
T2	5.0	37.0 ± 3.8	41.0 ± 4.1	1.09 ± 0.11
T3	5.0	24.8 ± 3.0	30.3 ± 3.4	1.22 ± 0.20
T4	5.5	26.0 ± 2.0	23.0 ± 2.0	0.88 ± 0.10
OT1	5.5	31.0 ± 5.1	46.0 ± 6.4	1.40 ± 0.09
OT2	6.0	31.1 ± 1.7	38.0 ± 2.0	1.22 ± 0.08
O7	5.5	30.0 ± 4.0	36.0 ± 4.6	1.20 ± 0.18
O6	4.5	60.0 ± 8.1	50.0 ± 7.0	0.83 ± 0.12
O5	4.5	778.0 ± 50.0	777.0 ± 50.0	1.00 ± 0.02
O4	4.5	206.5 ± 18.8	206.5 ± 18.9	1.00 ± 0.07
O3	5.5	13.9 ± 2.6	20.3 ± 3.11	1.47 ± 0.35
O2	5.5	20.0 ± 2.7	22.0 ± 2.8	1.10 ± 0.17
O1	3.0	66.0 ± 8.0	121.0 ± 13.0	1.83 ± 0.30

In table 2, we present some few additional  $^{137}\text{Cs}$  results together with the  $^{99}\text{Tc}$  activities in Fucus samples. There is no difference, both for  $^{137}\text{Cs}$  and  $^{99}\text{Tc}$ , between the activities obtained in the mediterranean and the atlantic sides of the Andalusian coast. Concerning the  $^{99}\text{Tc}$  results, very similar comments to those given in table 1 for  $^{137}\text{Cs}$  can be made. Thus, an average value of 0.2 mBq/g dry weight can be observed, which is in moderate agreement with values found in Galicia [2] and Portugal [10] coasts, of about 0.4 and 0.6 mBq/g dry weight, respectively, both during 1985.

Table 4

U-isotopes and  $^{210}\text{Po}$  activity concentrations (in mBq/g) for sediment samples taken at the Odiel (SO) and Tinto (ST) rivers. Sample SOT was taken at the confluence of both rivers. See fig. 2 for and easier comprehension of the table.

Sample	Activity concentration [mBq/l]			
	$^{238}\text{U}$	$^{235}\text{U}$	$^{234}\text{U}$	$^{210}\text{Po}$
ST2	100.0 ± 7.8	3.60 ± 0.72	110.0 ± 8.1	n.m. <sup>a</sup>
ST3	250.0 ± 1.7	11.0 ± 1.2	260.0 ± 1.7	252.0 ± 10.0
ST4	277.0 ± 13.0	10.3 ± 0.8	290.0 ± 14.0	341 ± 12.0
SOT	264.1 ± 29.6	n.d. <sup>b</sup>	275.7 ± 30.8	339.4 ± 13.3
SO7	1060.0 ± 75.0	48.0 ± 4.9	1060.0 ± 75.0	1194.8 ± 112.2
SO6	42.0 ± 3.9	2.80 ± 0.66	45.0 ± 4.2	41.6 ± 2.7
SO5	1100.0 ± 130.0	55.0 ± 10.0	1200.0 ± 130.0	820.9 ± 50.2
SO4	160.0 ± 11.0	7.7 ± 1.0	170.0 ± 12.0	615.2 ± 28.0

<sup>a</sup> n.m. = not measured.

<sup>b</sup> n.d. = not detected.

### 3.2. Levels in sediment and riverwater

U-isotopes and  $^{210}\text{Po}$  have been determined in sediment and riverwater samples collected at the Odiel and Tinto rivers (South-West of Spain).

Such rivers (see fig. 1 and 2) surround a large industrial complex, which includes several phosphate fertilizers factories near their mouths at the Atlantic Ocean. It is well known that such facilities produce a clear radiological impact in their immediate environment [11]. Our results, using U and  $^{210}\text{Po}$  as indicators, confirm such observations.

In table 3 the U-isotope activities found in waters of the Odiel and Tinto rivers are presented (see fig. 2 for an easier comprehension of table 3). In general, the activities in the Odiel river are higher than in the Tinto river. Thus, in the Odiel waters, a clear peak of activity can be seen. This corresponds to samples taken near the place where the phosphate fertilizer complex is located.

It seems, therefore, that such industries are directly releasing their wastes to the Odiel river. It does not occur so, for the case of the Tinto river. In fact, the U levels found in its waters are totally compatible with activities obtained in the Guadalquivir river [12], which crosses our region from East to West, and that have been taken as a background level for our study. The results of samples T1 and O1 are specially interesting. Such waters were taken near the sources of the Tinto and Odiel rivers, respectively. The natural low pH of such waters favours the redissolution of U from the bed of the rivers to the aqueous phase, which would explain the relatively high levels of activities found. Furthermore, this would account for the high  $^{234}\text{U}$  enrichment observed in these samples.

It would be interesting to study the form in which the wastes from the fertilizer factories are released

into their immediate environment. This work is currently being carried out in our group.

However, from the data we present in table 4, it seems that both river beds, those for Odiel and Tinto rivers, are accumulating U and  $^{210}\text{Po}$  activities. Indeed, the levels observed in sediments are clearly higher, both for U-isotopes and for  $^{210}\text{Po}$ , than other levels found in different rivers, including Spanish systems [13,14]. The case of sample SO6 is not surprising, since some other chemical materials, without radioactivity, are being released in such sampling point together with the wastes from the fertilizer industries. This would contribute to lowering the specific activity.

## References

- [1] E. Holm, J. Rioseco and M. García-León, Nucl. Instr. and Meth. 223 (1984) 204.
- [2] G. Manjón and M. García-León, An. Fís. B86 (1990) (in Spanish) 63.
- [3] C.I. Sánchez-Angulo and M. García-León, Nucl. Geophys. 2 (1988) 69.
- [4] A. Martínez-Aguirre, M.C. Morón and M. García-León, to be published in J. Radioanal. Nucl. Chem.
- [5] A. Martínez-Aguirre and M. García-León, to be published in J. Radioanal. Nucl. Chem. Lett.
- [6] W.W. Flynn, Anal. Chem. Acta 43 (1968) 221.
- [7] L. Hallstadius, Nucl. Instr. and Meth. 223 (1984) 266.
- [8] R. García-Tenorio, M. García-León, G. Madurga and C. Piazza, An. Fís. B82 (1986) 238 (in Spanish).
- [9] P.I. Mitchell, A. Vidal-Quadras, J.L. Font and M. Oliva, J. Environ. Rad. 6 (1988) 77.
- [10] A. Aarkrog, S. Boelskifte, E. Buch, G.C. Christensen, H. Dahlggaard, L. Hallstadius, H. Hansen, E. Holm and J. Rioseco, Risø National Laboratory Report-R-510 (1987) 74.
- [11] R.J. Guimond and J.M. Hardin, Radiat. Phys. Chem. 2 (1989) 309.
- [12] A. Martínez-Aguirre and M. García-León, in preparation.
- [13] F. Vera-Tomé and A. Martín-Sánchez, J. Radioanal. Nucl. Chem. 1 (1989) 73.
- [14] M.C. Morón, A. Martínez-Aguirre and M. García-León, Proc. Int. Conf. on Environmental Radioactivity in the Mediterranean Area, Barcelona, 1988 (SNE-ENS, 1988) p. 111.