



## Presence of Naturally Occurring Radioactive Materials in sludge samples from several Spanish water treatment plants

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### ABSTRACT

Sludge samples from eleven potable water treatment plants (PWTP), three waste water treatment plants (WWTP) and an industrial water treatment plant (IWTP), located in different areas of Spain, mainly in Catalonia, were analyzed for their radiological content in order to determine whether they could be considered as industries affected by naturally occurring radioactive material (NORM). In general, samples from the PWTPs showed higher activity values for the alpha and gamma emitting isotopes than the WWTPs and the IWTP. For example, samples from the area located in the north of Catalonia show values of  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  in the range of 84.4–792.1 Bq/kg, 3.3–26.8 Bq/kg and 63.8–585.9 Bq/kg, respectively. In general, for PWTP, the values obtained for the gamma emitter and alpha emitter isotopes showed that both the geology and the industrial activities correlate with the values measured. The magnitude of these results demonstrates the need to measure the radionuclide content of these samples before reaching a decision about their final disposal.

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### 1. Introduction

Radioactive elements occur naturally in the earth's rocks, soils and water in varying concentrations. Many industrial operations tend to concentrate these naturally occurring radioactive materials (NORM) in by-product waste streams, achieving relatively high activity concentrations of the so-called technologically enhanced NORM (TENORM). The problem of the build up of NORM by some industries is well known. However, these radioactive elements have been largely unregulated, even though different regulatory agencies have become increasingly concerned about the presence of these isotopes in the environment and also about the possible exposure of workers or the public [1,2,3].

In Spain, NORM was not subjected to regulation until the publication of Real Decreto 783/2001 [4]. In this law, a new "Regulation on Health Protection against Ionizing Radiation" was approved as a result of the transfer of European Council Directive 96/29 [5]. In article 62, paragraph VII, the regulation deals with "Natural Sources of Radiation" and the need to study those activities in which workers or members of the public could be exposed to significant doses of radiation [6].

As stated above, different industrial activities contribute to the increase of NORM levels. Among them are mining, milling and processing of uranium ores and mineral sands, fertilizer manufacture

and use, phosphate manufacture, burning of fossil fuels and metal refining [7,8,9].

Water treatment plants (WTPs) have also been considered by some authors as NORM industries [2,10,11,12]. In fact, the incoming water treated in these plants can contain such radionuclides as radium or uranium due to the geological media in which the waters flow. When this water is treated it passes through various filters to remove the contaminants. This treatment may lead to the generation of radioactive wastes such as sludge samples or also to the radiological contamination of the filters used.

The main aim of this study is the radiological characterization of certain gamma and alpha radioisotopes from sludge obtained from different Spanish water treatment plants.

### 2. Methods and sampling details

#### 2.1. Materials and reagents

All chemical reagents used in this study were of analytical grade. Hydrochloric acid (38%), nitric acid (65%), hydrogen peroxide (30%), ammonia solution (25%) and iron chloride (III) and xylene were supplied by J.T. Baker (Holland). Tri-n-butyl phosphate (TBP) was supplied by Fluka (Germany). A column (20 cm length and 10 mm internal diameter) which contained 7.5 g of BIO-RAD AG1-X8 resin (100–200 mesh chloride form) supplied by Eichrom (France) was used.

Uranium and thorium were electroplated onto stainless steel planchets (diameter 25.15 mm and thickness 0.63 mm) supplied

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by Tecnasa (Madrid, Spain). Samples were filtered with a 0.45  $\mu\text{m}$  filter supplied by Whatman (Maidstone, England).

To evaluate the alpha procedure recovery we used  $^{232}\text{U}$  and  $^{229}\text{Th}$  certified solutions with well-known activity concentration values of  $15.01 \pm 0.15 \text{ Bq/g}$  and  $20.91 \pm 0.29 \text{ Bq/g}$ , respectively, both provided by Ciemat (*Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas*) of Madrid (Spain).

A certified solution of ten gamma emitters (QCY-48) provided by Isotrak (Harwell, UK) covering an interval of energy between 60 to 1836 KeV was used for gamma spectrometry calibration. The standard and samples were measured in a 500-ml Marinelli beaker supplied by Tecnasa (Madrid, Spain).

## 2.2. Digestion method of sludge samples

The method employed involves ashing the sample before its acid digestion. To do this, the sample was previously dried in a stove at a temperature of  $110^\circ\text{C}$ , crushed in a ball mill and sifted in a sieve of  $250 \mu\text{m}$ . Subsequently, approximately 250 mg of the dry sample was introduced in a muffle furnace at  $550^\circ\text{C}$  for 12 hours and then transferred to a Teflon beaker. After this, the sample was spiked with 1 mL of  $^{232}\text{U}$  (42.4 Bq) and 1 mL of  $^{229}\text{Th}$  (61.0 Bq) certified solutions to evaluate the radiochemical yield. The next step was the acidic digestion of the sample, for which the EPA Method 3050B [13] was followed. This method consists in a sample attack with aqua regia (3:1  $\text{HNO}_3/\text{HCl}$ ), the final solution being evaporated to dryness. Afterwards, successive additions of 8 M  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  were performed until no further reaction was observed. Finally, after cooling, the solution was filtered through a  $0.45\text{-}\mu\text{m}$  pore-size syringe filter to remove the insoluble particles and then it was brought to a final volume of 50 mL with deionized water. This process completed, the procedure described in the next section was followed to separate uranium and thorium isotopes.

## 2.3. Radiochemical procedure

The methodology used to separate uranium and thorium isotopes was based on the procedures described by Holm *et al.* [14] and Vera Tomé *et al.* [15]. First, 30 mL of iron chloride (III) solution (30 mg/mL) were added to the solutions obtained after following the procedure described in section 2.2, and then the mixtures were agitated by using an electric-magnetic stirrer. The pH was then adjusted to 8 by adding a concentrated ammonia solution to coprecipitate uranium and thorium with iron. After stirring the mix for a further 30 minutes, the precipitate was allowed to settle for at least 4–6 hours and preferably overnight. The supernatant was then carefully siphoned off and discarded and the hydroxide slurry was transferred to a centrifuge tub and centrifuged at 4000 rpm for 10 minutes.

10 mL of 8 M  $\text{HNO}_3$  were added to the isolated precipitates and then uranium/thorium separation was performed by conducting a liquid-liquid extraction process with 5 ml of TBP and then the aqueous phase was discharged. Next, we added 20 ml of xylene and 15 mL of HCl 1.5 M and the aqueous fraction, which contains thorium and impurities, was separated and kept apart. This procedure was repeated three times and all the aqueous fractions were mixed (45 mL). To separate uranium, we took the organic phase and we added 15 mL of water and retained the aqueous phase. The procedure was repeated three times and all the aqueous fractions with uranium were mixed and then evaporated to dryness.

The acidic solution containing the thorium isotopes and impurities was evaporated and re-dissolved in 9 M HCl, and then this solution was passed through a column which contained BIORAD AG1-X8 resin to remove impurities. The thorium eluted in the 9 M HCl was then again evaporated.

When almost dry, the residues, which contain U or Th, were reconstituted by adding 1 mL of 0.3 M  $\text{Na}_2\text{SO}_4$ . This solution was then dried, the residue treated with 0.3 mL of concentrated  $\text{H}_2\text{SO}_4$  and, then, 5 mL of distilled water were added, along with two drops of thymol blue. This solution was heated and its pH was adjusted to 2.1–2.4 by the addition of concentrated  $\text{NH}_4\text{OH}$ . The solution was then transferred to an electrodeposition cell and submitted to electrolysis for 2 hours, under current density of  $1.5 \text{ A/cm}^2$ . One minute before the end of the electrolysis, 1 mL of concentrated  $\text{NH}_4\text{OH}$  was added in order to assure uranium and thorium deposit attachment on the stainless steel disk [16].

The electrodeposition apparatus supplied by Tecnasa, Spain was used to accumulate uranium and thorium in a cell of 25 mm internal diameter on stainless-steel disks of 20 mm in diameter. The anode was a polished platinum spiral wire.

## 2.4. Measurement techniques

The alpha spectrometer (EG&G ORTEC, Model 676A) includes an ion-implanted silicon detector (ORTEC, size:  $450 \text{ mm}^2$ ; alpha resolution: 25 keV FWHM at 5.48 MeV of  $^{241}\text{Am}$ ) in a vacuum chamber (Edwards Model E2M8), a detector bias supplier, a preamplifier, a linear amplifier, and a multichannel pulse height analyzer. During the measurement, the pressure of the chamber was maintained at 10–2 Torr.

Gamma emitters were measured with a high-resolution germanium detector (model 2020 Canberra Industries, Meriden, USA), equipped with a standard multi-channel analyzer. The operating conditions were a voltage of 4500 V, a negative polarity and a relative efficiency of 30%. Genie 2000 software (Canberra Industries, Meriden, USA) was used to acquire and subsequently analyze the information provided by the gamma spectra.

Conductivity and pH from water river samples were measured with a conductimeter, and pHmetre both supplied by (Crison, Barcelona, Spain).

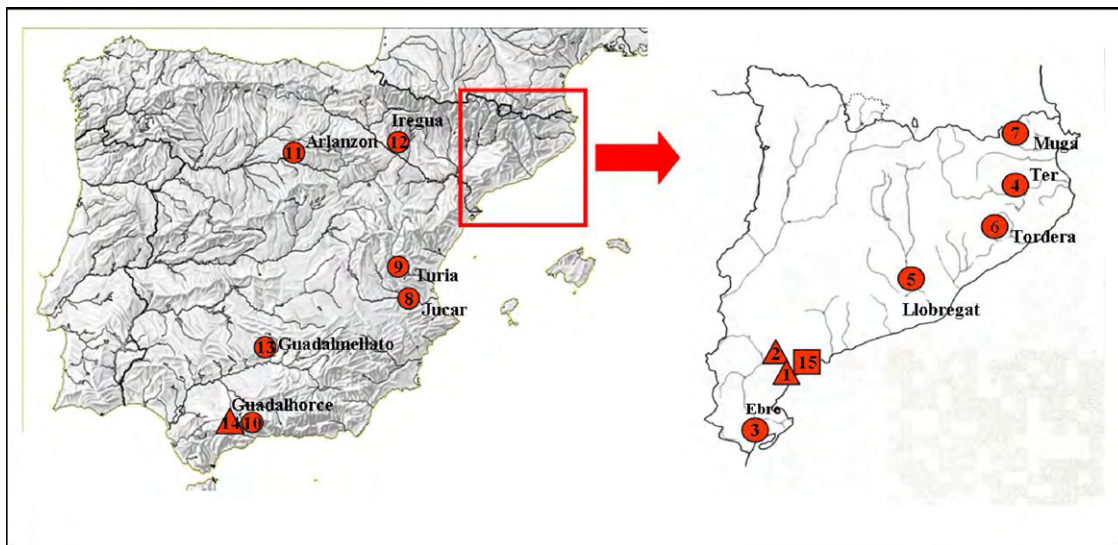
## 2.5. Samples

Sludge samples were obtained from fifteen different water treatment plants. All the plants were located in different areas of Spain as shown in Fig. 1. Basically most of the plants were located in the area of Catalonia and also we selected other plants from other Spanish regions. The selection was carried out taking into account that plants were of different geological areas and also we considered that they used different treatment processes. In particular, we analyzed the sludge from eleven potable water treatment plants (PWTP) (3–13), three waste water treatment plants (WWTP) (1, 2 and 14) and an industrial water treatment plant (IWTP) (15). These sludge samples were taken from the centrifuge and water was removed by decantation. Then they were transferred to a tray and dried in a stove at a temperature of  $110^\circ\text{C}$ . After that, the sample was crushed in a ball mill and sifted in a sieve of  $250 \mu\text{m}$ . Finally, to measure the gamma emitting isotopes, the sample was transferred to a Marinelli beaker of 500 ml. In the case of alpha emitting isotopes the sludge samples were treated as described above in sections 2.2 and 2.3.

To ensure the quality of the results of the procedures carried out in our laboratory, we also participated in different intercomparison exercises. In particular, one organized by the Spanish National Security Council (CSN) and another by the International Atomic Energy Agency (IAEA).

## 3. Results and discussion

As stated in the introduction to this paper, the European Union's Council Directive 96/29/Euratom [5] paid specific attention to nat-



**Fig. 1.** Map of Spain indicating the location of the different water treatment plants from which sludge samples were taken. In particular, the map shows the eleven potable water treatment plants (PWTP) (● 3–13), the three waste water treatment plants (WWTP) (▲ 1, 2 and 14) and also the industrial water treatment plant (IWTP) (■ 15) selected for this study.

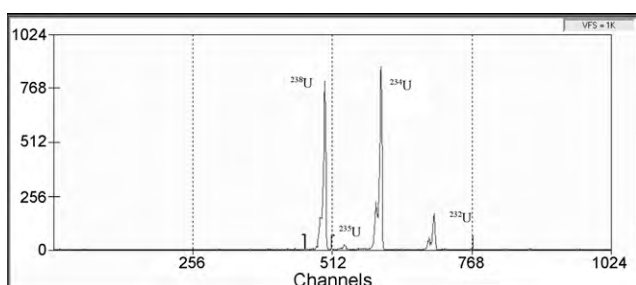
ural sources of radiation. EU Member States are obliged to identify any work activities that cannot be ignored from a radiological point of view and as a consequence most of the EU Member States have implemented national regulations concerning natural sources of radiation. Nevertheless, in many countries there is still a lack of knowledge regarding radiation protection problems with NORM, even though it is generally recognized that several kinds of NORM affected industries exist, among them water treatment plants.

In this context, sludge samples from fifteen Spanish water treatment plants were analyzed to determine the presence of radioactivity and evaluate their possible consideration as NORM industries. In particular, we selected eleven PWTPs located in different areas of Spain and with diverse geological characteristics. We included in this study three WWTPs and an IWTP.

For all the samples, uranium and thorium emitter isotopes were evaluated, and we also quantified a group of natural gamma emitters. In the following sections we discuss the main results obtained from these measurements.

### 3.1. Alpha emitters

**Fig. 2** contains an example (particularly from the water treatment plant number 3) of a spectrum of uranium isotopes from the sludge sample obtained from one of the evaluated PWTPs. In this figure, peaks for the different uranium isotopes can be observed. As is mentioned in Section 2,  $^{232}\text{U}$  was used to evaluate the radiochemical yield for uranium. We obtained an average yield of  $49 \pm 3\%$ . We used  $^{228}\text{Th}$  was used to evaluate the radiochemical yield for tho-



**Fig. 2.** Uranium spectrum obtained from the sludge sample from the PWTP numbered as 3.

rium and, in this case, we obtained an average yield of  $46 \pm 3\%$ . This value is in accordance with data reported in the literature: Lozano *et al.* [17] reported a mean recovery value of  $51 \pm 3\%$  and  $50 \pm 5\%$  for uranium and thorium respectively, using the same procedure that we used. However, it should be noted that the radiochemical yield values found in the bibliography can vary greatly depending on the sample matrix and also on the radiochemical procedure itself [6,18].

**Table 1** shows the average activity for uranium and thorium isotopes (Bq/Kg dry weight), the associated uncertainty values calculated using a level of confidence of 95% ( $k=1$ ) [19] and the  $^{234}\text{U}/^{238}\text{U}$  isotopic ratio. Two replicates have been carried out for each sample so standard deviation of the results has also been included in the table.

Throughout the results reported in **Table 1** and as is to be expected, in general, for uranium isotopes, PWTPs displayed higher activity values than the other types of water treatment plants. This behavior can be mainly attributed to the raw water used in each case and also in the water treatment process. The WWTP and the IWTP receive urban wastewaters and industrial discharges respectively. These sewage sludge samples corresponded to a mix of primary and secondary sewage, which was anaerobically digested and then dehydrated using press filters. The conventional treatment for sewage effluent basically employs: mechanical filtration, gravity settling, biological oxidation and chemical treatment. Sludge generated in municipal sewage treatment plants is essentially organic, although measurable quantities of metals, minerals and other compounds are present. However, the sludge from PWTPs were produced after coagulation/flocculation process. Each plant uses a characteristic coagulant, as we can see in **Table 2**. Once the sludge was formed, this was taken from the centrifuge and water was removed by decantation. The water treated in a PWTP can transport different radioisotopes which can be associated with such factors as the geology of the river course and also with the presence of industries close to the river upstream of the treatment plants. Also, it is important to consider the treatment process followed in each plant since this could have a great influence on the removal of radioisotopes, as several authors have demonstrated [20,21].

An examination of the behavior of the different PWTPs reveals relatively high activity values for uranium isotopes for plants 4, 6 and 7. These three plants are located in the same region, in the north

**Table 1**  
<sup>234</sup>U, <sup>235</sup>U, <sup>238</sup>U, <sup>230</sup>Th and <sup>232</sup>Th activities and uncertainty of the measurement for sludge samples analyzed by  $\alpha$ -spectrometry.

Type	Sample code	<sup>234</sup> U A (Bq/Kg dry weight)*	<sup>235</sup> U A (Bq/Kg dry weight)*	<sup>238</sup> U A (Bq/Kg dry weight)*	<sup>234</sup> U/ <sup>238</sup> U ratio	<sup>230</sup> Th A (Bq/Kg dry weight)*	<sup>232</sup> Th A (Bq/Kg dry weight)*
WWTP	1	36 ± 4 (6)	1.2 ± 0.8 (0.3)	29 ± 2 (2)	1.25	16 ± 4 (6)	4 ± 2 (1)
WWTP	2	54 ± 5 (12)	1.3 ± 0.7 (0.2)	42 ± 4 (9)	1.29	13 ± 5 (10)	13 ± 4 (10)
PWTP	3	153 ± 5 (62)	5 ± 1 (3)	132 ± 4 (55)	1.16	25 ± 1 (5)	14 ± 2 (7)
PWTP	4	790 ± 20 (152)	18 ± 2 (2)	540 ± 20 (145)	1.46	25 ± 3 (5)	11 ± 3 (4)
PWTP	5	84 ± 3 (8)	3.3 ± 0.2 (1)	64 ± 2 (10)	1.32	31 ± 6 (8)	25 ± 4 (4)
PWTP	6	730 ± 120 (182)	27 ± 5 (4)	590 ± 90 (120)	1.25	8 ± 2 (2)	11 ± 3 (3)
PWTP	7	480 ± 90 (45)	20 ± 5 (6)	390 ± 70 (55)	1.22	19 ± 7 (5)	30 ± 10 (11)
PWTP	8	41 ± 9 (15)	0.3 ± 0.2 (0.1)	26 ± 6 (10)	1.60	10 ± 4 (2)	7 ± 3 (2)
PWTP	9	150 ± 30 (55)	4 ± 1 (2)	80 ± 20 (18)	1.80	16 ± 3 (3)	4 ± 2 (1)
PWTP	10	24 ± 5 (6)	1.5 ± 0.5 (0.5)	19 ± 5 (4)	1.22	17 ± 4 (5)	21 ± 5 (7)
PWTP	11	120 ± 20 (46)	5 ± 1 (1)	120 ± 20 (32)	1.02	90 ± 20 (11)	19 ± 4 (8)
PWTP	12	170 ± 30 (54)	3 ± 1 (0.9)	100 ± 20 (42)	1.72	15 ± 4 (5)	16 ± 4 (6)
PWTP	13	180 ± 40 (55)	7 ± 2 (3)	140 ± 30 (45)	1.30	9 ± 4 (5)	15 ± 5 (4)
WWTP	14	29 ± 7 (3)	0.7 ± 0.3 (0.2)	23 ± 6 (5)	1.32	11 ± 3 (2)	8 ± 2 (3)
IWTP	15	44 ± 2 (5)	1.3 ± 0.1 (0.3)	43 ± 2 (2)	1.00	42 ± 1 (5)	8.4 ± 0.4 (1)

\*The uncertainty is calculated using a confidence level of 95% (k=1).  
In parenthesis: Standard relative deviation.

of Catalonia, an area in which granite predominates. Therefore, the relatively high activity values may be correlated with the geology of the area in which these plants are located. However, plant number 5, despite belonging to the same area, shows lower activity values for uranium. This fact can be explained by the different composition of the raw water used in each case, the different coagulants used and the water pH variations, since it has been reported by Gáfvert *et al.*, [10] that the removal uranium efficiency is very sensitive to the pH during flocculation-coagulation process. Table 2 shows the origin of the raw water used at all the PWTPs included in this study, the conductivity and the pH, and also the different coagulants used in the corresponding treatment process. In particular, PWTP 5 is fed with water from the Llobregat River, which has high salinity (conductivity is always over 1000  $\mu$ S/cm). This high salinity is related to the mining activities at the large salt deposits located in the upper part of the basin. Fernández-Turiel *et al.* [22] states that the raw water quality variability of both the Llobregat River (PWTP 5) and the Ter River (PWTP 4) could be related to the seasonal variations of the Mediterranean climate. However, the Sau-Susqueda-Pasteral reservoir system minimizes the influence of these effects on the Ter's raw water. It is important to note that the correlation between the uranium concentration and the salinity has been the subject of previous study. For example, Salas [23] demonstrated that there is a relationship between salt content and uranium absorption. Salas observed that a high salt concentration decreases the uranium absorption onto the particulates and, consequently, when water has a high salinity it reveals lower uranium activities in the sludge. The same behavior was observed for PWTPs 8 and 10, which also displayed low uranium activities and high conductivity values (1000  $\mu$ S/cm).

Another noteworthy fact is the difference between the coagulants used. As shown in Table 2, PWTPs 3 and 10 used FeCl<sub>3</sub> as coagulant whereas the other plants used an aluminum coagulant. In this sense, the work reported by Gáfvert *et al.* [10] is significant. These authors stated that, as a general trend, iron coagulant has slightly lower removal efficiency than aluminum coagulant. We observed the same trend for PWTP 10, which displayed lower uranium activities than the other plants studied. However, for PWTP 3, which also used iron coagulant, the uranium activities were relatively high. This may be due to the presence of a dicalcium phosphate factory close to the river upstream of PWTP 3. Production of dicalcium phosphate (DCP) from Moroccan phosphate rock started in 1960 and for 30 years the industrial waste from the plant was dumped in a reservoir, with no prior treatment. This produced an accumulation of wastes with high concentrations of <sup>238</sup>U and its by-products in the reservoir and, consequently, these isotopes are transported by water and can reach the water treatment plant [24,25].

The activity values of thorium isotopes measured for all the sludge samples were lower than was the case for uranium. This confirms the expected behavior, since this element has less affinity with water than uranium and most of the thorium will be present in suspended matter or sediment. Therefore, the concentration of soluble thorium in water will be very low. Also the values obtained for the different types of treatment plants do not show significant differences. The only noteworthy point is the value obtained for <sup>230</sup>Th in the sludge sample from PWTP 11 which also displayed a high activity value for its gamma parent <sup>234</sup>Th (860 ± 50 Bq/Kg). The raw water comes from the Demanda Mountain, which is about 30 kilometers from the capital, in the municipal district of Uzquiza,

**Table 2**  
River water, conductivity and pH of the water treated in each plant. And also, the coagulant used in the coagulation process applied in each PWTP.

sample code	type	River Water	conductivity $\mu$ S/cm	pH	coagulant
3	PWTP	Ebro	500	7.5	iron chloride
4	PWTP	Ter	400	6.5–9.5	aluminum sulphate
5	PWTP	Llobregat	1500	6.5–9.5	aluminum polichloride
6	PWTP	Tordera	300	6.5–9.5	aluminum polichloride
7	PWTP	Muga	500	6.5–9.5	aluminum polichloride
8	PWTP	Jucar	1000	7.5–9	aluminum polichloride
9	PWTP	Turia	700	7.5–9	aluminum polichloride
10	PWTP	Guadalhorce	1000	6.5–9.5	iron chloride
11	PWTP	Arlanzon	400	6.5–9.5	aluminum polichloride
12	PWTP	Iregua	400	7.5	aluminum sulphate
13	PWTP	Guadalmellato	289	7.5	aluminum polichloride



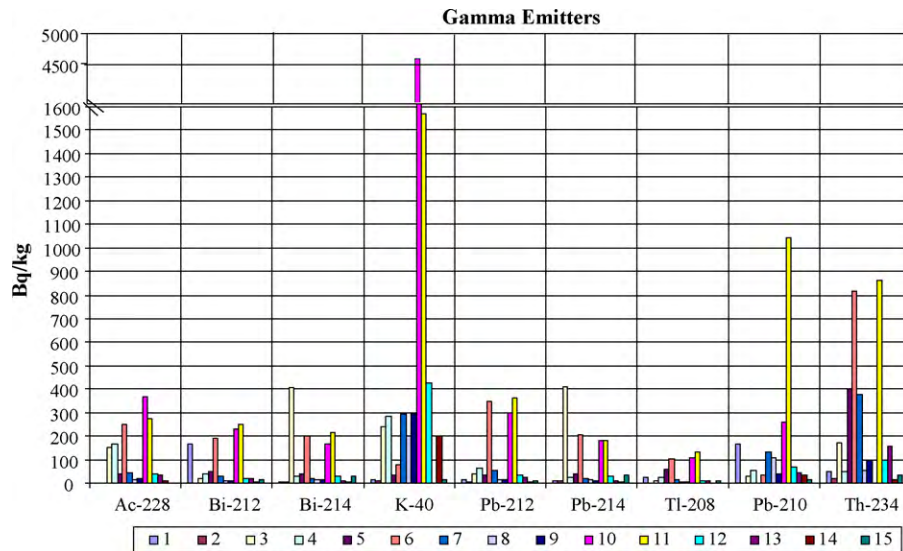


Fig. 3. Activity levels of NORM gamma emitters (Bq/Kg dry weight) obtained for the sludge samples coming from the different 15 water treatment plants included in the study.

which is located on the mountain slope. Since the water treated in this plant is taken directly from the source river, some authors, such as Tabeada *et al.* [26], have reported that thorium remains dissolved in the water, and it is not absorbed by the particulate matter.

Finally, when uranium isotopes are measured is important evaluate the isotopic ratio between  $^{234}\text{U}/^{238}\text{U}$ . As we can observe in Table 1, in the case of the IWTP included in this study the ratio is one, whereas for the rest of the plants this value shows that uranium is out of secular radioactive equilibrium, exhibiting an enrichment of  $^{234}\text{U}$  relative to  $^{238}\text{U}$ . The PWTPs numbered as 3–7, which are from Catalonia, show no significant differences between  $^{234}\text{U}/^{238}\text{U}$  ratios among them, being the values around 1.16–1.46 although they differ greatly in the uranium concentrations found. Also, the PWTP 8 and 9, are from the same area, dominated by carbonate rocks, these plants have similar values of the equilibrium ratios (1.6 and 1.8, respectively). The  $^{234}\text{U}$  enrichment observed in all the cases, is probably due to its instability in crystalline lattices after recoil following alpha emission from  $^{238}\text{U}$ . In this process, the chemical bond is weakened and the  $^{234}\text{U}$  oxidation state changes from tetravalent to a more soluble hexavalent form. Also, we would comment that some authors have been reported the  $^{234}\text{U}/^{238}\text{U}$  disequilibrium in the superficial water, due to the interaction between the water and the rocks and the rain water contribution [27–29].

### 3.2. Gamma emitters

Fig. 3 shows the distribution of the obtained activities (in Bq/Kg dry weight) for a group of gamma emitters quantified in the sludge samples from all fifteen water treatment plants.

The figure shows that  $^{40}\text{K}$  and the isotopes derived from the  $^{238}\text{U}$  and  $^{232}\text{Th}$  decay chains were found in the highest activities. The origin of those isotopes can be attributed to the raw water used in the corresponding plant as was indicated in the discussion of the behavior for uranium and thorium isotopes.

An examination of the results from Fig. 3 reveals that in general the PWTPs showed the highest values for some of the measured gamma emitting isotopes. Of all the results, it is noteworthy that for PWTP 3 the activity values for  $^{214}\text{Bi}$  and  $^{214}\text{Pb}$  were higher ( $405 \pm 9$  Bq/Kg and  $410 \pm 9$  Bq/Kg, respectively) than those obtained for the rest of plants (4–212 Bq/Kg and 4–198 Bq/Kg, respectively). These differences could be attributed to a combination of two factors:

- i) The presence of a dicalcium phosphate factory close to the river upstream of PWTP 3. As stated in the previous section and as Casacuberta *et al.* [24] published, in this reservoir there is a high accumulation of wastes with elevated concentrations of  $^{238}\text{U}$  and its by-products. However, it should be noted that this chain behaves differently depending on the isotope since, for example,  $^{210}\text{Pb}$  and  $^{234}\text{Th}$  have a greater affinity to associate onto particulates and consequently these radionuclides were not transported by the water to the PWTP.
- ii) Another explanation may be the different procedure followed in the water treatment plants, for example the different coagulants used. As reported above, PWTPs 3 and 10 used  $\text{FeCl}_3$  as coagulant whereas the other plants used an aluminum coagulant. Gáfvert *et al.* [10] stated that a general trend is for radium isotope behavior to be contrary to that for uranium. Thus iron-radium precipitate is more easily removed. This behavior can be observed in the relatively high concentration activities of radionuclides, such as  $^{214}\text{Bi}$ ,  $^{214}\text{Pb}$ ,  $^{212}\text{Pb}$  and  $^{212}\text{Bi}$  (see Fig. 3), found in the analyzed sludge samples from PWTP 3. This can be attributed to the removal of radium ( $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ ) from the water samples treated by means of processes such as flocculation, coagulation and precipitation with  $\text{FeCl}_3$ , as described by Baeza *et al.* [21], and the presence of the waste sludge accumulated in the Flix reservoir.

Finally, of note is the fact that, in the sludge samples from PWTPs 6, 10 and 11, we also observed relatively high concentrations of  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$ , and  $^{212}\text{Bi}$  in comparison with the values for the other plants analyzed. These radionuclides belong to the  $^{232}\text{Th}$  decay chain. Their presence may be attributed to the geology, the soil chemistry and water movement. In the case of PWTP (10), the high  $^{40}\text{K}$  activity values  $4800 \pm 600$  Bq/Kg are also significant. In particular, the high potassium content of this plant is related to the raw water and, in particular, this plant is a desalination plant

As we have stated in this section, we conclude that surface waters are one of the main factors that have an influence in the spread of radionuclides throughout the territory. Thus the role of rivers in the transportation and accumulation of radionuclides has to be taken into account when water is treated in a PWTP. For example, PWTP 3 only treats  $4.3 \text{ m}^3/\text{s}$  of the Ebro River which represents 1.4% of the total water transported by the river (at an average flow of  $300 \text{ m}^3/\text{s}$ ). The quantity of sludge produced by this plant is 692 T

per year, so the total sludge inventory produced for  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  was 195MBq/year and 203MBq/year, respectively.

#### 4. Conclusions

The results of this study show that sludge produced by a water treatment plant can concentrate radioactive constituents from source waters. The geology and industrial activities have an important influence on the radioisotopes present in the water and later on the sludges generated. Among the different isotopes found, are uranium and thorium emitting isotopes and their descendents and also  $^{40}\text{K}$ .

With all the results from the total inventory of the sludge samples analyzed, and considering that the European Union has no regulations on the disposal of sludge samples generated in water treatment plants, we pose the question of whether sludge samples from PWTP can be considered as NORM material. In any case, it would be important to consider this study as a starting point in this sense and to establish future aims to carry out more exhaustive studies to evaluate the possible effects on workers in contact with such kinds of materials or samples, and also on the population in general when such sludge samples are reused for different applications such as building materials.

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