Evaluation of the radioactive pollution in the salt-marshes under a phosphogypsum stack system

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Abstract

Next to the city of Huelva (SW of Spain), around 100 Mt of phosphogypsum (PG) are stored in stacks on the salt-marshes of the Tinto River estuary covering a surface of about 1000 ha. Due to the high content of ^{238}U series natural radionuclides of the PG, its acidic nature (pH about 3), and the fact that PG stacks were disposed without any kind of isolation from the substrate, they could produce a potential radioactive impact into the underlying sediments.

The aim of this work is to assess the pollution of the underlying sediments by natural radionuclides coming from the PG stacks. To this end, seven cores were taken, and PG and sediments samples collected at different depths were analysed. The activity concentrations of the

main long half-live natural radionuclides of interest were determined by applying both gamma-ray and alpha-particle spectrometry radiometric techniques.

The results of this study showed that the first decimeters of salt-marsh sediment act as a "barrier" for the radionuclides coming from the PG stacks decreasing rapidly its activity concentration in depth, affecting mainly sediments located in the first 20 cm below the contact due to mixing processes. While ^{230}Th, ^{226}Ra and ^{210}Pb pollution is mainly restricted to the first 20 cm of sediments, U-isotopes can reach higher depths (up to around 50 cm) by leaching processes due to their lower reactivity and higher concentration in the polluted leachates. The obtained results have high relevance for the design of the perimeter channel which is projected to build in the restoration project, suggesting that should has around 1 m deep under the base of the PG stacks, to ensure the full collection of polluting leachates, and to prevent their release into the estuary of the Tinto River.

Keywords

Phosphogypsum; natural radionuclides; radioactive pollution; radionuclide mobility; salt-marsh.

1. Introduction

On the salt-marshes of the Tinto River (SW Spain), close the Huelva city, large phosphogypsum (PG) stacks are located (Fig. 1). The confluence of the Tinto and Odiel Rivers form the Huelva estuary, which is an ecosystem of great interest and special characteristics, due to the acid mine drainage (AMD) provoked mainly by old abandoned sulphide mines located upriver, and the chemical industrial complex located at their mouths.

About 300 Mt of PG are produced worldwide every year (Yang et al., 2016). Only 15% of world PG production is recycled, and hence it is mainly disposed by dumping in large stacks, usually placed in coastal zones close to the factories, where PG is frequently exposed to weathering agents and may provoke severe environmental damages (Tayibi et al., 2009). The manufacturing of phosphoric acid (H_3PO_4) from the wet chemical attack of the phosphate rock with sulfuric acid (H_2SO_4) generate PG as a waste, which is more than 95% constituted by gypsum ($CaSO_4 \cdot 2H_2O$). Since 1965 the five acid phosphoric factories included in the industrial complex of Huelva (Spain), have produced annually around $2.5 \cdot 10^6$ tonnes of PG (Bolívar et al., 2002) until the end

of 2010, when the production of phosphoric acid stopped. The phosphate rock used in the factories of Huelva came mainly from Morocco (Bolívar et al., 1996a), and contained metal(oid)s in levels similar to typical soils, but with U-series radionuclides concentrations of about 1500 Bq kg^{-1} per nuclide (about 50 times higher than unperturbed soils), with ^{238}U in radioactive equilibrium with its daughters. About 20% of U, more than 70% of Th, and the majority of Ra, Pb and Po (> 95%) contained in the phosphate rock remains in the PG (Bolívar et al., 1996a, Bolívar et al., 2009). In the European Union, PG is currently considered a Naturally Occurring Radioactive Material (NORM) because of the high concentration of both ^{226}Ra and ^{230}Th radionuclides (IAEA, 2003; Directive 2013/59/Euratom*)*. On the other hand, the remaining phosphoric acid trapped between the PG particles explains the high acidity and polluting potential of the aqueous leachates produced by this waste (Pérez-López et al., 2010, Pérez-Moreno et al., 2018).

The potential contamination pathways from the PG stacks of Huelva into the environment, atmospheric by ^{222}Rn and radioactive particulate matter and surface sediments and waters of the Huelva estuary by the leachates emerging as edge outflows, have been previously studied in numerous works (Bolívar et al., 2002; Borrego et al., 2007; Hierro et al., 2013; Gázquez et al., 2014; Lopez-Coto et al., 2014; Hernandez- Ceballos et al., 2015; Perez-López et al., 2015, 2016; Papaslioti et al., 2018; Gutiérrez-Álvarez et al., 2019). The results of these works showed an increase in the concentration of metals and radionuclides in the surrounding environment. In this regard, the authorities in cooperation with the responsible companies, are designing an engineering a project for their remediation at this time.

Despite the numerous studies, and that the PG piles were placed on the marshes without any impermeable layer to prevent percolation, the impact on the sediments under the stacks only have been studied in a previous work (Guerrero et al., 2019). This study allowed to characterize the salt-marsh sediments under the stacks (mineralogy, granulometry, and geochemistry), but ^{238}U series radionuclides, which are key part of the potencial impact of the PG stacks were not analysed. The results obtained in this work will provide helpful information to assess the routes of contamination and develop restoration methodologies to others NORM repositories.

Considering the previous facts, the objective of this work is to determine the degree of affection of the salt-marsh sediments under the PG stacks of Huelva due to natural radionuclides coming from the stacks.

2. Study area

In the industrial process of Huelva, PG was transported as an aqueous slurry and disposed, without any type of isolating, forming large stacks on the salt-marshes of the Tinto River, accumulating about 100 million tonnes and covering an area of about 1000 ha, at a distance less than 1 km from the Huelva city.

The area where the generated PG during the production time was disposed is currently divided into 4 zones (Fig. 1). Zones 1 (around 400 ha) and 4 (around 150 ha) located to the south and north respectively were previously restored. On this basis, this study was not extended to these zones.

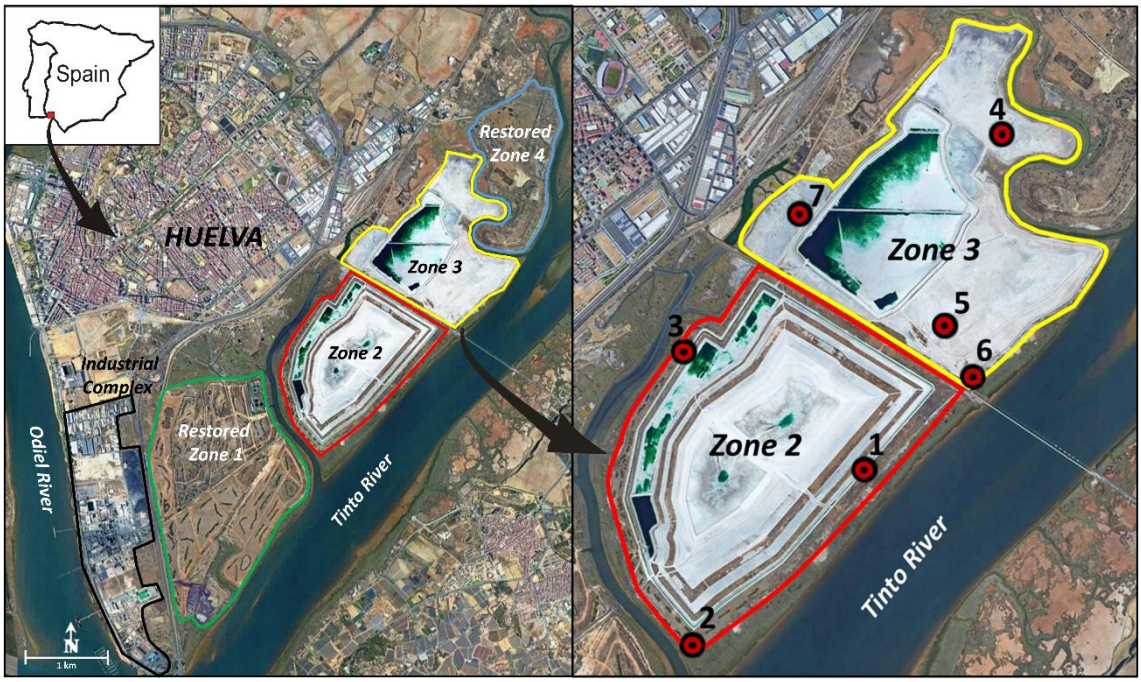

Fig. 1. Location map of the Huelva phosphogypsum stacks, determining the four zones and indicating the points were the seven cores were taken.

In zones 2 and 3 PG is directly exposed to weathering conditions, without any type of cover layer, and acidic waters (pH < 2) from the industrial process are stored in surface ponds (Fig. 1). These acidic waters are evaporating for the restoration project.

The Zone 2, with an extension of 250 ha, store around 25 Mt of PG. Until 1997, the PG was transported by seawater in open circuit and deposited above the salt-marsh generating a 5 m high PG pile. From 1998 until the end of 2010, due to a change in the environmental policy according to the OSPAR (OSPAR, 2002, 2007) convention, all the PG generated was placed in this zone by a close circuit pumped with fresh water, generating a pyramid-shaped stack of up to 20 m in height. In addition, a net of perimeter channels to collect lateral fluxes surrounds this zone.

The zone 3 covers a surface of 200 ha, and stores about 15 Mt of PG with an average height of 6 m over the marsh. In this sector, the PG was store before 1997, and a perimeter channel was constructed in 2015. Since the PG deposition stopped in this zone, its main role has been to store industrial process water in a central pond, which was part of the closed-circuit freshwater system fitted after the environmental policy change.

3. Material and methods

In November 2009, 7 cores were collected from the Zones 2 and 3 of the stacks (Fig. 1, Table S1). From the cores, 57 slices (11 PG and 46 sediment samples) with thickness of 5 cm and a diameter of 9 cm for the analysis of physicochemical parameters, chemical composition and the main long half-live natural radionuclides of interest were selected. Samples from different depths were taken, but most of them around the PG-sediment contact, in order to focus on the migration of natural radionuclides from the stacks to these upper sediment layers.

An aliquot of 20 g per slice was taken for the pH and electrical conductivity (EC) measurement. These portions were previously air drying, and the physicochemical parameters were determine by 1:2 (sample:water) mix. For chemical and radioactive analysis an aliquot of 30 g per slice were dried in an oven at 60 ºC to constant weight. The analysis of major and trace elements was conducted by ICP Mass in the Actlabs from Canada. The quality control (QC) was performed by the analysis at the beginning and end of each set of samples of Certified Standard Reference Materials. In addition, a duplicate for every 10 samples is run and internal control standards are analysed.

The radioactive characterization of all the samples was performed by applying two independent techniques: gamma-ray and alpha-particle spectrometry. ^{226}Ra, ^{228}Ra and ^{40}K were determined by

gamma-ray spectrometry with the same equipment and the methodology described in Pérez-Moreno et al. (2002). U-, Th-isotopes, and ^{210}Po were determined by alpha particle spectrometry (Martin and Hancock, 1992; Pérez-Moreno et al., 2018). Because of ^{210}Po come from the decay of ^{210}Pb and secular equilibrium is assumed between these radionuclides (more than 2 years elapsed between the sampling and the measurement), the activity concentration of ^{210}Po (half-life = 138 d) was interpreted as ^{210}Pb (half-life = 22.2 y). The QC for the alpha-particle spectrometry was made taking part in annual international proficiency tests (International Atomic Energy Agency [IAEA] and the Spanish Nuclear Safety Council [CSN]), and by analysing both blank and Certified Standard Reference Materials, IAEA-326 (soil) and IAEA-434 (phosphogypsum), every batch of 10 samples.

4. Results and discussion

4.1. Physicochemical parameters

The depth profiles of pH and EC for the different cores are displayed in Fig. 2. In order to make clearer the comparison between cores the PG-sediment contact is considered as "0 m depth", applying positive depth values for PG and negative for sediments. The pH of PG is homogeneous regardless the location of the cores, with a global mean value of 2.9 ± 0.2, and ranging from 2.1 (6P5) to 4.1 (3P2) (Table S2). The low pH values of PG are related with the remaining acids (mainly phosphoric), trapped between the particles of PG after the industrial process. The acidity of this waste favoured the liberation and mobility of metals, radionuclides, and other chemical species present into the PG. Table S3 shows the individual values of the physicochemical parameters for all the analysed samples.

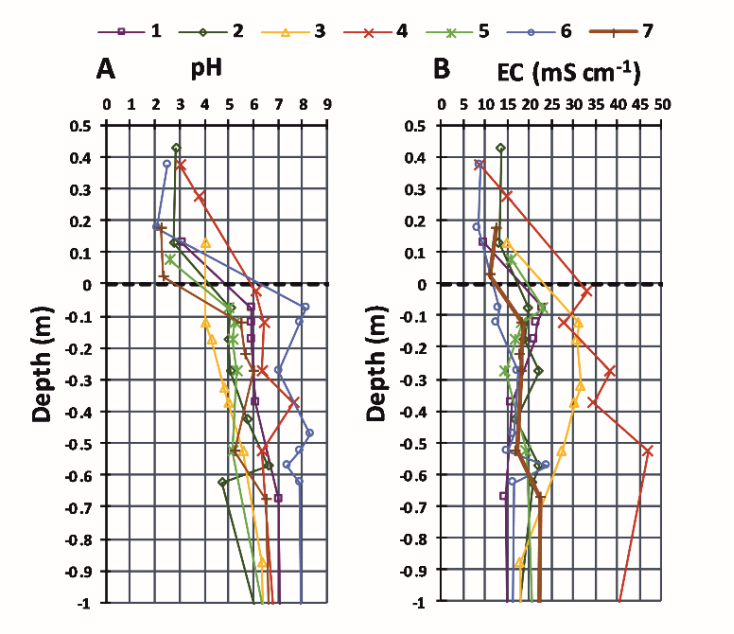

Fig. 2. Depth profiles of pH (A) and EC (B).

On the other hand, sediments samples taken in the first 50 cm below the contact showed a mean pH value of 5.9 ± 0.2, while the deeper ones showed a neutral mean value of 7.0 ± 0.3 (Table S2). The minimum pH was 4.0 in the sample 3S, which is located 10 cm under the contact. The acidic pH values of the shallower sediments are obviously due to the impact of the PG stack. Differences in the pH values are observed between cores. In this sense, cores 2, 5 and mainly 3, show lower pH values in the first 20-30 cm below the contact (Fig. 2A), probably due a higher influence of the PG acidity into the salt-marsh at these locations.

Regarding the EC, the PG shows a mean value of 12.2 ± 0.8 mS cm^{-1}, while for the sediments located in the first 50 cm below the contact the mean value was 22.6 ± 1.4 mS cm^{-1}, similar to mean value obtained for the deeper ones 19.5 ± 1.8 mS cm^{-1} (Table S2). Salt-marsh sediments show in general higher EC values than PG ones. This fact is due to salinity of the sediments in the studied estuarine environment. It is necessary to highlight the higher EC of sediment samples located in the cores 3 and 4, which show values above 30 mS cm^{-1} in the first 50 cm below the contact (Fig. 2B). Taking into account that Pérez-Lopez et al. (2015) determined a mean EC value of edge outflows from the PG of 40.3 ± 9.9 mS cm^{-1}, and the acidic of sediments in the core 3, the high EC values of this location could be related with the existence of leachates from the stacks. In the case of core 4, these higher EC values are probably related with natural processes.

170 **4.2. Natural radionuclides**

171 The variation in the activity concentrations of the most significant ^{238}U-series natural
172 radionuclides (^{238}U, ^{230}Th, ^{226}Ra and ^{210}Pb), ^{232}Th and ^{40}K with depth in the first meter after the
173 contact is shown in Fig. S2. The activity concentration for all the samples is included in the Table
174 S4. The activity concentration of ^{238}U-series radionuclides is higher in the PG and decrease rapidly
175 with depth from the contact zone. This behaviour is very clear in the cores 1, 2, 4, 5, and 7, where
176 the increase of natural radionuclide concentrations is only observed in the first 20 cm under the
177 contact, being the thickness of sediment affected even lower in some cores. This decrease in the
178 activity concentration with depth is not as clear and not as homogeneous in the cores 3 and 6,
179 which show a more a deeper affection, but only until around 50 cm under the contact zone (Fig.
180 S2C). In this sense and in order to clarify the impact of the PG stacks into de sediments, the
181 activity concentration of the natural radionuclides in the PG samples, the shallow sediments (0 -
182 20 cm under the contact) and deeper sediments (z > 20 cm under the contact) is displayed as
183 modified box and whisker plots in the Fig. 3. (the modified box and whisker plots consider the
184 existence of outliers).

185 "The main potential radionuclide pollution pathway from the PG stacks into the underlying
186 sediment is the migration of natural radionuclides due to the deep percolation of leachates. In this
187 regard, two properties should be taken into account for each radionuclide, the "mobility" and the
188 "reactivity" of the radionuclides. The mobility, can be defined as the capacity of a radionuclide
189 to be released from the solid phase (PG) into the aqueous media. This property was analyzed by
190 Pérez-Moreno et al. (2018), demonstrating that U is the most mobile radionuclide contained in
191 the PG, while Th has a very low mobility, and both Po and Ra present an intermediate mobility.
192 Due to this fact, the radionuclide concentrations in the acid waters from the perimeter channel
193 which collect the leachates from PG stacks are as follow: ^{238}U ≈ 300 Bq L-1, ^{210}Pb ≈ 10 Bq L-1,
194 and ^{226}Ra and ^{230}Th < 1 Bq L-1 (Gázquez et al., 2014; Pérez-Moreno et al., 2018). On the other
195 hand, the reactivity, or capacity to be adsorbed onto the surface of the salt-marsh sediments of
196 Th, Pb, and Po is very high, as a consequence, they are considered particle-reactive radionuclides
197 (Wei et al., 2011). The underlying salt-marsh is mainly composed by fine particle size sediments

198 (mainly clays) (Guerrero et al., 2019) which have a very low permeability and high specific
199 surface area, hence, a low percolation rate and high pollutant adsorption. Therefore, it is expected
200 that these reactive radioelements (Th, Pb, Po) remain adsorbed in few centimeters below the PG.
201 Accordingly, the in depth migration of these natural radionuclides must be mainly conducted by
202 molecular diffusion, while other pollutant transport processes, as dispersion and advection, only
203 are significant in some points where some coarser particle size strata are located.PG samples
204 present a ^{238}U mean activity concentration of 163 ± 27 Bq kg^{-1}, ranging from 45 ± 2 (5P5) to 354
205 ±10 Bq kg^{-1} (3P2) (Fig. 3A). ^{234}U is in secular equilibrium with ^{238}U in the PG samples, fact found
206 by many researchers in other locations in the world (Mazzilli et al., 2000; Boryło et al., 2009; El
207 Afifi et al., 2009). Samples located in the first 20 cm below the contact show a mean ^{238}U activity
208 concentration of 151 ± 39 Bq kg^{-1}, which is slightly smaller than the measured one in the PG, and
209 obviously due to the influence of the PG stacks. In deeper samples (z > 20 cm under the contact),
210 the activity concentration of ^{238}U decrase quickly until background values, with a mean value of
211 51 ± 5 Bq kg^{-1} and a median of 44 Bq kg^{-1}. These values of deeper sediments are in agreement
212 with the ^{238}U worldwide median concentration in unperturbed soils which is 35 Bq kg^{-1}, ranging
213 from 16 to 110 Bq kg^{-1} (UNSCEAR, 2000). ^{234}U show secular equilibrium in the salt-marsh
214 sediments with the parent nuclide of the decay chain, displaying therefore the same behaviour
215 that ^{238}U (Fig. 3A, B).

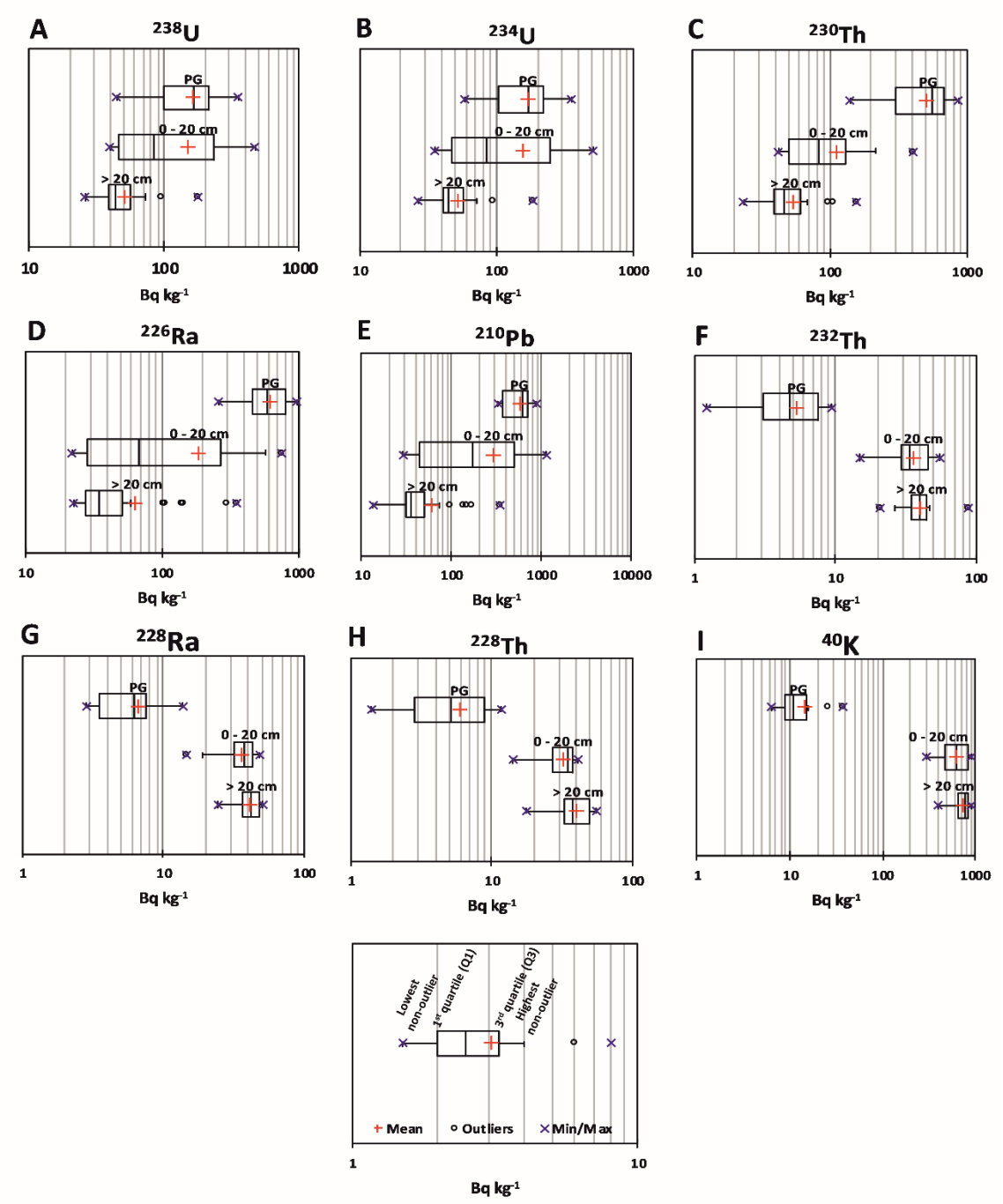

Fig. 3. Modified box and whisker plots of the analysed natural radionuclides in the PG samples, shallow sediments (0-20 cm under the contact) and deeper sediments (> 20 cm under the contact). Ordered by radioactive series and mass number.

Regarding ^{230}Th, shows a mean activity concentration of 519 ± 73 Bq kg^{-1} in the PG, and decrease until a mean value of 113 ± 25 Bq kg^{-1} in the first 20 cm under the contact, while deeper salt-marsh samples show a mean concentration of 55 ± 5 Bq kg^{-1} (Fig. 3C). Whereas in the case of U

223 isotopes, the mean activity concentration is similar in the PG and shallow sediments, ^{230}Th mean
224 activity concentration is five times lower in the sediments located near the contact than in the PG.
225 This fact is due to both, the very low mobility of this radionuclide as was previously discussed ,
226 and their higher reactivity (capacity to be adsorbed) onto the salt-marsh sediments, producing a
227 quicker decrease of its activity concentration with depth.
228 ^{226}Ra and ^{210}Pb showed a mean activity concentration in PG samples of 618 ± 74 and 566 ± 59
229 Bq kg^{-1} respectively (Fig. 3D, E), similar than the values obtained in previous studies for the whole
230 stacks (Bolívar et al., 1998; Más et al., 2006). Samples located in the first 20 cm under the contact
231 show a mean ^{226}Ra activity concentration of 185 ± 58 Bq kg^{-1}, and a mean ^{210}Pb activity
232 concentration of 281 ± 84 Bq kg^{-1}. In the case of deeper salt-marsh sediments showed a mean
233 activity concentration for ^{226}Ra and ^{210}Pb of 64 ± 14 and 59 ± 12 Bq kg^{-1} respectively, values even
234 higher than the third quartile (Fig. 3D, E) due to the existence of some samples with high extreme
235 values (outliers). It is remarkable that median values of ^{226}Ra and ^{210}Pb in shallow sediments was
236 68 and 170 Bq kg^{-1}, while in the deeper ones was 34 and 35 Bq kg^{-1} respectively. The median
237 ^{226}Ra value for deeper sediments (z > 20 cm below the contact) is similar than that the worldwide
238 concentration in natural soils 35 Bq kg^{-1} (range: 17 – 60 Bq kg^{-1}) (UNSCEAR, 2000),
239 demonstrating the low affection in depth of the salt-marsh due to PG-stacks influence.
240 It is interesting to comment the abnormally high activity concentrations (outliers) of natural
241 radionuclides from the ^{238}U series observed in the box and whisker plots in some samples located
242 more than 20 cm below the contact (Fig. 3A, B, C, D, E). These polluted samples were found in
243 the cores 3 and 6 (Fig. S2C, F), reaching a maximum depth until around 50 cm under the contact
244 zone. The $^{234\text{-}238}$U outliers were located in the core 3, while ^{230}Th, ^{226}Ra and ^{210}Pb outliers were
245 located mainly in the core 6.
246 It seems clear that salt-marsh sediments act as a "barrier" for the radioactive pollution, and the
247 influence of the PG stacks in the underlying sediments due to natural radionuclides is restricted
248 to the first decimetres (around 50 cm). It should take into account that the cores were taken after
249 more than 40 years from the start of PG storage, when the production of this waste stopped.
250 Obviously, the system will continue to evolve, but due to the characteristics of the salt-marsh
251 sediments (low permeability and high specific surface area) the penetration velocity of the

pollutants into deeper sediments is very low, even probably already reaching a steady-state in some cases. In addition, the PG acidic waters are under evaporation process during the restoration project, which also include the covering of the stacks with an impermeable geotextile, a 60 cm clay layer, and a final layer of 40 cm of soil. All these actions will avoid the main source of deep pollution, which is the generation of new polluted acid leachates. Therefore, the in-depth migration of these radionuclides into the salt-marsh sediments is not an important concern. On the other hand, these findings are also highly relevant due to suggest that the new perimeter channel planned to build in the restoration should has at least 1 m deep under the base of the PG piles to ensure the full collection of polluting leachates, and to prevent their release into the Tinto estuary.

Regarding the natural radionuclides from the ^{232}Th series, and ^{40}K, show very low activity concentrations in the PG samples, with values below the detection limit in some samples. Thus, the activity concentration of ^{228}Th, ^{232}Th and ^{228}Ra, show in general values below 10 Bq kg^{-1} while ^{40}K show activity concentration values below 20 Bq kg^{-1}, similar values than those observed in previous studies (Bolívar et al., 1998; Más et al., 2006). The mean activity concentration of ^{232}Th, ^{228}Ra, ^{228}Th and ^{40}K in the samples located in the first 20 cm under the contact were 36 ± 3 Bq kg^{-1}, 36 ± 2 Bq kg^{-1}, 36 ± 3 Bq kg^{-1}, and 640 ± 54 Bq kg^{-1} respectively, while in the deeper sediments samples the mean values were 41 ± 1 Bq kg^{-1}, 40 ± 2 Bq kg-1, 40 ± 2 Bq kg^{-1}, and 737 ± 25 Bq kg^{-1} respectively (Fig. 3F, G, H, I). The slightly decrease of concentration of these radionuclides in the shallower samples, seem to confirm the existence of mixing processes between PG and salt-marsh sediments, producing a decrease in the activity concentration of these radionuclides in the sediment directly in contact with the PG stacks. To understand the existence of this mixing processes we must look back to the initial conditions of PG storage, which was spilled as an aqueous slurry, as was indicated in the material and methods section, over the wet and low cohesive marsh sediments. Thus, a mixing between the PG and sediment particles during this first storing stage took place, polluting the sediments in direct contact with the base of the stacks. The activity concentration of ^{232}Th series radionuclides in salt-marsh sediments are pretty similar than the worldwide median concentration in soils which is 30 Bq kg^{-1} (range: 11-64 Bq kg^{-1}) (UNSCEAR, 2000), while the ^{40}K worldwide median concentration in common types of soils is

281 400 Bq kg^{-1} (range: 140 – 850 Bq kg^{-1}) (UNSCEAR, 2000), data notably lower than the values
282 obtained for the salt-marsh sediments analysed in this study.

283 **4.3. Activity ratios**

284 In the Fig. 4 are displayed as modified box and whisker plots the most representative activity
285 ratios (AR), following the same scheme than in Fig. 3. The Table S5 shows the values of these
286 activity ratios for all the analysed samples.

287 The analysis of the activity ratios ratifies some of the previously commented findings. In this way,
288 the activity ratios between natural radionuclides from the ^{238}U series and ^{232}Th series show high
289 values in the PG samples with mean activity ratios for $^{238}U/^{232}Th$, $^{226}Ra/^{228}Ra$, $^{230}Th/^{232}Th$ of 37 ±
290 7, 83 ± 9 and 110 ± 14 respectively (Fig. 4A, B, C). These ratios are in agreement with the found
291 ones in the raw material (phosphate rock) (Bolívar et al., 2009), and in the PG stacks (Más et al.,
292 2006). In the sediment samples located near the contact with the PG stacks, the mean value was
293 around 6 for $^{238}U/^{232}Th$ and $^{226}Ra/^{228}Ra$, and around 4 for $^{230}Th/^{232}Th$. While in the deeper sediment
294 samples (z > 20 cm under the contact) the mean value decreases up to around 1.4 for $^{238}U/^{232}Th$
295 and $^{230}Th/^{232}Th$, and around 1.7 for $^{226}Ra/^{228}Ra$, while median values are significantly lower,
296 mainly for $^{226}Ra/^{228}Ra$ activity ratio, which is 0.7. These values are similar to the found ones in
297 unpolluted salt-marshes of this geographical area in previous works (Bolívar et al., 1996b;
298 Aguado et al., 1998; Bolívar et al., 2002). It should be noted the existence of some outliers for
299 these activity ratios in the deeper samples, with maximum values of 8.7 ± 0.7 and 10.8 ± 1.2 for
300 $^{238}U/^{232}Th$ and $^{226}Ra/^{228}Ra$ respectively, determined in the core 3, and a maximum value of 3.9 ±
301 0.3 for $^{230}Th/^{232}Th$ activity ratio measure in the core 6. These abnormally high values for deeper
302 samples were located in all cases in the first 50 cm under the contact. The decrease of these
303 activity ratios with depth confirm the fact that the salt-marsh sediments act as a “barrier” for the
304 leachates from the PG stacks, and the impact is only observed in the first sediment decimetres.

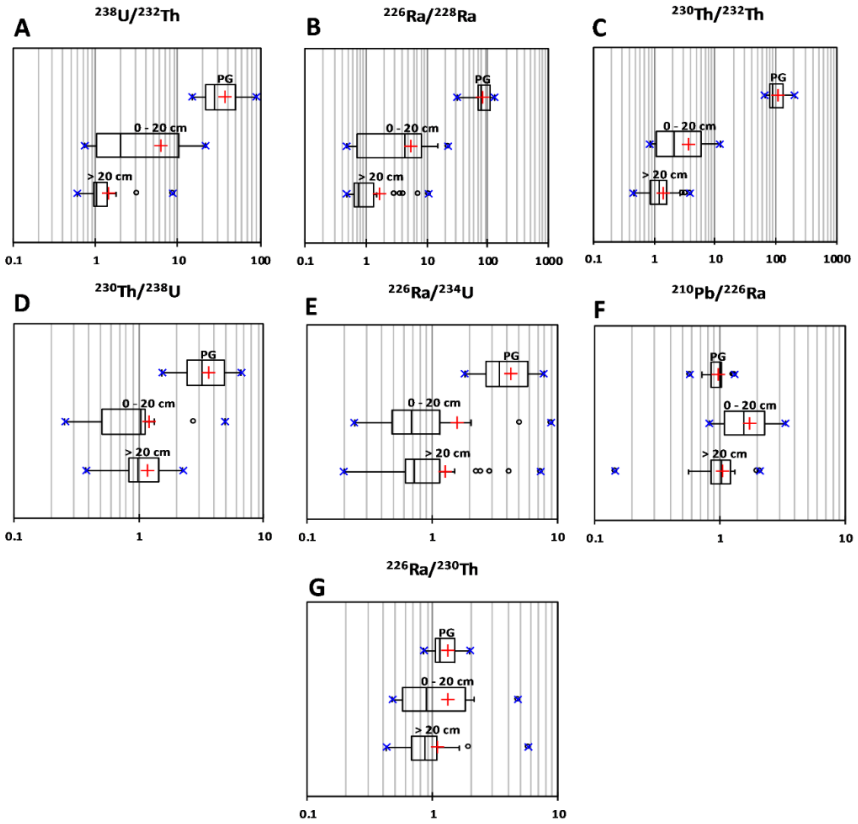

Fig. 4. Modified box and whisker plots of the most representative activity ratios in the PG samples, shallow sediments (0-20 cm under the contact) and deeper sediments (z > 20 cm under the contact).

The activity ratios between the ^{238}U-series radionuclides in the sediments provide information about their relative impact into the salt-marsh. PG samples show a mean ^{230}Th/^{238}U and ^{226}Ra/^{234}U activity ratio of 3.6 ± 0.5 and 4.3 ± 0.6, respectively, while in the shallow sediments these activity ratios show mean values close to the unity, with values of 1.2 ± 0.3 and 1.6 ± 0.6, respectively (Fig. 4D and E). The decrease of these activity ratios in the upper sediments is related with the lower reactivity, around 3 times lower, and the higher activity concentration in the leachates of U-isotopes, which provokes a deeper impact by these radionuclides. The concentration of ^{226}Ra in the leachates is two orders of magnitude lower than the 238U one. Therefore, the increase of ^{226}Ra in the sediments due to percolation is not detectable, and can be considered as negligible in relation to the increase of the U-isotopes activity concentrations. The samples located more than 20 cm below the contact present mean values around secular equilibrium (AR ≈ 1), taking into account the uncertainties, for these activity ratios.

With regard to $^{210}Pb/^{226}Ra$ activity ratio (Fig. 4F), to point out that mean values around secular equilibrium were determined for PG and deeper sediment samples, while in the first 20 cm below the contact the mean value was higher than 1 (1.7 ± 0.2), probably due to the unsupported ^{210}Pb by the atmospheric deposition existing before the PG stacks. Finally, the $^{226}Ra/^{230}Th$ activity ratio (Fig. 4 G), with a mean value of 1.3 for both PG and sediments located near the contact, and a mean value around secular equilibrium for the deeper sediments, confirm that these two radionuclides are affected by the same processes, polluting the upper sediments mainly by mixing.

4.4. Principal Component Analysis

In order to deepen in the understanding of the processes involved in the migration of natural radionuclides from the PG stacks into the underlying salt-marsh, a Principal Components Analysis (PCA) was performed (Fig. 5). PCA is a method for reduce a large number of variables, finding new variables (principal components), which are ordered so that the first few retain most of the variation present in all of the original variables, making the data easier to understand (Jolliffe, 2002).The PCA is used to study the relationship between variables and identify how groups of variables change with respect to each other. In this analysis, element concentrations were included to know its relationship with the natural radionuclides and improve the understanding of pollution processes that affects the salt-marsh sediments. The first two factors (F1 and F2) explain the 73.3% of the data set total variance.

The F1 factor (53.7% of the variance) show high positive scores for Al, K, Mg, Ti, Ba, Cr, Li, Ni, Th, V, and from ^{232}Th-series radionuclides (^{232}Th, ^{228}Th and ^{228}Ra), and ^{40}K (Fig. 5A). These elements and radionuclides are clearly related to unpolluted sediments, that is to say, with the geological background of this geographical area. On the other hand, the F1 factor is highly negatively contributed by Ca, S, Sr, Y, and natural radionuclides from the ^{238}U series (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra and ^{210}Pb), which are clearly related to the PG.

In the PCA for observations (Fig. 5B), most sediment samples are grouped in the positive part of this factor, but with very low scores, while all PG samples are situated in a reduced area of the negative F1 axis. It should be noted the location of some upper sediment samples (1S1, 3S1, 3S2, 5S1, 6S2, and 7S1) in the negative part of F1 axis, which are clearly affected by mixing processes

with PG (negative F1 represents direct contamination by PG-sediment mixing). These shallow sediment samples show a low contribution to F1 component, which confirms the low affection of the salt-marsh sediments by mixing processes with PG. This way, F1 component discriminates the PG samples and unpolluted salt-marsh sediments, and it is controlled in the negative part by direct PG pollution, due to mixing.

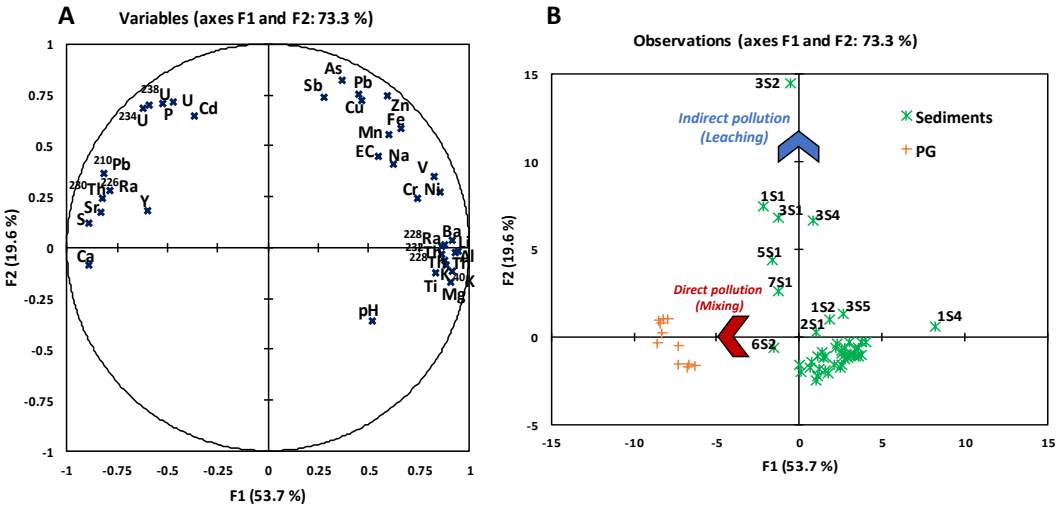

Fig. 5. PCA results. A: Loading plot of variables and B: score plot of observations.

Regarding the F2 factor (19.6% of the variance), there is a group of variables very related to PG, which show high positive scores on F2 axis (P, Cd, U, ^{238}U, ^{234}U). High concentrations of these elements and radionuclides in the PG leachates have been measured (Perez-López, 2015; Pérez-Moreno et al., 2018), which clearly demonstrate that the origin of these ones is the PG. The samples 1S1, 3S1, 3S3, and mainly 3S2, present very high positive scores along F2. Moreover, the core 3 show a deeper affection by natural radionuclides, mainly ^{238}U (Fig. S2C), and the lowest pH values (Fig. 2A), probably due to the higher grain size of the sediments located near the contact in this point (Guerrero et al., 2019).

It is very interesting the presence of P with high positive contribution in this factor. It was demonstrated that due to the high mobility of this element it is a good tracer to assess the impact of the PG stacks into the underlying salt-marsh substrate due to deep leachates (Guerrero et al., 2019), since this element is not increased by the AMD of the Tinto River. On the other hand, in the positive part of this component are located the natural U-isotopes which are the most mobile

and low reactive analysed radionuclides of this study as was previously observed. All of this indicate that F2 factor is closely related to the indirect polluting pathway of sediments, which is produced by leachates from the PG piles that infiltrate into upper decimetres of sediment.

To summarize, the PG-sediment mixing processes explain the radioactive pollution by ^{230}Th, ^{226}Ra, ^{210}Pb of the upper salt-marsh layers, while for $^{234\text{-}238}$U produce a deeper affection of the salt-marsh (up to around 50 cm) by leaching processes due to their higher mobility and lower reactivity. And finally, it is remarkable that most sediment samples are plotted in a small zone, with very low scores for the F1 and F2 factors (Fig. 5B), demonstrating that most of the salt-marsh sediments are not polluted by natural radionuclides from the PG piles.

5. Conclusions

The obtained conclusions in this work are:

1. The salt-marsh sediment produces a "barrier effect" for the ^{238}U series natural radionuclides coming from the PG stacks decreasing rapidly their activity concentration with depth, hence, most of the analysed sediments are not polluted by natural radionuclides from the PG stacks.

2. The sediments with a higher degree of affection are mainly located in the first 20 cm under the contact and are affected by mixing processes, while pollution of deeper sediments due to leaching processes only take place in some of the studied locations, affecting samples located maximum up to around 50 cm under the contact.

3. While ^{230}Th, ^{226}Ra and ^{210}Pb pollution is mainly restricted to the first 20 cm of sediments, U isotopes can reach higher depths (up to around 50 cm) by leaching processes due to their higher mobility and lower reactivity.

4. The obtained results in this research work have high relevance for the design of the projected perimeter channel in the restoration project, suggesting that should has at least 1 m deep under the base of the PG piles, to ensure the full collection of polluting leachates, and to avoid their release into the estuary of the Tinto River.

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7. References

Aguado, J.L., Bolívar, J.P., García-Tenorio, R., García-León, M., 1998. Behaviour and levels of natural radioactivity in sediments from the odiel river. Int. Ver. Theor. Angew. Limnol. 26, 893-895. https://doi.org/10.1080/03680770.1995.11900846.

Bolívar, J.P., García-Tenorio, R., García-León, M., 1996a. On the fractionation of natural radioactivity in the production of phosphoric acid by the wet acid method. J. Radioanal. Nucl. Chem. Letters 214(2), 77–78.

Bolívar, J.P., García-Tenorio, R., García-León, M., 1996b. Radioactive impact of some phosphogypsum piles in soils and salt marshes evaluated by γ-ray spectrometry. Appl. Radiat. Isot. 47 (9-10), 1069-1075. https://doi.org/10.1016/S0969-8043(96)00108-X.

Bolívar, J. P., García-Tenorio, R., and Más, J., 1998. Radioactivity of Phosphogypsum in South-West of Spain. Radiat. Prot. Dosim. 76(3), 185–189. https://doi.org/10.1093/oxfordjournals.rpd.a032263.

Bolívar, J.P., García-Tenorio, R., Más, J.L., Vaca, F., 2002. Radioactive impact in sediments from an estuarine system affected by industrial waste releases. Environ. Int. 27, 639–645. https://doi.org/10.1016/S0160-4120(01)00123-4.

Bolívar, J.P., Martín, J.E., García-Tenorio, R., Pérez-Moreno, J.P., Más, J.L., 2009. Behaviour and fluxes of natural radionuclides in the production process of a phosphoric acid plant. Appl. Radiat. Isot. 67, 345–356. https://doi.org/10.1016/j.apradiso.2008.10.012.

Boryło, A., Nowicki, W., Skwarzec, B., 2009. Isotopes of polonium (210Po) and uranium (234U and 238U) in the industrialised area of Wiślinka (North Poland). Int. J. Environ. A. Ch. 89(8-12), 677–685. https://doi.org/10.1080/03067310802654605.

Borrego, E., Más, J.L., Martín, J.E., Bolívar, J.P., Vaca, F., Aguado, J.L., 2007. Radioactivity levels in aerosol particles surrounding a large TENORM waste repository after application of

424 preliminary restoration work. Sci. Total Environ. 377, 27-35.
425 https://doi.org/10.1016/j.scitotenv.2007.01.098.
426 Directive, 2013. 2013/59/Euratom of 5 December 2013 Laying Down Basic Safety Standards for
427 Protection against the Dangers Arising from Exposure to Ionising Radiation, and Repealing
428 Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and
429 2003/122/Euratom.
430 El Afifi, E. M., Hilal, M. A., Attallah, M. F., EL-Reefy, S. A. 2009. Characterization of
431 phosphogypsum wastes associated with phosphoric acid and fertilizers production. J. Environ.
432 Radioact. 100(5), 407–412. https://doi.org/10.1016/j.jenvrad.2009.01.005.
433 Gázquez, M.J., Mantero, J., Mosqueda, F., Bolívar, J.P., García-Tenorio, R., 2014. Radioactive
434 characterization of leachates and efflorescences in the neighbouring areas of a phosphogypsum
435 disposal site as a preliminary step before its restoration. J. Environ. Radioact. 137, 79–87.
436 https://doi.org/10.1016/j.jenvrad.2014.06.025.
437 Guerrero, J.L., Gutiérrez-Álvarez, I, Mosqueda, F., Olías, M., García-Tenorio, R., Bolívar, J.P.,
438 2019. Pollution evaluation on the salt-marshes under the phosphogypsum stacks of Huelva due to
439 deep leachates. Chemosphere 230, 219-229. https://doi.org/10.1016/j.chemosphere.2019.04.212.
440 Gutiérrez-Álvarez, I., Guerrero, J.L., Martín, J.E., Adame, J.A., Vargas, A., Bolívar, J.P, 2019.
441 Radon behavior investigation based on cluster analysis and atmospheric modelling. Atmos.
442 Environ. 201, 50–61. https://doi.org/10.1016/j.atmosenv.2018.12.010.
443 Hernández-Ceballos, M.A., Vargas, A., Arnold, D., J.P. Bolívar., 2015. The role of mesoscale
444 meteorology in modulating the 222Rn concentrations in Huelva (Spain) - impact of
445 phosphogypsum piles. J. Environ. Radioact.145, 1-9.
446 https://doi.org/10.1016/j.jenvrad.2015.03.023.
447 Hierro, A, Martín J.E., Olías, M., Vaca F., Bolívar, J.P., 2013. Uranium behaviour in an estuary
448 polluted by mining and industrial effluents: The Ría of Huelva (SW of Spain). Water res. 47,
449 6269-6279. https://doi.org/10.1016/j.watres.2013.07.044.
450 IAEA, 2003. Extent of environmental contamination by naturally occurring radioactive material
451 (NORM) and technological options for mitigation. Technical Reports Ser. No 419, IAEA.

Jolliffe, I.T., 2002. Principal Component Analysis, second edition, New York: Springer-Verlag New York, Inc.

Lopez-Coto, I., Más, J.L., Vargas, A., Bolivar, J.P., 2014. Studying radon exhalation rates variability from phosphogypsum piles in the SW of Spain. J. Hazard. Mater. 280, 464-471. https://doi.org/10.1016/j.jhazmat.2014.07.025.

Martin, P., Hancock, G., 1992. Routine Analysis of Naturally Occurring Radionuclides in Environmental Samples by Alpha-particle Spectrometry. Research Report 7. Australian Government Publishing Service, Canberra.

Más, J.L., San Miguel, E.G., Bolívar, J.P., Vaca, F., Pérez-Moreno, J.P., 2006. An assay on the effect of preliminary restoration tasks applied to a large TENORM wastes disposal in the south-west of Spain. Sci. Total Environ. 364, 55-66. https://doi.org/10.1016/j.scitotenv.2005.11.006.

Mazzilli, B., Palmiro, V., Saueia, C., Nisti, M., 2000. Radiochemical characterization of Brazilian phosphogypsum. J. Environ. Rad. 49(1), 113–122. https://doi.org/10.1016/S0265-931X(99)00097-1.

OSPAR, 2002. Discharges of Radioactive Substances into the Maritime Area by Nonnuclear Industry. Radioactive Substances Series. Publication No. 161. OSPAR Commission, London, 60 pp.

OSPAR, 2007. PARCOM Recommendation 91/4 on Radioactive Discharges: Spanish Implementation Report. Radioactive Substances Series. Publication No. 342. OSPAR Commission, London, 49 pp.

Papaslioti, E.M., Pérez-López., R, Parviainen, A., Sarmiento, A.M., Nieto, J.M., Marchesi, C., Delgado-Huertas, A., Garrido. C., 2018. Effects of seawater mixing on the mobility of trace elements in acid phosphogypsum leachates. Mar. Pollut. Bul. 127, 695–703. https://doi.org/10.1016/j.marpolbul.2018.01.001.

Pérez-López, R., Nieto, J.M, López-Coto, I, Aguado, J.L., Bolívar, J.P., Santiesteban, M., 2010. Dynamics of contaminants in phosphogypsum of the fertilizer industry of Huelva (SW Spain): From phosphate rock ore to the environment. Appl. Geochem. 25, 705–715. https://doi.org/10.1016/j.apgeochem.2010.02.003.

480 Pérez-López, R., Nieto, J.M., de la Rosa, J.D., Bolívar, J.P., 2015. Environmental tracers for
481 elucidating the weathering process in a phosphogypsum disposal site: implications for restoration.
482 J. Hydrol. 529, 1313-1323. https://doi.org/10.1016/j.jhydrol.2015.08.056.
483 Pérez-López R., Macías, F., Cánovas C.R., Sarmiento, A.M., Pérez-Moreno, S.M., 2016.
484 Pollutant flows from a phosphogypsum disposal area to an estuarine environment: An insight
485 from geochemical signatures. Sci Total Environ. 553, 42–51.
486 https://doi.org/10.1016/j.scitotenv.2016.02.070.
487 Pérez-Moreno, J.P., San Miguel, E.G., Bolívar, J.P., Aguado, J.L., 2002. A
488 comprehensivecalibration method of Ge detector for low level spectrometry measurement. Nucl.
489 Instrum. Meth. A 491, 152-162. https://doi.org/10.1016/j.jhazmat.2018.02.001.
490 Pérez-Moreno, S.M., Gázquez, M.J., Pérez-López, R., Vioque, J., Bolívar, J.P., 2018. Assessment
491 of natural radionuclides mobility in a phosphogypsum disposal area. Chemosphere 211, 775-783.
492 https://doi.org/10.1016/j.chemosphere.2018.07.193.
493 Tayibi, H., Choura, M., López, F.A., Alguacil, F.J., López-Delgado, A., 2009. Environmental
494 impact and management of phosphogypsum. J. Environ. Manag. 90 (8), 2377–2386.
495 https://doi.org/10.1016/j.jenvman.2009.03.007.
496 UNSCEAR, 2000. Sources and effects of ionizing radiation. Volume I: Sources: Report to the
497 General Assembly of the United Nations Scientific Committee on the Effects of Atomic
498 Radiation, United Nations, New York.
499 Wei, C.-L., Lin, S.-Y., Sheu, D. D.-D., Chou, W.-C., Yi, M.-C., Santschi, P. H., & Wen, L.-S.,
500 2011. Particle-reactive radionuclides (^{234}Th, ^{210}Pb, ^{210}Po) as tracers for the estimation of export
501 production in the South China Sea. Biogeosciences, 8(12), 3793–3808. doi:10.5194/bg-8-3793-
502 2011
503 Yang, L., Zhang, Y., Yan, Y., 2016. Utilization of original phosphogypsum as raw material for
504 the preparation of self-leveling mortar. J. Clean. Prod. 127, 204-213.
505 https://doi.org/10.1016/j.jclepro.2016.04.054.