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2 **1. Introduction**

3 Due to the relatively high concentration of ^{238}U (and its decay chain daughters) in
4 phosphate rocks (PR), phosphate industries constitute one of several minerals related
5 industry sectors for which some of the processes involved may warrant radiation
6 protection measures through the system of regulatory control for practices (IAEA,
7 2013), also known as Naturally Occurring Radioactive Material (NORM) industries.
8 The activities of these industries regarding radiation are now regulated in Europe by the
9 European Directive 2013/59/EURATOM (EURATOM, 2013). Both legislations
10 establish uniform basic safety standards for the protection of the health of individuals
11 subject to occupational, medical and public exposures against the dangers arising from
12 ionizing radiation (EURATOM, 2013).

13 Phosphate deposits contain calcium and phosphorus and can be of sedimentary marine,
14 igneous, metamorphic or biogenic origin (IAEA, 2013), although the majority of the
15 phosphate production plants use sedimentary marine deposits. This is the case of
16 Morocco, from where the European phosphate plants obtain the phosphate rock as raw
17 material. Typical activity concentrations of ^{238}U in these deposits are 1600 - 1700
18 $\text{Bq}\cdot\text{kg}^{-1}$ (in equilibrium with decay progeny) (Azouazi et al., 2001). These
19 concentrations are of about two orders of magnitude higher than average concentrations
20 in natural soils ($30 \text{ Bq}\cdot\text{kg}^{-1}$; UNSCEAR, 2000), and in PR from igneous origin (e.g.
21 Kola (Russia), $40 \text{ Bq}\cdot\text{kg}^{-1}$ of ^{238}U and $30 \text{ Bq}\cdot\text{kg}^{-1}$ of ^{232}Th) (Sabiha-Javied et al., 2010).
22 Once in the plant, phosphate ore is converted into commercial products. In most cases
23 (85%) the PR is acid digested (wet process) and is later converted into intermediate or
24 final products, including phosphoric acid (70%), and a variety of other products such as
25 animal feed supplements (i.e. Dicalcium Phosphate, DCP) (IAEA, 2013).

26 During the industrial processing of these materials, exposure to gamma radiation from
27 radionuclides of the ^{238}U decay series is the main concern for radiation protection.
28 However, exposure to radionuclides in inhaled dust particles can also be relevant
29 (IAEA, 2013), and has been investigated in various phosphate industries (Papastefanou,
30 2001; San Miguel et al., 2009). ^{222}Rn can also emanate from accumulated ^{226}Ra (White
31 and Rood, 2001) and may also be responsible for a significant fraction of the total dose
32 to workers. Gamma-radiation dose rates are generally higher near digestion tanks,
33 piping, filters and residual stockpiles, due to radionuclide accumulation, increasing the
34 ambient equivalent dose (Gäfvert et al., 2001; Bolívar et al., 2009). Therefore, the
35 manipulation and treatment of the phosphate rock ore and the different by-products
36 could lead to an increase of the radiological doses to workers.

37 The industrial plant studied here produces dicalcium phosphate (DCP) used as an
38 inorganic feed supplement for farm animals (Casacuberta et al., 2009; 2011).
39 Differently to most of the phosphate plants that use sulfuric acid to digest the PR,
40 hydrochloric acid is used in this plant (Casacuberta et al., 2011). Previous studies in the
41 same plant were focused on the radiological fluxes of the production process, showing

42 that the equilibrium between the radionuclides of the ^{238}U decay series is disrupted due
43 to the different chemical behavior after the PR digestion with hydrochloric acid
44 (Casacuberta et al., 2011) and they are distributed in different proportions in the final
45 product and by-products. Casacuberta et al. (2011) also described the accumulation of
46 significant amounts of ^{226}Ra in pipes during the DCP production process that can
47 increase the external gamma-radiation dose to workers in the plant.

48 The aim of this study is to establish a radiological risk assessment to the workers of the
49 DCP industry. Several surveillances in the DCP plant were carried out between 2011
50 and 2014 to determine the concentrations of the most significant radionuclides in
51 aerosols, the ^{222}Rn concentrations in air and to map the gamma-radiation dose rates.
52 External and internal doses were assessed for workers in order to determine whether
53 annual doses exceed the $1\text{ mSv}\cdot\text{y}^{-1}$ limit reference value established by the European
54 Directive 2013/59/EURATOM (EURATOM, 2013).

55

56 **2. Materials and Methods**

57 2.1 Description of the DCP production plant

58 The plant is located in the Iberian Peninsula (Europe) and nowadays it has a total
59 production capacity of 360 t of DCP per day. The production process can be divided
60 into three main lines (sludge, DCP and water effluents), and therefore wet and dry
61 production areas can be identified (Figure 1). Details are described in Casacuberta et al.
62 (2011). Most steps of the production process are located outdoors, although there are
63 some indoor areas such as offices, control areas, packaging store and milling area. Wet
64 process areas in the sludge line include the PR digestion area and the decantation area.
65 In the DCP line, the precipitation and filtering areas are also wet process areas. The dry
66 process areas are the PR milling in the sludge line and the DCP drying, loading and
67 packaging areas in the DCP line.

68

69 2.2 Sampling, measurements and data collection

70 The criteria used to design the sampling procedure of aerosols, Rn measurements and
71 and ambient dose equivalent $\text{H}^*(10)$ was considering the most occupied workplaces and
72 transiting areas by plant operators.

73 *2.2.1 Aerosols*

74 Sampling of aerosols was carried out in November 2011 and March 2012 at 8 different
75 locations of the DCP production plant (Fig. 1). Between $10 - 30\text{ m}^3$ of air were filtered
76 using a SAIC Radeco vacuum-pump system at 25 cm above the ground. Aerosol
77 particles ($> 0.3\ \mu\text{m}$) were retained onto pre-weighted glass fibre filters (LB-5211 type,
78 Radeco). Filters were cut into two identical sections for the subsequent analysis of
79 radionuclides.

80 The equivalent to half of each sample was used to quantify the concentration of ^{210}Pb
81 and ^{210}Po , following the method described in Masqué et al. (2002). Briefly, the filter
82 was first acid digested after addition of ^{209}Po as an internal tracer. The residue was
83 dissolved in 100 mL of HCl 1N and polonium isotopes were auto-plated onto 2.2 cm
84 silver discs for 6 – 7 h at 70 °C with constant stirring. Any polonium activity remaining
85 in the solution was removed by a second deposition onto silver discs, re-spiked with
86 ^{209}Po and stored for more than 6 months. The ^{210}Pb concentration was obtained after a
87 second plating and measurement of the ingrowth of ^{210}Po . The silver discs were
88 measured using a Canberra Alpha Analyst spectrometry system equipped with
89 Passivated Implanted Planar Silicon (PIPS). The determination of the initial activities of
90 ^{210}Pb and ^{210}Po were carried out following Rigaud et al. (2013).

91 The other half-filter sections were used for the quantification of ^{238}U and ^{230}Th , also by
92 alpha spectrometry. The radiochemical separation of U and Th, was carried out by
93 extraction chromatography using UTEVA resins and electrodeposition onto 2.2 cm
94 diameter silver discs, as described in Casacuberta et al. (2012). ^{232}U and ^{229}Th were
95 used as internal yield tracers.

96 2.2.2 Atmospheric ^{222}Rn

97 Measurements at 9 indoor and 22 outdoor sites were carried out using passive
98 positioned between 50 and 100 cm above the ground and active ^{222}Rn detectors (25 cm
99 above the ground) during two different periods: 18 – 19 July and 8 – 9 November 2011.
100 We used the Karlsruhe®FN dosimeters based on Makrofol®DE for the passive
101 measurements of integrated ^{222}Rn concentrations in 7 indoor and 7 outdoor sites. After
102 four months of exposure, detectors were collected and the Makrofol foils were
103 electrochemically etched with laboratory standard conditions. The track counting was
104 performed with a semi-automatic system. These detectors were calibrated at the Public
105 Health England (PHE) radon chamber, for which the calibration factor is regularly
106 checked by participating in national and international comparisons. The detection limit
107 (D_L) for a four month measurement period was $9 \text{ Bq}\cdot\text{m}^{-3}$ (Moreno et al., 2008).
108 Polyethylene membranes were used to protect radon detectors from environment
109 conditions (high dust concentration and humidity) (Moreno et al., 2013; 2015).

110 An AlphaGuard monitor (Saphymo GmbH), consisting of an ionization chamber, and a
111 RAD 7 monitor (DurrIDGE Co), consisting of an electrodepositing chamber with a
112 semiconductor, were used for monitor continuously the ^{222}Rn concentration at 3 indoor
113 sites (service, rock discharge and packaging buildings) from 12 h to 18 h, integrating
114 the data in 30 min intervals. The RAD 7 monitor was also used to perform short
115 timescale measurements (about 1 h) at all the other sites.

116

117 2.2.3 Gamma-radiation dose rates

118 Three campaigns to determine external gamma-radiation dose rates were carried out in
119 July 2011, November 2011 and May 2012 at various locations of the DCP production
120 plant (50 cm above the ground), using an Eberline E-600 connected to a SHP-270
121 probe, calibrated for measuring ambient dose equivalent $H^*(10)$. Pipes were also
122 measured in order to determine the ^{226}Ra -derived dose with a Canberra Inspector 1000
123 equipped with a gamma NaI(Tl) probe. Personal equivalent dose $H_p(10)$ was measured
124 during the pipe removal and maintenance in February 2014, using an electronic personal
125 dosimeter, Dosicard (Canberra).

126

127 2.3 Dose assessment quantification

128 The operational annual effective above background dose received by the plant operators
129 was calculated considering the sum of annual occupational exposures of a worker
130 according to the European Directive 1996/29/EURATOM (EURATOM, 1996).

$$131 \quad E = E_{External} + \sum_j (h(g)_{j,inh} \cdot J_{j,inh}) + \sum_j (h(g)_{j,ing} \cdot J_{j,ing}) + E_{Rn} \quad (1)$$

132 where $E_{External}$ is the corresponding effective dose from external exposure and
133 $\sum_j (h(g)_{j,ing} \cdot J_{j,ing})$, $\sum_j (h(g)_{j,inh} \cdot J_{j,inh})$ are the committed effective doses due
134 to ingestion and inhalation, respectively, and E_{Rn} is the operational annual effective dose
135 due to the ^{222}Rn inhalation. Given the characteristics of the studied site, the exposure
136 due to ingestion is considered negligible (IAEA, 2013). $h(g)_{j,inh}$ (in $\text{Sv}\cdot\text{Bq}^{-1}$) is the
137 committed effective dose per unit-intake for inhaled radionuclide j by an individual in
138 the group of age g and $J_{j,inh}$ (in Bq) is the relevant intake via inhalation of the
139 radionuclide j in a year. According to Article 9 of EURATOM (2013), the occupational
140 exposure to ^{222}Rn inhalation in workplaces needs to exceed the national reference level
141 ($300 \text{ Bq}\cdot\text{m}^{-3}$) to be considered in the operational annual effective dose, which is then
142 calculated according to UNSCEAR (2000).

143 The estimate of the internal dose by inhalation was carried out only for radionuclides of
144 the ^{238}U decay series using the conversion factors from the ICRP (2012): $1.6\cdot 10^{-6}$
145 $\text{Sv}\cdot\text{Bq}^{-1}$ for ^{238}U , $2.8\cdot 10^{-5} \text{ Sv}\cdot\text{Bq}^{-1}$ for ^{230}Th , $1.1\cdot 10^{-6} \text{ Sv}\cdot\text{Bq}^{-1}$ for ^{210}Pb and $2.2\cdot 10^{-6}$
146 $\text{Sv}\cdot\text{Bq}^{-1}$ for ^{210}Po . These parameters correspond to an activity median aerodynamic
147 diameter (AMAD) of $5 \mu\text{m}$ and to the M class (intermediate rate of absorption) except
148 for ^{210}Pb , for which the default class was F (fast rate of absorption).

149

150 3. Results and Discussion

151 3.1 Aerosols

152 Concentrations of ^{238}U (in equilibrium with ^{234}U), ^{230}Th , ^{210}Pb and ^{210}Po in aerosols
153 determined at different locations in the DCP plant are shown in Table 1. Results were

154 divided into “wet process” and “dry process” locations, as it would be expected to find
155 less airborne dust particle in the former compared to the latter. Indeed, locations in the
156 “dry process” areas (F3, F4 and F8) had mean concentrations of $51 \text{ mg}\cdot\text{m}^{-3}$ while “wet
157 process” locations (F1, F2, F6 and F7) and service building averaged $2 \text{ mg}\cdot\text{m}^{-3}$,
158 respectively. This is due to the fact that dust accumulates mainly in storage and milling
159 of PR areas, as well as in DCP storage areas. Activity concentrations of ^{238}U ranged
160 from 0.36 ± 0.03 to $92 \pm 5 \text{ mBq}\cdot\text{m}^{-3}$, with the highest concentration detected in the DCP
161 loading trucks area. The same trend was observed for ^{210}Pb with values ranging between
162 0.67 ± 0.04 and $147 \pm 6 \text{ mBq}\cdot\text{m}^{-3}$. In the case of ^{230}Th and ^{210}Po , the range of values
163 were between 0.24 ± 0.04 and $33 \pm 2 \text{ mBq}\cdot\text{m}^{-3}$ and between <0.007 and $34 \pm 6 \text{ mBq}\cdot\text{m}^{-3}$,
164 respectively, with the maximum concentration measured in the PR milling area. In
165 general, the highest activity concentrations in aerosols were observed in the “dry
166 process” locations such as storage and milling of PR areas and DCP storage areas
167 because those areas have more suspended aerosol concentrations (see Table 1).

168 Samples collected in the PR milling area (F-3) showed activity ratios close to unity
169 (Table 1). This corroborates that dust particles in this location ($43 \text{ mg}\cdot\text{m}^{-3}$) are
170 composed of PR. On the other hand, the airborne dust particle in loading trucks (F-8)
171 and packaging areas (F-4) (91 and $18 \text{ mg}\cdot\text{m}^{-3}$, respectively) had higher concentrations
172 of both ^{238}U and ^{210}Pb compared to ^{230}Th and ^{210}Po . These concentrations are in
173 agreement with the radionuclide activity ratio of DCP (Table 1), described in
174 Casacuberta et al. (2011). The $^{210}\text{Pb}/^{210}\text{Po}$ ratio in the packaging area (1.7 ± 0.3) reflects
175 the ingrowth of ^{210}Po from the decay of ^{210}Pb present in old DCP dust accumulated
176 around the area.

177 Aerosol samples collected in the “wet processes” areas were less enriched in
178 radionuclides. Samples with the lowest activities (F-1 and F-2) **showed slightly higher**
179 **specific activities above** the measured background for ^{238}U and ^{210}Po (Table 1) and for
180 the range reported by Preiss et al. (1996) for ^{210}Pb of $0.2 - 0.5 \text{ mBq}\cdot\text{m}^{-3}$ in Europe.
181 Samples located in the digestion section (F-6 and F-7), that are also outdoor locations,
182 showed higher concentrations of ^{210}Pb (5.5 ± 0.3 and $1.69 \pm 0.08 \text{ mBq}\cdot\text{m}^{-3}$,
183 respectively) compared to the rest of the wet process areas. This may be related to the
184 highest ^{222}Rn concentration measured in the digestion and decanter areas in the DCP
185 plant (Table 2), adding to the ^{210}Pb naturally present in air and DCP suspended dust.
186 Thus, the ratios obtained for the wet process areas sampling points F-6 and F-7 were not
187 exactly in agreement with PR and DCP dust ratios.

188 The concentrations in aerosols collected in the office and the service building (F-5)
189 were higher than in most locations at the wet processes areas, especially for ^{238}U , ^{210}Pb
190 and ^{210}Po , likely due to the spreading of DCP dust originating from the nearby DCP
191 drying facility. However, because the presence of old DCP accumulated in the area
192 allows ingrowth of ^{210}Po when in the packaging area, the $^{210}\text{Pb}/^{210}\text{Po}$ ratio in this sample
193 is lower than the DCP ratio (Table 1).

194

195 3.2 Atmospheric ²²²Rn

196 ²²²Rn concentrations in air measured with the passive detectors ranged from <D_L (9
197 Bq·m⁻³) to 211 ± 61 Bq·m⁻³ (Table 2). This maximum value corresponds to the indoor
198 sludge line area where the phosphate rock ore is denaturalized, milled and dissolved
199 with hydrochloric acid. Complementary measurements taken with active detectors in the
200 same area confirm this result: the highest ²²²Rn mean values of 186 ± 16 Bq·m⁻³ (July
201 2011) and 318 ± 58 Bq·m⁻³ (November 2011) were obtained in the 1st and 2nd
202 underground floors, respectively, where the PR is discharged, stored and milled. The
203 use of active detectors also highlight the fact that, respect to 1st underground floor,
204 maximum punctual levels of 760 ± 98 Bq·m⁻³ in July 2011 (Figure 2A) and 480 ± 80
205 Bq·m⁻³ in November 2011 (Figure 2B) were reached. In addition to the possible natural
206 background contribution (10 Bq·m⁻³, UNSCEAR, 2010), this high concentration in the
207 two floors air of the semi-closed corridors under the silos is due to the easily ²²²Rn
208 exhalation from the accumulated PR powder produced during the milling process.
209 Passive measurements next to the open top of the digester tanks (Table 2; P15) also
210 registered significantly high ²²²Rn concentration (121 ± 17 Bq·m⁻³) compared to the
211 other outdoor areas in the sludge line where maximum values did not exceed 25 Bq·m⁻³.
212 This high outdoor ²²²Rn concentration on top of the digesters is attributed to the boiling
213 process that occurs during the HCl chemical reaction with the PR, leading to ²²²Rn
214 release to the air. Results of the active measurements did not reach the highest value
215 measured in the digester tanks with the passive measurements. However, the
216 concentration in the 1st floor of the milling area (67 ± 29 Bq·m⁻³) suggests that the ²²²Rn
217 emanation may also occur, although to a lesser extent, in the decantation area. Outdoor
218 ²²²Rn concentrations in the rest of the sludge line area were, in general, higher (from <
219 D_L to 47 ± 18 Bq·m⁻³) than the world mean value for outdoor areas (10 Bq·m⁻³,
220 UNSCEAR, 2010).

221 ²²²Rn concentrations measured with passive detectors (long-term or integrated
222 measurements) in the DCP line ranged from D_L to 48 ± 10 Bq·m⁻³. The complementary
223 short timescale measurements with active detectors showed mean values similar to the
224 integrated measurements, with activity concentrations that ranged from < D_L to 52 ± 19
225 Bq·m⁻³, with the highest measurements recorded in those areas located next to the
226 sludge line area (precipitation and filtering areas). These concentrations of ²²²Rn in air
227 above the natural background in the DCP production plant may be due to: (i) the scales
228 formation with ²²⁶Ra (Casacuberta et al., 2011) that leads to ²²²Rn emanation, as shown
229 in previous studies in NORM industries (White and Rood, 2001) and the ²²²Rn
230 emanation due to ²²⁶Ra accumulation in ebonite, and; (ii) the emanation of ²²²Rn from
231 the phosphate rock ore processing in the milling and digestion.

232 Indoor areas such as services and office building areas, where workers spent most of
233 their working hours, registered mean ²²²Rn concentrations below 300 Bq·m⁻³. ²²²Rn
234 concentrations measured with passive detectors were 152 ± 20 Bq·m⁻³ in the laboratory
235 and 180 ± 22 Bq·m⁻³ in the control room (Table 2). Those values agree with the
236 concentration measured with the active detectors in November 2011 with mean values

237 of $193 \pm 47 \text{ Bq}\cdot\text{m}^{-3}$ in the office and $203 \pm 84 \text{ Bq}\cdot\text{m}^{-3}$ in the laboratory. Results obtained
238 with active detectors in July 2011 were generally lower with mean values of 48 ± 36
239 $\text{Bq}\cdot\text{m}^{-3}$ and $43 \pm 24 \text{ Bq}\cdot\text{m}^{-3}$, respectively. Maximum punctual values recorded with
240 active detectors were $285 \pm 55 \text{ Bq}\cdot\text{m}^{-3}$ in July 2011 in offices (Figure 2C) and 459 ± 68
241 $\text{Bq}\cdot\text{m}^{-3}$ in the laboratory (Figure 2D).

242

243 3.3 Gamma-radiation dose rates

244

245 The ambient dose equivalent $H^*(10)$ values measured in the DCP production plant are
246 listed in Table 3 and it is shown in Figure 3. Doses in the DCP line were generally low,
247 ranging from background ($0.05 - 0.08 \mu\text{Sv}\cdot\text{h}^{-1}$) to $0.57 \mu\text{Sv}\cdot\text{h}^{-1}$. The highest doses were
248 recorded in the sludge line (up to $27 \mu\text{Sv}\cdot\text{h}^{-1}$), particularly in the digestion and the
249 decantation areas of the plant and in the scrap metal disposal controlled area, where
250 pipes and metal devices from the DCP plant have been accumulated after its substitution
251 in the production plant.

252 In the digestion area, the walls of the digesters tanks tend to accumulate ^{226}Ra due to
253 scales formation (Casacuberta et al., 2011). Scales composition is determined by the
254 particular chemical conditions of the different production stages (Beddow et al., 2006)
255 and it is usually characterized by conglomerates of calcium sulphate, fluorides and
256 phosphates that include a fraction of dissolved ^{226}Ra and their daughters in the
257 crystalline structure. Gamma-radiation doses ranged from 0.87 to $4.1 \mu\text{Sv}\cdot\text{h}^{-1}$,
258 increasing at closer distances to the digesters tanks, being highest in contact with those
259 digesters that accumulated waste muds ($4.1 \mu\text{Sv}\cdot\text{h}^{-1}$) (Figure 3, A3), followed by the
260 values measured in contact with the walls of the digestion tanks ($3.5 \mu\text{Sv}\cdot\text{h}^{-1}$ in the first
261 floor and $3.3 \mu\text{Sv}\cdot\text{h}^{-1}$ in the second floor). Several zones close to the digestion area were
262 also influenced by the presence of ^{226}Ra . Gamma-radiation doses in the milling area
263 were higher than background, with values ranging from 0.10 to $0.31 \mu\text{Sv}\cdot\text{h}^{-1}$, the highest
264 in the vicinity of the digestion area.

265 In the decantation area, gamma-radiation doses measured close to pipes internally
266 coated with ebonite were significantly high, ranging from 0.23 to $27 \mu\text{Sv}\cdot\text{h}^{-1}$. Ebonite is
267 a type of rubber used to protect the pipes from acid corrosion. The maximum values of
268 13 and $27 \mu\text{Sv}\cdot\text{h}^{-1}$ were obtained in contact with the pipe that connects decanter tank 1
269 with decanter tank 2 (Figure 3, A1) and in contact with the pipe from decanter tank 1 to
270 re-digestion tank 1A (Figure 3, A2), respectively. The measurements of gamma-
271 radiation doses with NaI(Tl) and the visual inspection of some dismantled pipes
272 confirmed the presence of large amounts of ^{226}Ra in the ebonite and the absence of
273 scales, suggesting that the use of ebonite enhances the accumulation of ^{226}Ra inside the
274 pipes. The measurement of pipes extracted from the production process revealed that
275 those internally coated with ebonite presented doses of $0.18 - 13 \mu\text{Sv}\cdot\text{h}^{-1}$, while pipes
276 that were not coated with ebonite showed values similar to the background (up to 0.08
277 $\mu\text{Sv}\cdot\text{h}^{-1}$) (Table 4). Relatively high doses were measured in some other zones in the
278 decantation area, such as in the sludge compressor area ($4.8 \mu\text{Sv}\cdot\text{h}^{-1}$, Fig 3, A6), likely

279 due to the high concentrations of ^{226}Ra in sludge and fluids present in this area
280 (Casacuberta et al., 2011).

281 In the precipitation and filtering zones located in the wet DCP line area the doses ranged
282 from 0.19 to $0.54 \mu\text{Sv}\cdot\text{h}^{-1}$, substantially lower than in the digestion and decantation
283 areas (Table 3). Doses slightly above background could be caused by white scales
284 formation with low concentrations of ^{226}Ra (Casacuberta et al., 2011) or by the adjacent
285 sludge line.

286 In drying, storing and services areas (Table 3) the values obtained are comparable to
287 background (from background to $0.13 \mu\text{Sv}\cdot\text{h}^{-1}$) and the apparent faint increment may be
288 caused by the ^{226}Ra accumulation in the adjoining areas from the plant, without
289 significantly contributing to the external dose to workers, although they spend most of
290 their working time in this area.

291 Finally, outside the DCP production plant area (Fig 3. A4), dismantled pipes with
292 ebonite and devices extracted from the plant due to maintenance operations provide also
293 gamma-radiation dose levels above background due to the accumulation of ^{226}Ra after
294 being used in the DCP plant for several years. The median ambient dose equivalent
295 $\text{H}^*(10)$ was $1.0 \mu\text{Sv}\cdot\text{h}^{-1}$, with maximum values around $8.1 \mu\text{Sv}\cdot\text{h}^{-1}$ (Fig 3, A4) in
296 contact with scrap containers or pipes.

297

298 3.4 Occupational Effective Dose

299

300 In order to estimate the occupational dose to DCP plant workers, two types of working
301 tasks are considered: i) those related to operators that check routinely the correct
302 functioning of the plant and; ii) those related to workers that carry out maintenance
303 tasks of the plant, such as cleaning and fixing tanks and pipes. Both types of operators
304 are exposed to external radiation, airborne dust particle and ^{222}Rn inhalation. In both
305 cases the committed effective dose due to the inhalation of aerosols was quantified
306 using the concentrations of ^{238}U , ^{230}Th , ^{210}Pb and ^{210}Po and a breathing flux of $1.2 \text{m}^3\cdot\text{h}^{-1}$
307 1 (ICRP-66; 1994). The sample F1, collected at the stairs next to Digester-2 on the 3rd
308 floor, was considered as background for the atmospheric particles inhalation dose
309 source (Table 5).

310

311 *3.4.1. Plant Operators*

312

313 Results of the occupational effective dose estimated for the plant operators that check
314 routinely the correct functioning of the plant are shown in Table 5. Doses were
315 quantified using the annual occupation time of each worker in the different areas within
316 the DCP production plant (Table 5).

317 The effective external dose ranges from 0.08 to $0.16 \text{mSv}\cdot\text{y}^{-1}$, being the highest in the
318 sludge line due to the accumulation of ^{226}Ra in the ebonite and pipes (scales). Although

319 the external dose rates are generally high in the DCP line, the limited time that operators
320 spend in the area results in an annual external dose to workers of $0.08 \text{ mSv}\cdot\text{y}^{-1}$. The
321 external dose measured in the services area is slightly higher ($0.11 \text{ mSv}\cdot\text{y}^{-1}$) due to the
322 greater occupational time of workers in this area.

323 The committed effective doses due to inhalation of airborne dust particles are
324 significantly lower than the external dose, ranging from <0.01 to $0.02 \text{ mSv}\cdot\text{y}^{-1}$. On the
325 other hand, because the annual mean ^{222}Rn concentration in workplaces does not exceed
326 the European legislation reference level ($300 \text{ Bq}\cdot\text{m}^{-3}$), the occupational exposure to
327 ^{222}Rn inhalation is not considered in the total operational annual effective dose.

328 The total occupational annual effective dose to workers (internal and external) resulted
329 into $0.37 \text{ mSv}\cdot\text{y}^{-1}$. Although the DCP and sludge lines presented greater dose rates
330 during the short timescale measurements (Table 5), the limited time spent by workers in
331 these areas limited its contribution to the annual doses. The occupational annual
332 effective dose derived from the external dose and inhalation of aerosols obtained in the
333 DCP production plant is higher than the $0.17 \text{ mSv}\cdot\text{y}^{-1}$ (inhalation of aerosols 0.07
334 $\text{mSv}\cdot\text{y}^{-1}$ and external dose $\sim 0.10 \text{ mSv}\cdot\text{y}^{-1}$) reported by Gäfvert et al. (2001) in a
335 phosphoric acid plant in Sweden where PR is also digested with hydrochloric acid. On
336 the other hand, Bolívar et al. (2009) estimated a total gamma-radiation external dose of
337 less than $0.5 \text{ mSv}\cdot\text{y}^{-1}$ in a phosphoric acid production plant in Spain, where phosphoric
338 rock is digested with sulphuric acid.

339

340 *3.4.2 Maintenance operators*

341 Although most of the work carried out by operators is mainly focused on the routine
342 checking of process parameters, there are several maintenance works that are performed
343 during short periods of time (few hours) in areas with high ^{226}Ra concentrations (pipes
344 or tanks). The two major maintenance operations in the sludge line areas were analyzed:
345 i) the cleaning of the digesters and, ii) the substitution of pipes (Table 6). In the first
346 case the accumulated external dose in 2 h was $2.2 \mu\text{Sv}$. The pipe substitution operation
347 increased the external dose of workers by $5.0 \mu\text{Sv}$ in 2 h. The short duration of these
348 operations does not lead to a significant increase of the external dose of the workers.

349

350 **4 Conclusions**

351 This work presents the first comprehensive radiological risk assessment in a phosphate
352 industry plant that produces Dicalcium Phosphate. This was carried out by considering
353 the external gamma-radiation dose rates, the internal dose due to inhalation of airborne
354 dust particles and the assessment of ^{222}Rn concentration in air.

355 The highest external gamma-radiation dose rates (up to $27 \mu\text{Sv}\cdot\text{h}^{-1}$) were measured in
356 the digestion and decantation areas, mainly due to the formation of scales in the digester
357 tanks and pipes, and to the presence of ebonite, a rubber material used to protect the
358 pipes from the acid corrosion. However, the limited time spent by workers in those

359 areas resulted in an effective gamma-radiation external dose of less than $0.16 \text{ mSv}\cdot\text{y}^{-1}$.
360 Considering also the DCP line and service building, the total effective external dose for
361 workers was $0.35 \text{ mSv}\cdot\text{y}^{-1}$.

362 Inhalation of aerosols resulted in a negligible ($<0.02 \text{ mSv}\cdot\text{y}^{-1}$) committed effective dose
363 to workers.

364 Concentrations of ^{222}Rn were measured using different methods (passive and active) in
365 different locations within the plant. The highest mean concentrations ($211 \pm 61 \text{ Bq}\cdot\text{m}^{-3}$)
366 were found in indoor areas, where PR is discharged, stored and milled. Mean ^{222}Rn
367 concentrations in the service building were relatively high (up to $180 \text{ Bq}\cdot\text{m}^{-3}$),
368 especially in those measurements performed in November 2011. Mean ^{222}Rn
369 concentrations were always below the European legislation reference level ($300 \text{ Bq}\cdot\text{m}^{-3}$)
370 and therefore the ^{222}Rn occupational dose was excluded in the total operational annual
371 effective dose. However, ^{222}Rn concentrations were highly variable, with several short-
372 timescale measurements (Figure 3) higher than $300 \text{ Bq}\cdot\text{m}^{-3}$, with a maximum punctual
373 measurement of up to $750 \text{ Bq}\cdot\text{m}^{-3}$, which may require complementary studies to
374 understand the temporal variability of ^{222}Rn in the DCP plant.

375 The results obtained for external dose and inhalation of aerosols in the DCP production
376 plant resulted in a total occupational annual effective dose of 0.37 mSv considering an
377 annual occupational time of 1720 h. This annual dose to workers in the DCP plant
378 studied here is significantly lower than the limits established by the EURATOM (2013)
379 for non-radiation workers and members of the public ($1 \text{ mSv}\cdot\text{y}^{-1}$). This study highlights
380 the importance of performing dose evaluations in NORM industries in order to be able
381 to apply the proper countermeasures (e.g. limiting the residence time to exposure areas,
382 air ventilation, dust cleaning...) so that the dose to workers is as low as reasonably
383 achievable (ALARA).

384

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471

472 **Figures**

473

474 **Figure 1.** Sampling locations of aerosols (dot, F#), passive (cross, P#) and active (circle,
475 A#) integrated ^{222}Rn measurements in the DCP plant. Sampling at different plant levels
476 from ground indicated in brackets.

477 **Figure 2.** Radon short timescale concentrations obtained during an hourly period with
478 active monitors in different locations from the DCP plant.

479

480 A) (A.9) Rock discharge area (basement -2) Radon concentration obtained with the
481 active monitor AlphaGUARD for 18 hours between 18th and 19th July 2011.

482 B) (A.9) Rock discharge area (basement -2) Radon concentration obtained with the
483 active monitor AlphaGUARD for 18 hours between 8th and 9th November 2011.

484 C) (A.23) Office ^{222}Rn concentration obtained with active monitor RAD7 for 16 hours
485 between 18th and 19th July 2011 (left figure) and for 13 hours between 8th and 9th
486 November 2011 (right figure).

487 D) (A.24) Laboratory ^{222}Rn concentration obtained with active monitor RAD7 for 16
488 hours between 18th and 19th July 2011 (left figure) and for 14 hours between 8th and 9th
489 November 2011 (right figure).

490 **Figure 3.** Ambient dose equivalent $\text{H}^*(10)$ rate in above ground level (A) and level 1
491 (B) from the DCP Plant ($\mu\text{Sv}\cdot\text{h}^{-1}$). Sampling points are indicated with dots. The most
492 significant dose rates correspond to the pipe that connects decanter tank 1 with decanter
493 tank 2 (A1), the pipe from decanter tank 1 to re-digestion tank 1A (A2), the sands from
494 the digester tanks cleaning operations (A3), the dismantled pipes with ebonite and
495 devices extracted from the plant (A4), the digester tanks (A5) and the sludge
496 compressors (A6)

497

498 **Tables**

499 **Table 1.** Concentrations of ^{238}U , ^{230}Th , ^{210}Pb and ^{210}Po ($\text{mBq}\cdot\text{m}^{-3}$) in aerosols at
500 different locations in the DCP production plant. Isotope ratios were quantified for
501 aerosols, raw material (PR) and final product (DCP).

502 **Table 2.** Indoor and outdoor mean radon concentrations obtained with short timescale
503 (about 1 h) or continuous (about 18 h) measurements using active detectors (A) in July
504 2011 and November 2011. Radon concentrations measured by passive detectors (P)
505 during a four months period (July-November 2011) are also shown.

506 **Table 3.** Median ambient dose equivalent $H^*(10)$ and range of values measured in
507 several areas in the DCP plant.

508 **Table 4.** Ambient dose equivalent $H^*(10)$ in several pieces extracted from the
509 production process. Detailed for each piece the ebonite containing.

510 **Table 5.** Occupational annual effective dose received by the plant operator in different
511 areas of the production plant due to effective external dose and committed effective
512 dose due to inhalation of aerosols.

513 **Table 6.** Dose evaluation for plant operators in two maintenance operations in the DCP
514 plant.