^{210}Pb enhancement in rivers affected by the phosphate rock processing in southwestern Spain

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ABSTRACT

The activity levels of ^{210}Pb in solution and bottom sediments were measured in the estuary formed by the Odiel and Tinto rivers in southwest Spain. The levels in both water and sediment samples indicate that the discharges from two fertilizer factories in the area enhance the radioactivity of such samples.

1. INTRODUCTION

Recently, high radioactivity levels of U, Th and ^{226}Ra isotopes were found in solution, suspended matter and bottom sediments of the Odiel and Tinto rivers located in southwestern Spain [1–3]. The anomaly was attributed to two fertilizer factories located in an industrial complex surrounded by these two rivers (Fig. 1). These factories release their wastes directly to the Odiel river or store them in uncovered piles near the Tinto river channel. In this paper, we have extended previous work to the study of ^{210}Pb in solution and bottom sediments.

2. SAMPLES AND EXPERIMENTAL METHODS

Seven points on the Odiel river, four on the Tinto river and one at the confluence of both rivers (Fig. 1) were sampled for water and bottom sediments in July 1990 (dry season) and in February 1991 (wet season) to evaluate seasonal variations in ^{210}Pb activities. The pH of the waters was measured at the time of sampling. The suspended matter was separated by filtration through Nucleopore filters of 0.45 μm pore size. Immediately, the filtrate was acidified to pH ~2 with concentrated HNO_3. The small size fraction ($d < 63$ μm) was separated from sediment samples in order to determine the ^{210}Pb content. Determinations of percent organic matter and percent of water were carried out on each bottom sediment sample.

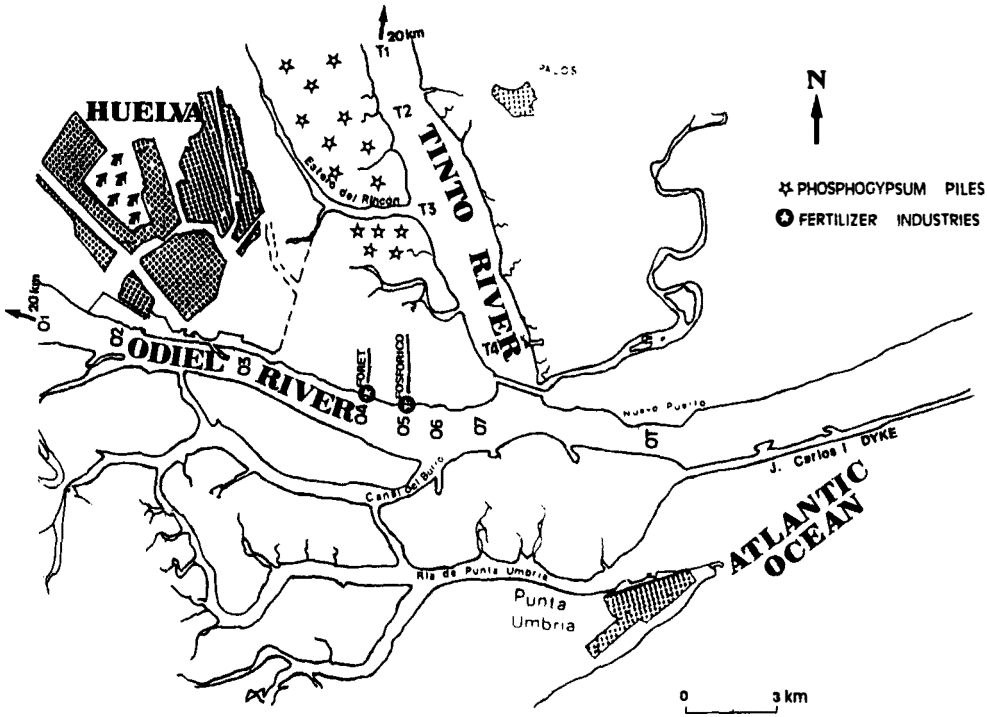

Fig. 1. Map of the Odiel and Tinto rivers which shows the sampling stations along both river channels. The fertilizer factories and the phosphogypsum storage area are also shown.

^{210}Pb was determined through the measurement of its daughter ^{210}Po by α-spectrometry, after secular equilibrium was achieved. The samples were spiked with known activities of ^{208}Po to determine the chemical recovery of the total procedure. Samples were first acid digested with concentrated HNO_3 followed by aqua regia and, finally dissolved in 8 M HNO_3. Po was separated using a solvent extraction method with TBP as the organic phase and 8 M HNO_3 as the inorganic phase. After vigorous shaking Po remains in the inorganic phase whereas other radionuclides join the organic phase. The solution containing the Po was evaporated to dryness and self deposition of Po onto silver planchets was encouraged by shaking gently at 60°C. The planchet was finally measured by α-spectrometry with ion implanted detectors. Further details on the radiochemical procedure are presented in Morón et al. [4].

3. RESULTS AND DISCUSSION

To simplify the subsequent discussion we will first present the results for water samples from both rivers for all sampling campaigns, followed by those obtained for bottom sediments. Samples O represent those taken in the Odiel

river, T in the Tinto river and OT in the confluence of both rivers. Sediment samples are identified as SO, ST and SOT for the Odiel, Tinto and the confluence respectively. The index represents the sampling station along each river (Fig. 1).

3.1. Waters

The results obtained for the analysis of ^{210}Pb in water samples taken during the low tide in 1990 (dry season) and 1991 (wet season) are presented in Table 1. The levels of ^{210}Pb in the Odiel river area under study range from 3.7 ± 0.5 to 289 ± 22 mBq l^{-1} with the maxima, in summer and in winter, in front of one of the fertilizer outfalls (Fig. 2). The levels decrease quickly downstream from this point, due, probably, to precipitation of Fe and Mn during mixing downstream [5]. This activity pattern is similar to those obtained previously for other radionuclides [1,2] reflecting the presence of a local source of radioactivity (the fertilizer industries) along the river channel. The minimum levels found in summer are clearly higher than those in winter, probably due to a lower water stream flow of the river in the dry season. In the case of the Tinto river the levels along the channel are quite constant, ranging from 17.0 ± 1.5 to 26.6 ± 3.0 mBq l^{-1} in summer 1991, with a slight decrease downstream of the channel. In 1991, the levels range from 15.3 ± 3.1 to 45.6 ± 2.7 mBq l^{-1}. In both campaigns the

TABLE I

Data of ^{210}Pb in mBq l^{-1} in water samples (low tide) taken from the Odiel and Tinto river basins in 1990 (dry season) and 1991 (wet season). The pH of the waters at the time of sampling is also given. N.M means not measured

	1990		1991	
Code	pH	^{210}Pb	pH	^{210}Pb
O1	2.86	21.1±2.5	3.90	N.M.
O2	6.37	7.9±1.0	5.52	7.8±0.7
O3	6.42	10.2±3.4	5.90	3.7±0.5
O4	6.35	289±22	5.96	36.4±2.6
O5	6.32	34.4±2.2	6.03	8.4±0.8
O6	6.48	12.2±1.4	6.06	7.4±1.1
O7	6.40	14.0±1.0	6.02	50.6±3.9
T1	2.41	41.7±3.1	2.88	N.M.
T2	5.54	26.6±3.0	3.22	45.6±2.7
T3	5.82	19.5±1.5	5.56	15.3±3.1
T4	6.10	17.0±1.5	6.40	30.7±5.7
OT	6.56	11.7±1.0	6.23	10.5±1.2

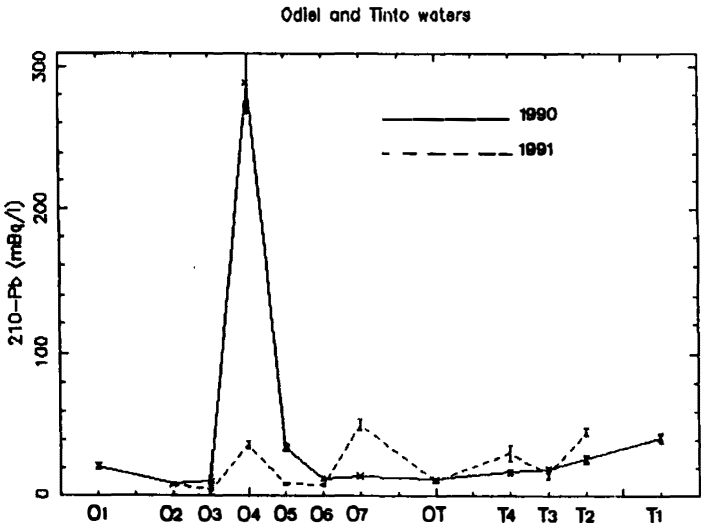

Fig. 2. ^{210}Pb in mBq l^{-1} in water samples taken from the Odiel and Tinto rivers in 1990 and 1991.

maximum level in the Tinto river was found in station T2. This station is located close to an artificial stream coming from the phosphogypsum storage area. In fact, the pH of the water at this station is lower than at the rest of the stations, at 3.22 in 1991 (Table 1), which reflects the wastes released at this point. We also observe that the level of ^{210}Pb found at station T4 of the Tinto river is quite similar to that found at station O7 of the Odiel river. This fact could be explained by the influence that contaminated waters from the Odiel river have on the Tinto river channel. Thus, contaminated water from the Odiel river can flow upstream into the Tinto river when the tide changes from low to high.

In the Netherlands, Koster et al. [6] obtained levels of ^{210}Pb of 0.9 mBq l^{-1} in waters of the Oosterchelde system while in the area around a fertilizer factory in the Nieuwe Waterweg system they found 10 mBq l^{-1}. In general, the authors assumed levels below 1 mBq l^{-1} as a background level, those higher than 3 mBq l^{-1} as probably enhanced and finally, those higher than 5 mBq l^{-1} as clearly enhanced. Lewis [5] reported dissolved ^{210}Pb in normal river waters to be less than 0.2 mBq l^{-1}. By contrast in acid river waters, dissolved ^{210}Pb was found to reach 230 mBq l^{-1} in the Colorado system and 2.8 mBq l^{-1} in the west branch of the Susquehannah river [7]. Comparing the levels of ^{210}Pb in the Odiel and Tinto rivers for both sampling campaigns we should consider both rivers to be clearly enhanced in ^{210}Pb activity by the fertilizer industries, particularly in the area close to the outfalls. The background level away from the outfalls appears to be around 7 mBq l^{-1}.

We will consider separately the case of samples O1 and T1, which were collected at the source of both rivers, far from the fertilizer industries (20 km

upstream in both cases) and unaffected by their wastes. Both sampling stations present levels of ^{210}Pb much higher than the usual values in fresh river waters. This fact must be related with the acid pH of the waters (Table 1) at both stations. These acid pHs produce a dissolution of ^{210}Pb from soil particles and consequently a higher ^{210}Pb activity in solution, as was previously found in the Colorado river and in the Susquehannah river [6,7]. This effect of dissolution from bottom sediments by the acid pH of the waters was also found for other radionuclides in the same sampling stations [1–3].

3.2. Sediments

The small size fraction ($d \leq 63$ μm) of 7 bottom sediments from the Odiel river, 4 from the Tinto and 1 from the confluence of both rivers sampled in 1990 and 1991 were separated for ^{210}Pb determinations. The results obtained together with percent of water and percent of organics for each sediment sample are presented in Table 2.

Levels of ^{210}Pb are quite high in the area close to the fertilizer industries in the Odiel river, with a maximum level of 799 ± 48 mBq g^{-1} in 1990 and 534 ± 25 mBq g^{-1} in 1991. These levels of radioactivity at stations O4 to O7 are much higher than the background level, ≤100 mBq g^{-1} reported elsewhere [6]. Only in two stations (Fig. 3), upstream from the industries, in both sampling campaigns, does the level of ^{210}Pb fall in the non enhanced range (≤100 mBq g^{-1}). ^{210}Pb activity levels at station O7 were much lower (≤100 mBq g^{-1}) in the 1990

TABLE 2

Data of ^{210}Pb in mBq g^{-1} in the small size fractions of bottom sediments taken from the Odiel and Tinto river basins in 1990 (dry season) and 1991 (wet season). Percent of water and percent of organics in the sediment samples are also given. N.M. means not measured

Code	% Water	% Organics	^{210}Pb	% Water	% Organics	^{210}Pb
SO1	52.58	5.73	N.M.	61.18	15.40	N.M.
SO2	26.64	11.76	13.9±1.3	24.53	3.09	8.0±0.7
SO3	60.58	9.51	27.2±1.5	57.21	8.25	40.9±2.7
SO4	52.53	10.91	212±10	39.13	11.57	284±14
SO5	65.51	5.26	438±21	59.83	9.74	420±31
SO6	58.18	9.47	799±49	67.93	12.95	534±25
SO7	65.35	9.47	78.6±3.7	55.64	9.58	411±24
ST1	79.63	8.38	N.M.	39.80	2.25	N.M.
ST2	38.78	4.34	96.7±6.1	51.37	8.96	33.1±3.3
ST3	59.29	9.64	39.8±1.9	56.8	11.72	233±9
ST4	61.46	8.64	74.4±4.8	56.03	10.93	47.9±2.5
OT	64.98	8.69	149±11	66.77	11.49	204±16

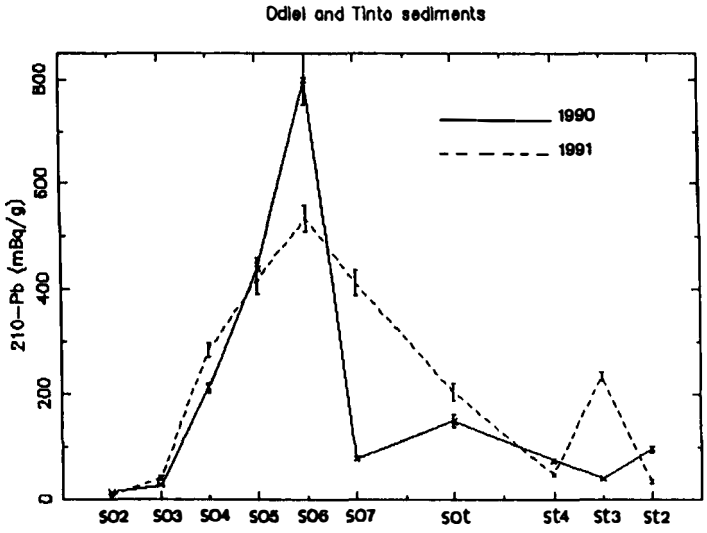

Fig. 3. ^{210}Pb in mBq g^{-1} in bottom sediment samples taken from the Odiel and Tinto rivers in 1990 and 1991.

sampling campaign than in that of 1991. This must be related to some drainage activities carried out in the area in 1990.

In the Tinto river the levels range from 33.1 ± 3.3 to 233 ± 9 mBq g^{-1} in the fine fraction for both years. ^{210}Pb levels in the Tinto river sediments, for the same sampling campaigns, are much lower than in the Odiel river. Moreover, there is a clear peak of activity in station T3 in the sampling campaign of 1991 (Fig. 3), with levels much higher than the typical background level. This station is located at the confluence with a small natural stream, Estero del Rincón, (Fig. 1) which crosses the phosphogypsum storage area, and could transport some gypsum particles with high activity levels. These particles will eventually be deposited on the Tinto river bed at the confluence. High activity levels of other natural radionuclides were also found at the same station in 1988 and 1989 [1,2]. The stations upstream from the industries at the Odiel river and also stations ST2 and ST4 of the Tinto river, however, present levels of ^{210}Pb much lower and similar to the background level (≤100 mBq g^{-1}). In general, no correlations between ^{210}Pb content and organic or granular composition were found in either river, and the activity patterns obtained are similar to those found for other radionuclides in previous years [1,2].

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