Journal of Hazardous Materials 198 (2011) 57–64

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Distribution of naturally occurring radioactive materials in sediments from the Ebro river reservoir in Flix (Southern Catalonia, Spain)

M. Mola[a,b], M. Palomo[a,b], A. Peñalver[a,b], C. Aguilar[a,b], F. Borrull[a,b,*]

[a] Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain
[b] Unitat de Radioquímica Ambiental i Sanitària (URAIS), Consorci d'Aigües de Tarragona (CAT), Ctra Nacional 340, km 1094, 43895 L'Ampolla, Spain

ARTICLE INFO

Article history:
Received 18 July 2011
Received in revised form
29 September 2011
Accepted 2 October 2011
Available online 6 October 2011

Keywords:
Naturally occurring radioactive materials
Dicalcium phosphate plant
Industrial waste
Sludge

ABSTRACT

Industrial waste containing radioactive isotopes (from U-decay series) was released into Ebro river basin due to the activity of a dicalcium phosphate (DCP) plant for a period of more than two decades. Gross alpha, gross beta, ^{40}K, ^{226}Ra and ^{210}Pb activities were determined in several sludge samples taken at different depths from different points in the area of influence of the DCP plant located in Flix. Samples were collected from two different zones: one in front of the DCP plant and the second in front of a wastewater treatment plant installed several years after the DCP plant. The data obtained verify the influence of industrial DCP production on radioactivity levels present in the area.

1. Introduction

Natural radionuclides are normally found in the environment in concentrations that seldom become a matter for regulatory concern. However, some human activities can increase the activity concentration of some of these isotopes. Many studies have associated the accumulation of natural radioactivity with the presence of certain industries, such as petroleum extraction, uranium mining and the production of phosphate-based products [1–5].

These natural radioactive elements have been largely unregulated, although different regulatory agencies have become increasingly concerned about their presence in the environment as well as about the possible exposure of workers and the public [6–8]. Specific legislation regarding the limits of contamination of natural radioactive waste has not been introduced, however, guidelines have been published, such as the IAEA Draft Safety Guide DS161 [9], that provide recommendations about radioactivity limits in solid waste, mainly derived from non-nuclear industries [10].

In Spain, Naturally Occurring Radioactive Materials (NORM) were not subject to regulation until the publication of Royal Decree 783 in 2001 [11], which was recently modified in 2010 through Royal Decree 1439 [12] approved as a result of the transfer of European Council Directive 96/29 [13]. These regulations apply directly to those responsible for activities involving natural sources of radiation, making it mandatory to conduct studies to determine whether such activities contribute to a significant increase in the radiation exposure of workers or members of the public.

As mentioned above, the production of phosphate-based products is considered a NORM activity [14–16]. Using sedimentary phosphate rocks as a raw material in an industrial process leads to the input of several different radionuclides, mainly ^{238}U and its decay chain progeny, resulting in increased natural radioactivity in the immediate environment. The products obtained through these processes can be used for several different processes, and it is important to highlight that the results of these industrial processes should be evaluated and regulated, as they can be of radiological concern to workers and the public.

Various Spanish studies have verified natural radionuclide accumulations resulting from phosphoric acid production, for example in Huelva (southern Spain) and in Flix (north-eastern Spain) [17–21]. For instance, Villa et al. [19] studied an area of the Estuary of the Tinto and Odiel rivers (Huelva) and evaluated the ^{226}Ra and ^{210}Pb activities in bottom sediment samples collected from 1999 to 2005, the influence of the waste dumped by the phosphate industry and its temporal evolution. In conclusion, the authors observed that the activities decreased considerably due to the self-cleaning and dilution of this contamination after direct releases into maritime areas ceased in 1998 [22,23].

Our study focuses on the dicalcium phosphate (DCP) plant located in Flix. The production process of DCP from Moroccan phosphate rock started in 1973 and continued for about 25 years. Several studies have focused their attention on this process and

* Corresponding author.
E-mail address: francesc.borrull@urv.cat (F. Borrull).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.10.011

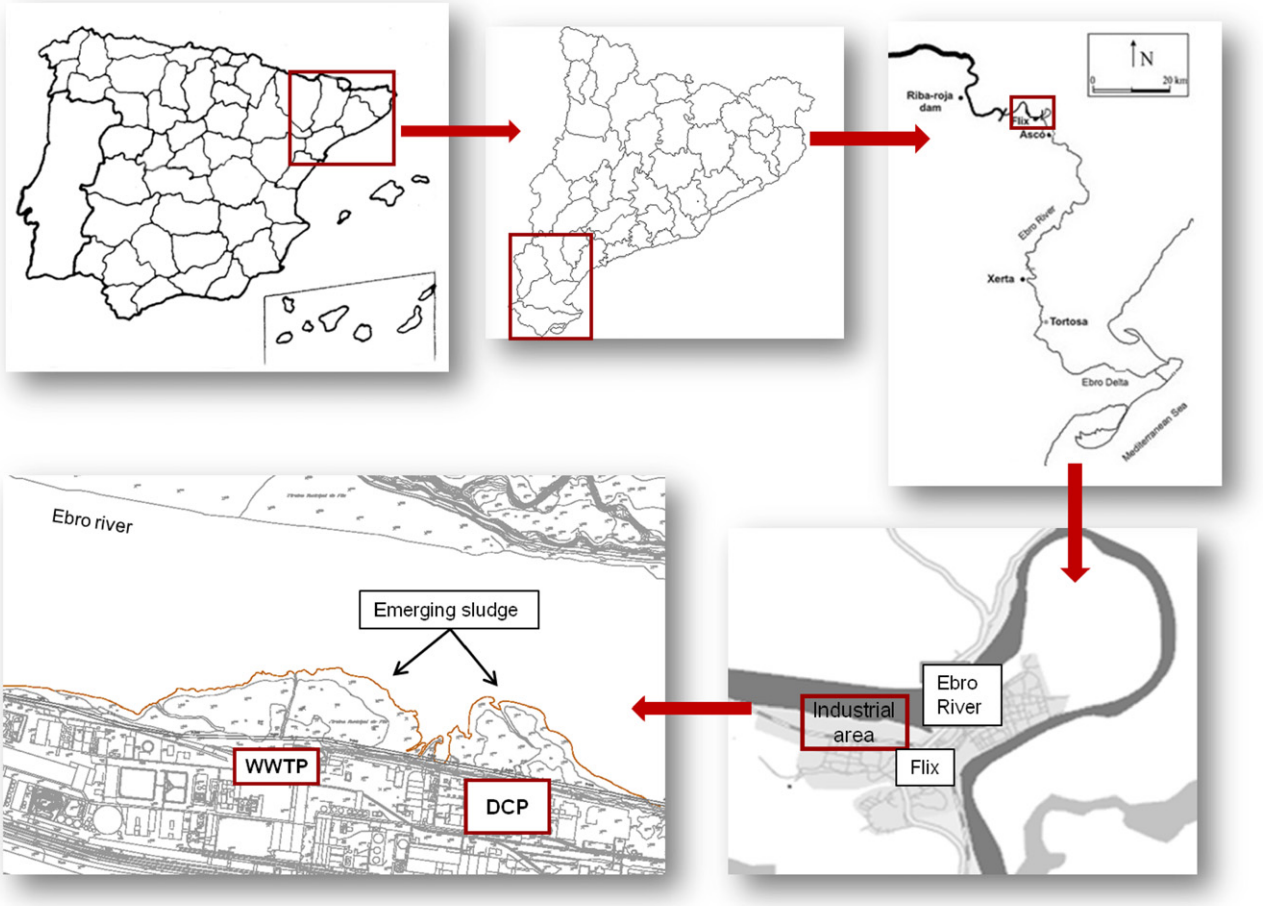

Fig. 1. Area of study close to the DCP factory in which the emerging sludge samples were deposited in the Ebro river is shown (South-Western Catalonia, Spain).

some authors have concluded that it leads to the presence of large amounts of radioactivity in both end products and by-products [4,14]. One of the primary problems with the Flix plant is that it released its waste streams into a reservoir of the Ebro river without any prior treatment until the late nineties, when Spanish Royal Decree 11 [24] was approved.

Some of the published studies carried out in the Flix reservoir area have shown the problem of accumulated residues resulting from DCP production. These studies had two basic aims: to evaluate the concentration of different radioisotopes accumulated in the sludge and to evaluate the possible influence of the DCP industry on the Ebro river ecosystem. In relation to the former, Costa [20] measured the concentrations of ^{238}U, ^{226}Ra and ^{210}Pb and found values approximately 308, 92 and 38 times higher than the natural levels of these isotopes in the bed of the same river. Another study by Casacuberta et al. [21] demonstrated the influence of the industrial activity of the DCP plant on increased radioactive levels in the surrounding area.

Several studies published previously by our group [25,26] have looked at the second objective mentioned above—the effect of the DCP industry on the ecosystem. In one such study, radioactivity levels in two different species of algae were evaluated (*Cladophora glomerata* and *Cynodon dactylon*) [26] from samples taken at different points along the course of the River Ebro. Our results showed that the presence of the DCP plant has had a significant influence on levels of radioactivity, as the highest activity values were observed in algae samples taken from the area surrounding the plant (Flix).

These studies, as well as others focusing on different types of contaminants such as PCBs, heavy metals and others derived from similar industries, make it clear that the early extraction of this contaminated sludge is crucial in order to prevent a possible environmental problem in the river course. In this respect, it is important to point out that as this article is being written a project is underway to remove the sediment sludge from the Ebro area [27,28].

The main goal of this study is to evaluate the radiology of the sludge accumulated in the Flix reservoir at different depths. In particular, our purpose was to establish a possible relationship between our results and the industrial activity conducted at the DCP plant. Since most of the research published to date has studied sediments taken at a superficial level, one of our main aims is to evaluate whether the radioisotopes in the area located in front of the DCP plant are distributed uniformly.

2. Sampling details and methods

2.1. Samples

In this study, sludge samples were collected from different points within the area of influence of the DCP plant in Flix. Fig. 1 shows the area of study close to the DCP factory where the emerging sludge samples from that factory were released into the Ebro river (Catalonia, Spain).

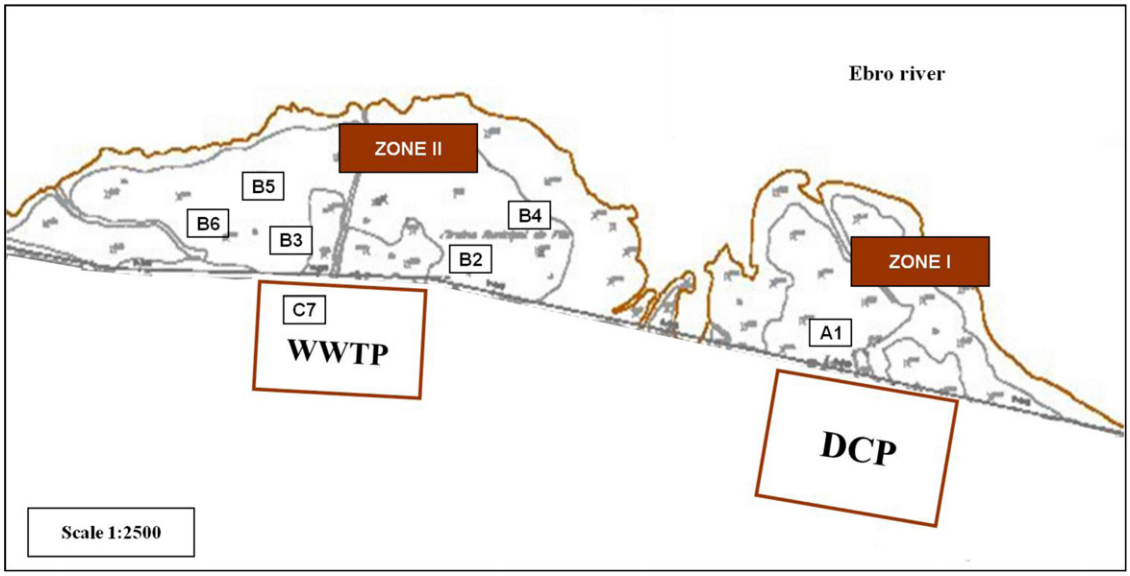

Fig. 2. Location of the seven different sampling points included in this study in front of the area of influence of the DCP plant. Sludge samples were collected from seven different points: A1 is located in the zone called Zone I (in front of the DCP plant) and sampling points B2, B3, B4, B5 and B6 are located in Zone II (in front of the WWTP). C7 is a sampling point located outside of the area of influence of the plant. For each sampling point, sludge samples were collected at different depths ranging between 1 and 11 m.

Fig. 2 shows the sampling area, which was near the plant and in the River Ebro. Specifically, the figure shows two different zones where sludge had accumulated. Zone I is located in front of the DCP plant, where sludge samples were collected from a single sampling point at different depths (A1). Zone II is situated in front of a wastewater treatment plant (WWTP) for the plant and sludge samples were collected from five different sampling points at different depths (B2, B3, B4, B5 and B6) here as well. Finally, we also took sludge samples from a sampling point (C7) which is theoretically not affected by DCP emissions since it is located out of the area where the DCP plant released its waste streams. For all the sampling points, sludge samples were collected at different depths ranging between 1 and 11 m. Therefore, a total of 46 sludge samples were taken. Approximately 750 g of damp sludge sample was taken at each sampling point and placed in a plastic container. Samples were transported to the laboratory where they were transferred to a tray and dried in an oven at a temperature of 110 °C. The samples were then crushed in a ball mill and sifted in a 250 μm sieve.

2.2. Detectors and preparation of samples

To measure gross alpha activity, a zinc sulphide (ZnS) scintillator counter (photo multiplier tube and base preamplifier, model 2000, Canberra, USA) with a voltage of 0.76 kV was used. A certified solution of ^{241}Am with a nominal activity concentration of 4.7 ± 0.4 KBq g^{-1} provided by Amersham International plc. (Buckinghamshire, England) was used to determine the alpha detection efficiency. A planchet containing ^{241}Am with an activity of 100 Bq was prepared from the standard certified solution, and this was used for monthly calibration. The background of each detector was determined by counting an empty planchet for 5000 min.

Gross beta activity was measured with a 10 channel low level alpha/beta counter detector type (Model Berthold LB770, Germany), with a voltage of 1650 V. The background of each detector was determined by counting an empty planchet for 900 min and monthly calibration was performed by using one planchet containing ^{241}Am with an activity of 100 Bq and another planchet of ^{90}Sr/^{90}Y with an activity of 100 Bq. These planchets were prepared from certified solutions of ^{241}Am (4.7 ± 0.4 KBq g^{-1}) and ^{90}Sr/^{90}Y (4.7 ± 1.5 KBq g^{-1}), both provided by Amersham International plc. (Buckinghamshire, England). Source thickness is important in the determination of gross alpha and beta activities in soil and also water samples due to the self-absorption and energy losses. In this sense, we have prepared different planchets containing ^{241}Am and ^{90}Sr standards and increasing amounts of sodium nitrate provided by Merck (Darmstadt, Germany), ranging from 0 to 100 mg for gross alpha determination and from 0 to 700 mg for gross beta determination. The obtained thicknesses in the self-absorption planchets ranged between 0 and 5 mg cm^{-2} and between 0 and 25 mg cm^{-2} for gross alpha and gross beta determination, respectively. Afterwards, in the measurement of the different samples, we applied the corresponding correction factor.

Gamma emitters were measured with a high-resolution germanium detector (HPGe) (model 2020 Canberra Industries, Meriden, USA), equipped with a standard multi-channel analyser. The operating conditions were a voltage of 4500 V, negative polarity and a relative efficiency of 20%. Genie 2000 software (Canberra Industries, Meriden, USA) was used to acquire and subsequently analyse the information provided by the gamma spectra. The background of the detector was determined by counting a 60 mL plastic beaker containing milliQ water for 20 h and monthly calibration was performed by using a standard certified solution which was spiked with a known activity concentration of Pb-210 to cover the entire energy range. Both solutions were provided by the *Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas* (CIEMAT) (Madrid, Spain).

For gross alpha and gross beta activity measurements, 0.05 g of dry sludge sample was weighed into a striated stainless steel planchet supplied by Tecnasa (Madrid, Spain), 2 mL of distilled water was added and dried at a temperature not exceeding 150 °C, in accordance with the procedure stipulated by national laboratories [29]. The samples were then measured using two cycles of 1000 min in each case.

For the measurement of gamma spectra, 60 g of each sample were placed in a 60 mL beaker, which was introduced in the spectrometer and then measured for 20 h. In the case of ^{226}Ra, each beaker was sealed and stored for three weeks prior to its measurement in order to ensure secular equilibrium between ^{226}Ra and its short-lived daughters (^{214}Pb and ^{214}Bi). ^{226}Ra activity values were

determined from the photopeaks of its daughter nuclides in secular equilibrium.

3. Results and discussion

In this study the gross alpha and gross beta activity indexes, and the activities of some natural (^{226}Ra and ^{210}Pb) and artificial (^{137}Cs) gamma emitters were measured in sediments of the Ebro river reservoir near the town of Flix. Most of the samples were taken from the area of influence of a DCP plant. Our main aim was to establish a possible relationship between the uniformity in the distribution of radioactive content found in the samples analysed and the industrial activities undertaken at the plant. In the following subsections we discuss the primary results yielded by our study.

We would like to stress that for the purpose of improving and ensuring the quality of the results of all the procedures carried out in our laboratory we participate periodically in both national and international proficiency/inter-comparison exercises with mineral samples such as soil and phosphogypsum.

3.1. Special cases: C7 profile and the presence of ^{137}Cs

Sampling point C7 was included as a reference. This point, as mentioned earlier, is not affected by the emissions resulting from the industrial activity carried out in the evaluated area, so the sludge samples taken from C7 should, in theory, not contain any contributions resulting from DCP or WWTP dumping.

Fig. 3 shows the different values obtained for gross alpha, gross beta and ^{226}Ra activities for the samples taken at different depths for C7 and their error bars (corresponding to counting uncertainties). We obtained values of between 103 and 309 Bq kg^{-1} for gross alpha, between 448 and 876 Bq kg^{-1} for gross beta and between 28 and 63 Bq kg^{-1} for ^{226}Ra. We compared these results with others reported in the literature in which sludge samples from different areas not influenced by an industrial activity such as a DCP plant were analysed for their radiological content. For instance, Spain has a monitoring program for supervising the radiological quality of the environment called the *Programa de Vigilancia Radiológica Ambiental* (PVRA) which is established under the regulations of the Nuclear Safety Council (CSN) [30]. We selected the results obtained for soil samples from Zaragoza, a city located upstream on the River Ebro, outside of the area of influence of the Flix DCP plant, for comparison purposes. We found that the activity values published by the CSN (between 480 and 670 Bq kg^{-1} for gross beta) were similar to those obtained for C7, and to those reported by United

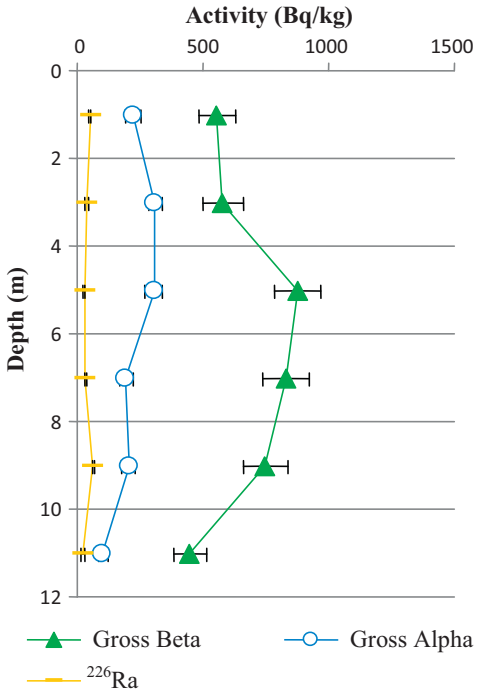

Fig. 3. Vertical profiles for gross alpha, gross beta and ^{226}Ra activities (Bq kg^{-1}) vs. depth for the sludge sample collected in sampling point C7. Error bars are derived from counting uncertainties at $k = 2$.

Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (values between 6 and 250 Bq kg^{-1} for ^{226}Ra) [31]. Therefore, we concluded that C7 could be used as good reference, as it is not influenced by DCP. The measurement of an artificial isotope, ^{137}Cs, was also considered as a reference because its activity profile can be very useful in understanding the temporal distribution of the radionuclides in the sediments taken from the area of influence of the DCP plant in Flix. The presence of this artificial radionuclide at certain depths can be related to the nuclear weapons testing carried out in the atmosphere between 1950 and 1960 as well as to the fallout produced by the Chernobyl accident in 1986, and it has been used to date different sediments [32,33].

Fig. 4 shows the different profiles obtained for ^{137}Cs activity and the corresponding uncertainties for some of the sampling points examined to illustrate the behaviour of this artificial isotope.

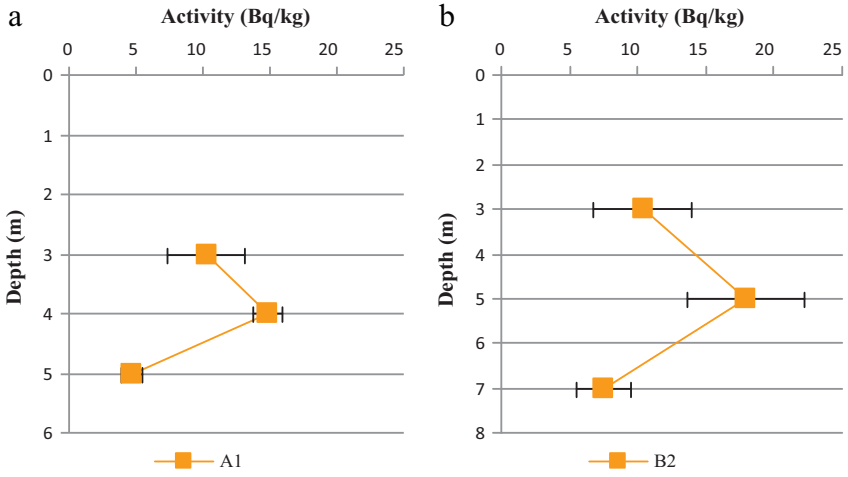

Fig. 4. Vertical profiles for ^{137}Cs (Bq kg^{-1}) vs. depth from sludge samples collected in sampling points A1 (Fig. 4a) and B2 (Fig. 4b). Error bars consider counting uncertainties at $k = 2$.

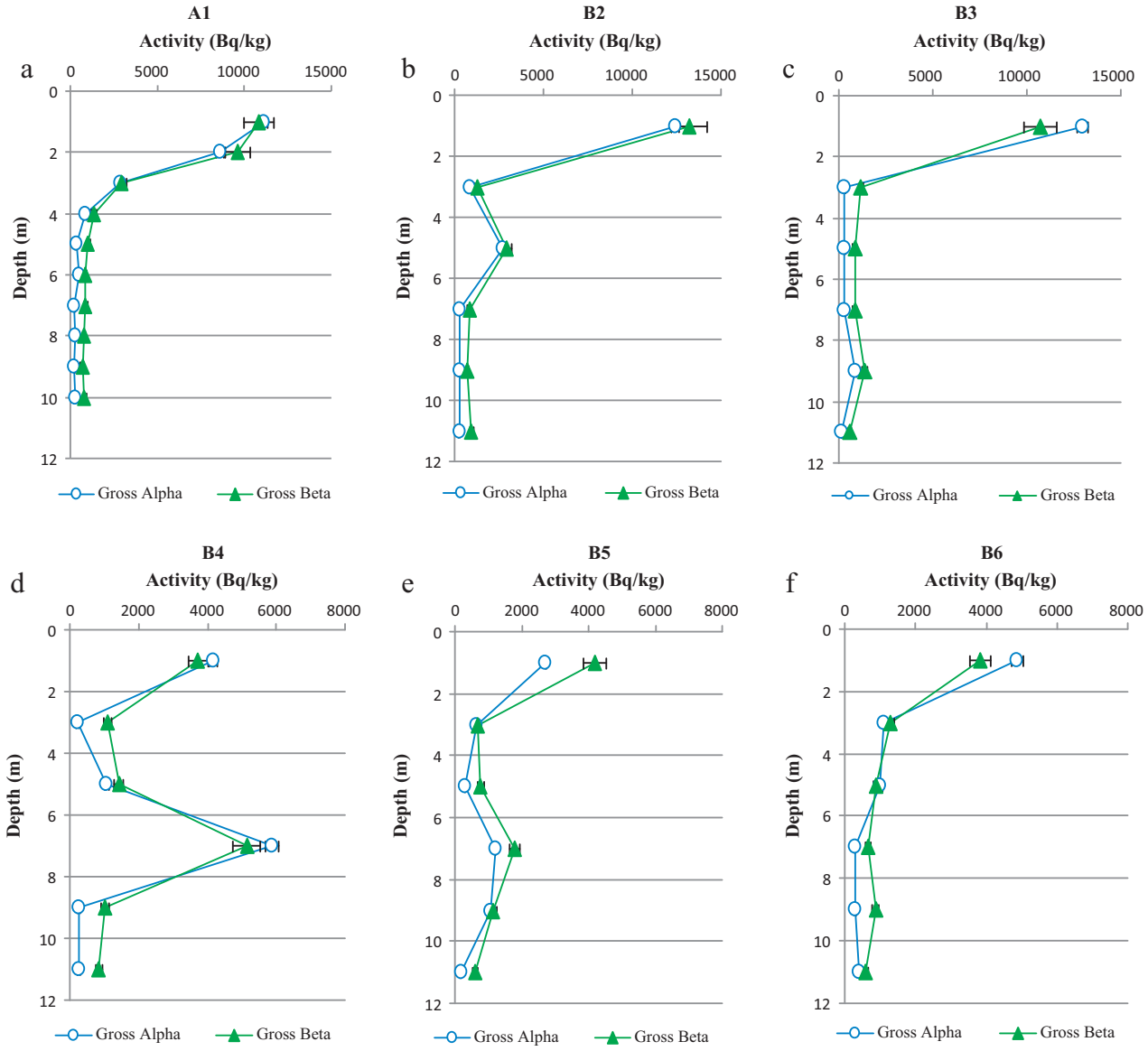

Fig. 5. Vertical profiles for gross alpha and gross beta activities (Bq kg^{-1}) vs. depth obtained for the sludge samples collected in the different sampling points: A1 (Fig. 5a), B2 (Fig. 5b), B3 (Fig. 5c), B4 (Fig. 5d), B5 (Fig. 5e) and B6 (Fig. 5f). Error bars consider counting uncertainties at $k = 2$.

Specifically, the figure shows the profiles obtained for sampling points A1 (located in Zone I) and B2 (in Zone II). A similar behaviour has been found with regard to the distribution of ^{137}Cs in the two sampling points. In both cases this artificial radioisotope could be quantified starting at a certain depth, at approximately 3 m, and up to 5 m in A1 and 7 m in B2. This confirms that this radioisotope was introduced into the environment from a certain date, probably in the fifties, when this specific radionuclide was released into the atmosphere because of the nuclear weapons testing performed between 1950 and 1960. Moreover, due to the Chernobyl nuclear accident in 1986 it was an additional input of this isotope. The activity values obtained ranged from 5 to 20 Bq kg^{-1}. It is important to note that the data we obtained also allows us to establish, by comparison, when the main releases from the DCP industrial plant occurred.

3.2. Gross alpha activity index

One of the parameters measured for all the samples was the gross alpha activity index, which is likely influenced by the DCP plant. Our results are shown in Fig. 5, which gives the profiles of the six different sampling points in the two different testing zones. A different distribution was found at all these sampling points than at C7 (see Fig. 3), with higher activity values for gross alpha obtained at these six sampling points, mainly in the upper layers (between 1 and 2 m), followed by a general decrease in activity values. Error bars corresponding to the uncertainties we encountered are also shown in the figure.

The results yielded by sampling point A1 (Fig. 5a), which is located just in front of the DCP plant, reveals some interesting data. A maximum concentration of gross alpha activity was found in this sample at 1 m (11118 ± 234 Bq kg^{-1}) followed by a marked decrease up to a depth of 5 m (339 ± 44 Bq kg^{-1}). At that depth and deeper, activity remained more or less constant. Therefore, it can be concluded that the influence of the DCP plant decreased as depth increased, since the results obtained were similar to those found at sampling point C7. This behaviour in site A1 might be explained by the profile obtained for ^{137}Cs and through some bibliographic data regarding the historical evolution of the DCP plant [34]. We can attribute the higher values

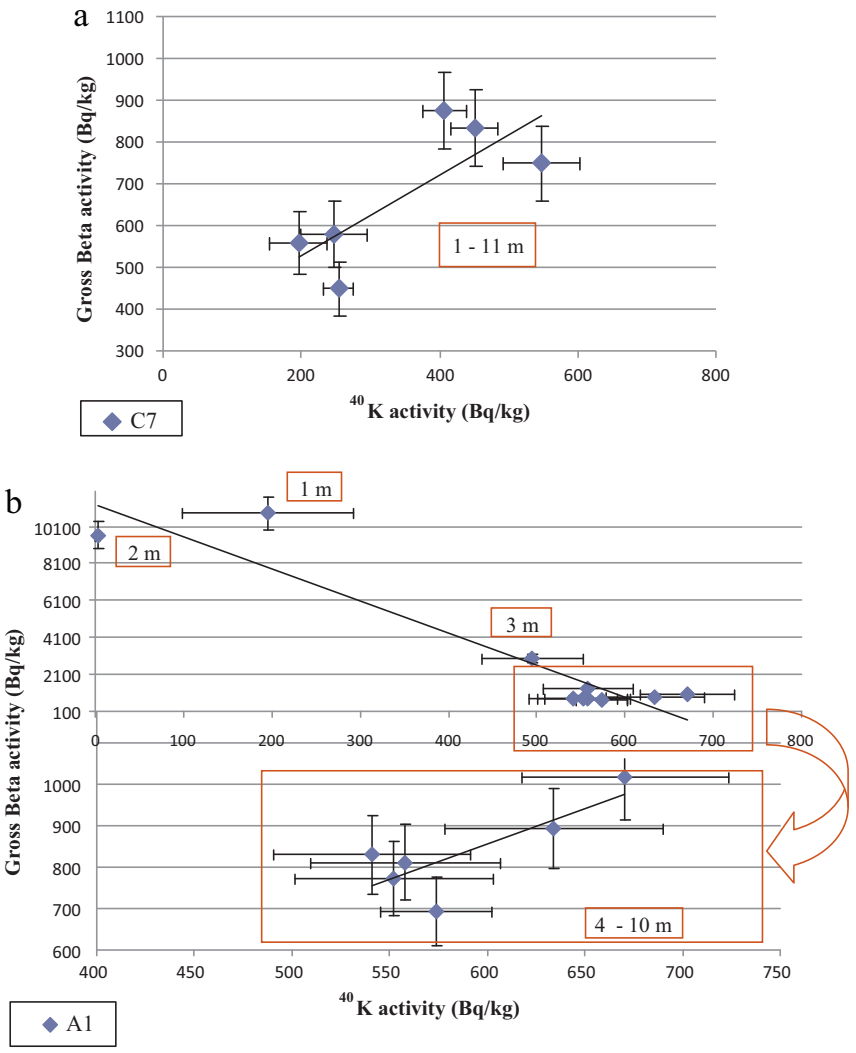

Fig. 6. Gross beta activities (Bq kg^{-1}) vs ^{40}K activities (Bq kg^{-1}) for sludge samples from sampling point C7 (Fig. 6a) and A1 (Fig. 6b). The corresponding depths are also indicated in the figure.

of activity in the upper layers to the higher productivity of the DCP industry during the period from 1992 to 1997. So the main contribution to the radioactivity in these sludge samples took place after the Chernobyl nuclear accident. This assessment was reached by comparing the profiles for this sampling point (Figs. 4a and 5a), which demonstrated the prior introduction of ^{137}Cs.

Samples from five different points (B2, B3, B4, B5 and B6) were collected in Zone II, which is located in front of the WWTP. Fig. 5b–f shows the results obtained from those samples. For instance, in the B3 profile, maximum activity was found at a depth of 1 m (12992 ± 275 Bq kg^{-1}), while at 3 m activity was determined at 303 ± 30 Bq kg^{-1}. These values suggest that the measured activity remained more or less constant over time. A very similar behaviour was found in sampling point B2. The other three sampling points (B4, B5 and B6) yielded activity values in the upper layer that were approximately three times lower than in B2 or B3.

In the activity profiles for some sampling points, such as B4, a pronounced increase in measured activity was found at a certain depth, for example, between 7 and 9 m. Taking into account the evolution of the industrial activity at the site, this might be attributed to a sporadic release of waste.

3.3. Gross beta activity index

We also measured gross beta activity for all the sludge samples. The corresponding values obtained are also presented in Fig. 5, which shows that the trend for gross beta activity is very similar to that obtained for gross alpha activity.

One of the main contributors to gross beta activity in different soils is ^{40}K [31] and we believe that this isotope also plays a relevant role in the different samples analysed in this case. However, due to the DCP industrial activity, other beta isotopes may have also contributed to gross beta activity. To verify this, the relationship between ^{40}K activity and gross beta activity with their error bars is shown in Fig. 6. Specifically, the graphs obtained for C7 and A1 are shown as examples to illustrate this behaviour. Data for C7 are primarily shown because this sampling point is out of the area of influence of the DCP plant, so a linear correlation between the two measured parameters is expected. This trend is shown in the figure corresponding to sample point C7 (Fig. 6a). However, in sampling point A1 (Fig. 6b) no linear correlation between the two parameters was found in the upper layers (the first 1–3 m of depth in the profile), which suggests that other beta isotopes from the ^{238}U chain apart from ^{40}K have contributed to gross beta activity. According to various previous studies reported in the bibliography, such as those

Table 1
Activity concentration and uncertainty ($K=2$) of ^{226}Ra, ^{210}Pb and ^{40}K (Bq kg^{-1}) in different depths from sludge samples.

Code	A1			B2			B4		
depth (m)	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})
1	5847 ± 97	2499 ± 606	196 ± 97	2760 ± 53	1118 ± 277	164 ± 22	566 ± 15	356 ± 97	323 ± 61
2	2479 ± 48	1127 ± 272	<69	–	–	–	–	–	–
3	341 ± 11	259 ± 8	495 ± 57	242 ± 10	125 ± 64	561 ± 66	38 ± 3	<55	883 ± 64
4	114 ± 4	86 ± 38	558 ± 51	–	–	–	–	–	–
5	34 ± 3	<55	671 ± 53	687 ± 20	319 ± 99	624 ± 78	185 ± 9	129 ± 67	600 ± 36
6	40 ± 6	<18	541 ± 50	–	–	–	–	–	–
7	43 ± 5	<54	634 ± 56	31 ± 5	<18	641 ± 52	996 ± 25	820 ± 208	411 ± 84
8	35 ± 3	<19	552 ± 51	–	–	–	–	–	–
9	30 ± 5	<53	574 ± 29	30 ± 3	<19	597 ± 54	42 ± 6	<56	712 ± 33
10	34 ± 5	<55	558 ± 49	–	–	–	–	–	–
11	–	–	–	26 ± 5	<18	534 ± 28	39 ± 5	<54	645 ± 54

Code	B3			B5			B6		
depth (m)	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})	^{226}Ra (Bq kg^{-1})	^{210}Pb (Bq kg^{-1})	^{40}K (Bq kg^{-1})
1	4182 ± 77	1337 ± 330	285 ± 28	896 ± 21	312 ± 83	200 ± 29	1034 ± 28	433 ± 115	332 ± 53
2	–	–	–	–	–	–	–	–	–
3	50 ± 7	<22	440 ± 34	131 ± 8	67 ± 26	<40	172 ± 9	<29	291 ± 58
4	–	–	–	–	–	–	–	–	–
5	48 ± 6	<19	557 ± 5	38 ± 6	<18	549 ± 48	172 ± 10	<29	301 ± 25
6	–	–	–	–	–	–	–	–	–
7	93 ± 6	44 ± 34	441 ± 25	301 ± 10	82 ± 38	336 ± 52	29 ± 5	<18	531 ± 98
8	–	–	–	–	–	–	–	–	–
9	134 ± 8	54 ± 35	543 ± 53	150 ± 8	53 ± 40	438 ± 44	30 ± 5	<19	606 ± 52
10	–	–	–	–	–	–	–	–	–
11	27 ± 4	<18	398 ± 45	22 ± 6	<22	490 ± 29	30 ± 5	27 ± 21	471 ± 49

by Martínez et al. [35] and Azouazi et al. [36], low levels of ^{40}K in the sedimentary material are indicators of the presence of high levels of the other isotopes, mainly ^{210}Pb and other ^{238}U descendants and point to the intrusion of NORM from industries which use phosphate rocks as a raw material in the production of fertilizer. Also, according to UNSCEAR [31] and the study published by Khater et al. [37] the raw material used in the phosphate industry is very poor in ^{40}K. This leads us to conclude that apart from ^{40}K, other contributors have played a role in the gross beta activity measured in this study, such as ^{210}Pb and ^{214}Pb, which are derived from the ^{238}U decay series.

3.4. Gamma emitters

Gamma activity was measured to verify the presence of some of the main individual isotopes that may have contributed to the gross alpha and gross beta activities measured previously. To this end, we measured activity resulting from ^{226}Ra, ^{210}Pb and ^{40}K. The resulting values are shown in Table 1 along with the corresponding uncertainty values. In the case of ^{210}Pb (46.5 KeV) the uncertainties were higher than the other radionuclides due to the Compton effect and the high background, which is characteristic of the low energy spectrum in which this radionuclide emits. Comparing the values reported in Table 1 with the corresponding profiles for gross alpha and gross beta activities (see Fig. 5), the same trend emerges higher activity values for such isotopes (^{226}Ra and ^{210}Pb) were obtained in the upper layer (at a depth of 1 m). Specifically, results comparable to those published in Costa's study [20] were obtained in terms of the values determined in the upper layers.

The results from sampling point A1 also lead to several important conclusions. Maximum concentrations of ^{226}Ra and ^{210}Pb activity in this sample were found at 1 m (5847 ± 97 Bq kg^{-1} and 2499 ± 606 Bq kg^{-1}, respectively) and then dropped off considerably until a depth of 5 m (34 ± 3 Bq kg^{-1} of ^{226}Ra and <MDA for ^{210}Pb). These values are not significantly different from those measured at sampling point C7. Therefore, we can conclude that ^{226}Ra and ^{210}Pb contribute to a great extent to the gross activity measured and their origin can be related to the industrial activity carried out in the testing area. In the case of B4, B3, B5 and B6, higher concentrations of these isotopes were obtained at a depth of 1 m. Moreover, for some sampling points such as B4, a pronounced increase in the measured activity was obtained at a certain depth in the corresponding activity profiles. This was in accordance with the profiles obtained for gross alpha and gross beta activity values.

4. Conclusions

Sludge samples in two different zones within the area of influence the DCP industry in Flix were measured for their radiological content. Samples closer to the surface were found to have higher activity values and this trend was more pronounced in Zone I (located in front of the DCP plant) than in Zone II (located in front of the WWTP).

The individual evaluation of different isotopes from the ^{238}U chain led us to conclude that ^{226}Ra and ^{210}Pb contributed to a great extent to the gross activity measured and their origin is related to the industrial activity carried out in the testing area.

The distribution of the radioactivity over time and in relation to the industrial activity might be explained through the data obtained by ^{137}Cs measurement. We found concordance in the accumulation of radionuclides and the activity carried out in the DCP plant.

Acknowledgments

The authors are greatly indebted to the *Consorci d'Aigües de Tarragona* (*CAT*) for their invaluable collaboration and to the *Generalitat de Catalunya, Departament d'Innovació, Universitats i Empresa* through project 2009 SGR 223. Finally, we also appreciate the cooperation of UTE Flix and UTE Ebre-Flix, which provided us with the samples included in this study.

References

[1] F.S. Al-Saleh, G.A. Al-Harshan, Measurements of radiation level in petroleum products and wastes in Riyadh City Refinery, J. Environ. Radioact. 99 (2008) 1026–1031.

[2] F.P. Carvalho, J.M. Oliveira, M. Malta, Analyses of radionuclides in soil, water and agriculture products near the Urgeiriça uranium mine in Portugal, J. Radioanal. Nucl. Chem. 281 (2009) 479–484.

[3] Q.H. Hu, J.Q. Weng, J.S. Wang, Source of anthropogenic radionuclides in the environment: a review, J. Environ. Radioact. 101 (2010) 426–437.

[4] P.M. Rutherford, M.J. Dudas, R.A. Samek, Environmental impacts of phosphogypsum, Sci. Total Environ. 149 (1994) 1–38.

[5] M. Palomo, S. Peñalver, C. Aguilar, F. Borrull, Presence of naturally occurring radioactive materials in sludge samples from several Spanish water treatment plants, J. Hazard. Mater. 181 (2010) 716–721.

[6] R.S. O'Brien, M.B. Cooper, Technologically enhanced naturally occurring radioactive material (NORM): pathway analysis and radiological impact, Appl. Radiat. Isot. 49 (1998) 227–239.

[7] United States Environmental Protection Agency (USEPA), A Regulators' Guide to the Management of Radioactive Residuals from Drinking Water Treatment Technologies, United States, Environmental Protection Agency. Environmental Radioactivity Services Pty Ltd., Australia, 2005.

[8] D. Vearrier, J.A. Curtis, M.I. Greenberg, Technological enhanced naturally occurring radioactive materials, J. Toxicol. Clin. Toxicol. 47 (2009) 393–406.

[9] International Atomic Energy Agency (IAEA), Radioactivity in material not requiring regulation for purposes of radiation, IAEA safety standards series, No. DS161, 2003.

[10] D. Wymer, Application of international safety standards to work involving exposure natural radiation, International Conference Naturally Occurring Radioactive Materials, NORM IV, ISBN 83-87610-62-3, 2004.

[11] Royal Decree 783/2001, de 6 de julio, por el que se aprueba el Reglamento sobre Protección Sanitaria contra Radiaciones Ionizantes. BOE 26 de julio de 2001.

[12] Royal Decree 1439/2010, de 5 de noviembre, por el que se modifica el Reglamento sobre protección sanitaria contra radiaciones ionizantes, aprobado por Real Decreto 783/2001, de 6 de julio.

[13] European Council Directive 96/29/EURATOM, 13 May 1996, Laying down basic safety standards for the protection of the health of workers and the general public against the dangers arising from ionizing radiation.

[14] N. Casacuberta, Naturally occurring radionuclides in the dicalcium phosphate industry and their transfer to poultry. Ph.D. thesis, Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona (UAB), Bellaterra, Spain, 2011.

[15] C.H.R. Saueia, B.P. Mazzilli, M.H.T. Taddei, Sequential radioanalytical method for the determination of U and Th isotopes, ^{226}Ra and ^{210}Po using alpha spectrometry in samples of Brazilian phosphate industry, J. Radioanal. Nucl. Chem. 281 (2009) 201–204.

[16] J. Paridaens, H. Vanmarcke, Radium contamination of the banks of the river Laak as a consequence of the phosphate industry in Belgium, J. Environ. Radioact. 54 (2001) 53–60.

[17] J.M. Abril, R. García-Tenorio, R. Periañez, S.M. Enamorado, L. Andreu, A. Delgado, Occupational dosimetric assessment (inhalation pathway) from the application of phosphogypsum in agriculture in South West Spain, J. Environ. Radioact. 100 (2009) 29–34.

[18] J.M. Abril, R. García-Tenorio, G. Manjón, Extensive radioactive characterization of a phosphogypsum stack in SW Spain: ^{226}Ra, ^{238}U, ^{210}Po concentrations and ^{222}Rn exhalation rate, J. Hazard. Mater. 164 (2009) 790–797.

[19] M. Villa, F. Mosqueda, S. Hurtado, J. Mantenero, G. Manjón, R. Periañez, F. Vaca, R. García-Tenorio, Contamination and restoration of an estuary affected by phosphogypsum releases, Sci. Total Environ. 408 (2009) 69–77.

[20] E. Costa, Processos de sedimentació i distribució de radioactivitat natural i artificial en sistemes aquàtics continentals de Catalunya (embassaments de Flix i tram català del riu Ebre, Camarassa i llacs pirinencs). PhD thesis, Universitat Autònoma de Barcelona (UAB), Bellaterra, Spain, 2004.

[21] N. Casacuberta, P. Masqué, J. García-Orellana, J.M. Bruach, M. Anguita, J. Gasa, M. Villa, S. Hurtado, R. García-Tenorio, Radioactivity contents in dicalcium phosphate and the potential radiological risk to human populations, J. Hazard. Mater. 170 (2009) 814–823.

[22] Oslo and Paris Commissions (OSPAR Commission), Discharges of Radioactive Substances into the Maritime Area by Non-Nuclear Industry, 2002.

[23] Oslo and Paris Commissions (OSPAR Commission), PARCOM Recommendation 91/4 on Radioactive Discharges, Spanish Implementation Report, 2007.

[24] Royal Decree 11/1995, de 28 de diciembre, por el que se establecen las Normas Aplicables al Tratamiento de las Aguas Residuales Urbanas.

[25] M. Palomo, S. Peñalver, C. Aguilar, F. Borrull, Radioactivity evaluation of Ebro River water and sludge treated in a potable water treatment plant located in the south of Catalonia (Spain), Appl. Radiat. Isot. 68 (2010) 474–480.

[26] M. Palomo, A. Peñalver, C. Aguilar, F. Borrull, Impact of industries in the accumulation of radionuclides in the lower part of the Ebro River (Catalonia, Spain), Radioprotection 45 (2010) 459–475.

[27] Ley 11/2005, de 22 de junio, por la que se modifica la Ley 10/2001, de 5 de julio, del Plan Hidrológico Nacional. BOE núm. 149.

[28] F. Gracia, F.J. Hijós, M.G. Mañueco, M.A. Rodríguez-Trellés, Proyecto para la eliminación de la contaminación química en el Embalse de Flix (Tarragona), Congreso Nacional del Medio Ambiente (CONAMA), 2004.

[29] M. Llaurador, I. Vallés, A. Abelairas, A. Alonso, M.F. Díaz, R. García, M.J. de Lucas, O. Tejión, J.A. Suárez-Navarro, M. Villa, Draft version 5: Procedimientos para la determinación de los índices de actividad alfa total y beta total en suelos y sedimentos, National Laboratories, Spain, 2006.

[30] Nuclear Safety Council (CSN), Programas de vigilancia radiológica ambiental, 2006–2008.

[31] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), Source and Effects of Ionizing Radiation, United Nations Annex B: Exposures from Natural Radiation Sources, New York, 2000.

[32] T. Semizhon, S. Röllin, Y. Spasova, E. Klemt, Transport and distribution of artificial gamma-emitting radionuclides in the River Yenisei and its sediment, J. Environ. Radioact. 101 (2010) 385–402.

[33] E.G. San Miguel, J.P. Bolívar, R. García-Tenorio, Vertical distribution of Th-isotope ratios, ^{210}Pb, ^{226}Ra and ^{137}Cs in sediments cores from an estuary affected by anthropogenic releases, Sci. Total Environ. 318 (2004) 143–157.

[34] M. Hierro, P. Muñoz, J.A. Collazos, A. Gisbert, F.J. Madariaga, J. Sánchez, J.M. Armora, J. Torres, J.L. Peña, Centenario de la fábrica de la sociedad electroquímica de Flix a Erkimia 1897–1997 (1997). ISBN 84-7782-486-X.

[35] A. Martínez-Aguirre, M. García-León, Radioactive impact of phosphate ore processing in a wet Marshland in Southwestern Spain, J. Environ. Radioact. 34 (1997) 45–57.

[36] M. Azouazi, Y. Ouahidi, S. Fakhi, Y. Andres, J.C. Abbe, M. Benmansour, Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco, J. Environ. Radioact. 54 (2001) 231–242.

[37] E.M. Ashraf Khater, R.H. Higgy, M. Pimpl, Radiological impacts of natural radioactivity in Abu-Tartor phosphate deposits, Egypt, J. Environ. Radioact. 55 (2001) 255–267.