



## Radioactivity contents in dicalcium phosphate and the potential radiological risk to human populations

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### ABSTRACT

Potentially harmful phosphate-based products derived from the wet acid digestion of phosphate rock represent one of the most serious problems facing the phosphate industry. This is particularly true for dicalcium phosphate (DCP), a food additive produced from either sulphuric acid or hydrochloric acid digestion of raw rock material. This study determined the natural occurring radionuclide concentrations of 12 DCP samples and 4 tricalcium phosphate (TCP) samples used for animal and human consumption, respectively. Metal concentrations (Al, Fe, Zn, Cd, Cr, As, Hg, Pb and Mg) were also determined. Samples were grouped into three different clusters (A, B, C) based on their radionuclide content. Whereas group A is characterized by high activities of  $^{238}\text{U}$ ,  $^{234}\text{U}$  ( $\sim 10^3 \text{ Bq kg}^{-1}$ ),  $^{210}\text{Pb}$  ( $2 \times 10^3 \text{ Bq kg}^{-1}$ ) and  $^{210}\text{Po}$  ( $\sim 800 \text{ Bq kg}^{-1}$ ); group B presents high activities of  $^{238}\text{U}$ ,  $^{234}\text{U}$  and  $^{230}\text{Th}$  ( $\sim 10^3 \text{ Bq kg}^{-1}$ ). Group C was characterized by very low activities of all radionuclides ( $< 50 \text{ Bq kg}^{-1}$ ). Differences between the two groups of DCP samples for animal consumption (groups A and B) were related to the wet acid digestion method used, with group A samples produced from hydrochloric acid digestion, and group B samples produced using sulphuric acid. Group C includes more purified samples required for human consumption. High radionuclide concentrations in some DCP samples (reaching  $2 \times 10^3$  and  $10^3 \text{ Bq kg}^{-1}$  of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , respectively) may be of concern due to direct or indirect radiological exposure via ingestion. Our experimental results based on  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  within poultry consumed by humans, suggest that the maximum radiological doses are  $11 \pm 2 \mu\text{Sv y}^{-1}$ . While these results suggest that human health risks are small, additional testing should be conducted.

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### 1. Introduction

Phosphorus is an essential element for all living cells and a key element in the transport of cellular energy. During the last several decades, inorganic phosphate rock of both igneous and sedimentary origin has been used as a source of phosphorus in the production of fertilizers and feed supplements for farm and domestic animals [1]. However, these compounds may be enriched in significant quantities of naturally occurring radionuclides [2], due to the similar ionic radii of uranium ( $\text{U}^{4+}$ ) and calcium ( $\text{Ca}^{2+}$ ), e.g. U substitutes for Ca in the apatite lattice of sedimentary phosphate rocks [3]. The range of  $^{238}\text{U}$  and  $^{226}\text{Ra}$  concentrations in marketable phosphate rocks is broad (about  $10\text{--}5000 \text{ Bq kg}^{-1}$ ), mostly due to its geological composition. For example, sedimentary phosphate ores such as those found in Tanzania, Florida (USA) and Morocco tend to have high

$^{238}\text{U}$  ( $> 10^3 \text{ Bq kg}^{-1}$ ) and low  $^{232}\text{Th}$  ( $< 100 \text{ Bq kg}^{-1}$ ) concentrations, magmatic ores such as apatite from Kola (Russia) or Brazil, contain appreciable amounts of  $^{232}\text{Th}$  (up to  $400 \text{ Bq kg}^{-1}$ ) relative to  $^{238}\text{U}$  ( $< 400 \text{ Bq kg}^{-1}$ ) [2,4–6].

Phosphate-based products such as dicalcium phosphate (DCP), monocalcium phosphate (MCP) and tricalcium phosphate (TCP), each containing  $\sim 20\%$  phosphorus, are important in modern live-stock production. These compounds are mostly used for cattle, pig and poultry diets [7–9] as well as a human diet supplement. The most common production process is based on wet acid digestion of the phosphate rock with sulphuric acid [6,10,11], although hydrochloric acid is also used [12]. Both acids lead to the enhancement of several radionuclides within the final product (e.g. DCP) and waste/by-products that are subsequently considered to be Naturally Occurring Radioactive Materials (NORM).

The main concern regarding these NORM materials, and particularly DCP, MCP and TCP, is that they may directly enter into the food chain. Hence they pose a potential radiological risk to animal and human populations. The lack of legal limits

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regarding the radionuclide content of NORM materials may lead to misconceptions regarding radiological consequences to animal and human populations.

The goals of this research are to: (i) evaluate the concentrations of natural radionuclides in a representative number of DCP and TCP samples commercialized in Spain in 2006; (ii) understand the origins of the radionuclide concentration patterns, as well as the metal concentrations, observed within sample groups; and (iii) estimate the dose to consumers via the ingestion of chicken meat fed with food containing certain amounts of DCP and TCP, with particular emphasis on  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  because of their potentially high contribution to internal radiological doses through ingestion.

## 2. Materials and methods

### 2.1. Sample description

A total of 16 DCP samples produced for commercial use in Catalonia (Spain) during the first half of 2006 were provided by the *Agència Catalana de Seguretat Alimentària* of the *Departament de Salut de la Generalitat de Catalunya* for analysis. Twelve of these samples were DCP used as livestock feed supplement and duplicates of each sample type were analyzed. Four other samples consisted of TCP used in human dietary supplements (Table 1). No details regarding initial rock type or subsequent industrial processing were provided.

### 2.2. Gamma emitters

Gamma emitters such as  $^{234}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{231}\text{Pa}$ , and  $^{228}\text{Th}$ , and  $^{40}\text{K}$  were quantified by gamma-ray spectrometry. Between 500 and 1000 g of dry homogenized sample were placed into 500 cm<sup>3</sup> Marinelli Jars. The jars were then sealed and stored for 3 weeks prior to quantification in order to ensure secular equilibrium between

$^{226}\text{Ra}$  and its short-lived daughters. Samples were measured for  $(80\text{--}150) \times 10^3$  s using a coaxial HPGe detector (GMX, EG&G Ortec) equipped with an iron, copper and lead shielding. The detection system basically consists of a high pure germanium crystal in a cryostat. The crystal is inversely polarized and the pulse is electronically stored to the multichannel analyzer (MCA). The MCA consists of 8192 channels set to allow the determination of emission lines ranging from 40 to 3000 keV. The efficiency calibration of the detector was confirmed using the SRM-4276 solution standard supplied by the National Institute of Standards and Technology, which consists of a mixture of  $^{125}\text{Sb}$  (in equilibrium with  $^{125\text{m}}\text{Te}$ ),  $^{154}\text{Eu}$  and  $^{155}\text{Eu}$ . Resolution at 1.33 MeV of  $^{60}\text{Co}$  is 1.9 keV, 20% relative efficiency and Genie 2000 as the software.

Thorium-234 activities were determined through the emission line at 63.29 keV. The  $^{226}\text{Ra}$  activities were determined from the three photopeaks of its daughter nuclides in secular equilibrium:  $^{214}\text{Pb}$  at 295 keV and 352 keV, and  $^{214}\text{Bi}$  at 609 keV. Thorium-228 concentrations were determined via  $^{212}\text{Bi}$  decay, using its emission line of 727.2 keV. The activity of  $^{228}\text{Ra}$  was determined via  $^{228}\text{Ac}$  decay at 911 keV. The  $^{235}\text{U}$  gamma emitter daughter,  $^{231}\text{Pa}$ , was determined at 330.1 keV. Finally,  $^{40}\text{K}$  was determined via its emission line at 1461 keV.

### 2.3. Alpha emitters

Polonium-210, uranium and thorium isotopes were quantified by alpha spectrometry after radiochemical purification. For the quantification of  $^{210}\text{Po}$  activity, between 150 and 250 mg of DCP or TCP was spiked with a known amount of  $^{209}\text{Po}$  as internal tracer, and microwave digested using a mixture of HCl, HNO<sub>3</sub> and HF [13]. Boric acid (H<sub>3</sub>BO<sub>3</sub>) was added in order to remove borofluorides. After digestion and evaporation, the residue was dissolved in 100 mL 1 M HCl. After the addition of ascorbic acid to reduce Fe<sup>3+</sup>,

**Table 1**

Description of the analyzed samples of dicalcium phosphate (DCP) and tricalcium phosphate (TCP).

Sample code	Batch/lot	Collection date	Additional information		
			Raw material	Source region	Phosphoric acid production place
DCP for animal consumption					
1	890R	4-Apr-06	Phosphate rock	Morocco	nd
	890G	4-Apr-06	Phosphate rock	Morocco	nd
2	883R	4-Apr-06	Phosphate rock	Morocco	nd
	883G	4-Apr-06	Phosphate rock	Morocco	nd
3	899B	4-Apr-06	Phosphate rock	Morocco	nd
	883B	11-Apr-06	Phosphate rock	Morocco	nd
4	899R	11-Apr-06	Phosphate rock	Morocco	nd
	899G	4-Apr-06	Phosphate rock	Morocco	nd
5	896B	7-Apr-06	Phosphate rock	Morocco (Bu Craa)	Huelva (Spain)
	897G	7-Apr-06	Phosphate rock	Morocco (Bu Craa)	Huelva (Spain)
6	896G	7-Apr-06	Phosphate rock	Morocco (Bu Craa)	Huelva (Spain)
	896R	7-Apr-06	Phosphate rock	Morocco (Bu Craa)	Huelva (Spain)
7	897B	7-Apr-06	Phosphate rock	Negev's Dessert	Israel
	897R	7-Apr-06	Phosphate rock	Negev's Dessert	Israel
8	891B	11-Apr-06	Phosphate rock	Negev's Dessert	Israel
	891G	11-Apr-06	Phosphate rock	Negev's Dessert	Israel
9	900B	11-Apr-06	Phosphate rock	Morocco	nd
	900G	11-Apr-06	Phosphate rock	Morocco	nd
10	891R	11-Apr-06	nd	nd	nd
	893B	11-Apr-06	nd	nd	nd
11	895G	20-Apr-06	nd	nd	Liban
	895B	11-Apr-06	nd	nd	Liban
12	893R	20-Apr-06	nd	nd	Liban
	893G	11-Apr-06	nd	nd	Liban
TCP for human consumption					
13	sha-1	1-May-06	Tricalcium phosphate	nd	nd
14	sha-2	1-May-06	Tricalcium phosphate	nd	nd
15	sha-3	1-May-06	Tricalcium phosphate	nd	nd
16	sha-4	1-May-06	Tricalcium phosphate	nd	nd

nd: no data.

**Table 2**Radionuclide concentrations of the  $^{238}\text{U}$  decay series in DCP and TCP samples for animal and human consumption commercialized in Catalonia in 2006.

Sample code	$^{238}\text{U}$ (Bq kg $^{-1}$ )	$^{234}\text{Th}$ (Bq kg $^{-1}$ )	$^{234}\text{U}$ (Bq kg $^{-1}$ )	$^{230}\text{Th}$ (Bq kg $^{-1}$ )	$^{226}\text{Ra}$ (Bq kg $^{-1}$ )	$^{210}\text{Pb}$ (Bq kg $^{-1}$ )	$^{210}\text{Po}$ (Bq kg $^{-1}$ )
DCP for animal consumption							
1	1131 ± 18	845 ± 10	899 ± 15	41 ± 3	96.9 ± 0.7	2183 ± 112	570 ± 29
2	1246 ± 20	978 ± 40	982 ± 16	38.7 ± 0.9	86 ± 8	2089 ± 117	684 ± 45
3	1257 ± 20	1010 ± 92	1032 ± 17	44 ± 1	88 ± 5	2207 ± 99	1336 ± 165
4	1173 ± 19	935 ± 33	929 ± 15	92 ± 3	131 ± 3	2260 ± 93	1043 ± 58
5	1432 ± 23	1003 ± 26	1418 ± 23	2007 ± 42	15.8 ± 0.4	41 ± 5	17 ± 7
6	1450 ± 16	1142 ± 27	1436 ± 16	2286 ± 47	16.7 ± 0.3	34 ± 10	22 ± 8
7	1341 ± 20	866 ± 9	1369 ± 21	1453 ± 30	8.5 ± 0.3	8.8 ± 0.9	12 ± 6
8	3128 ± 31	2236 ± 21	3144 ± 31	4512 ± 109	6.3 ± 0.4	8 ± 6	10 ± 5
9	999 ± 16	831 ± 8	784 ± 13	34 ± 3	65 ± 3	1851 ± 97	786 ± 55
10	1022 ± 17	855 ± 22	808 ± 13	40 ± 1	111 ± 3	2060 ± 66	692 ± 67
11	1126 ± 9	909 ± 13	1106 ± 0	206 ± 9	14 ± 1	36 ± 3	30 ± 4
12	1046 ± 17	697 ± 13	943 ± 15	63 ± 2	18 ± 3	204 ± 82	16 ± 37
TCP for human consumption							
13	24.7 ± 0.7	11 ± 1	22 ± 1	10.3 ± 0.3	7.3 ± 0.3	2.2 ± 0.3	4.3 ± 0.6
14	15.0 ± 0.4	<6.4	14.9 ± 0.4	45 ± 1	16.2 ± 0.6	7.7 ± 0.5	7.0 ± 0.7
15	5.8 ± 0.3	<5.4	5.3 ± 0.3	16 ± 1	2.3 ± 0.4	7.3 ± 0.5	9.9 ± 1.2
16	2.0 ± 0.2	<5.6	2.0 ± 0.2	53 ± 6	<1.4	1.8 ± 0.5	5.3 ± 0.8

both  $^{209}\text{Po}$  and  $^{210}\text{Po}$  were plated onto a silver disc. Plating time was approximately 6–7 h at 70 °C with constant stirring. Lead-210 was determined through the measurement of its granddaughter  $^{210}\text{Po}$ . In this case, samples were digested and quantified 1 year after sample collection to ensure the radioactive equilibrium between  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the analyzed samples. Appropriate decay and in-growth corrections were applied to determine concentrations at sampling time.

A modified version of the method described in Martínez-Aguirre and García-León [14] was used for the quantification of uranium and thorium isotopes. Approximately 1 g of dried sample was spiked with  $^{229}\text{Th}$  and  $^{232}\text{U}$  and digested with  $\text{HNO}_3$ . The final residue was redissolved in 8 M  $\text{HNO}_3$ . The aqueous phase (8 M  $\text{HNO}_3$ ) was mixed with tributylphosphate (TBP), shaken for 5 min, and decanted, leaving the actinides remaining in the organic phase. Separation of U and Th was accomplished by using repeated extractions of a mixture of 15 mL xylene, 1.5 M HCl and  $\text{H}_2\text{O}$ . While Th was extracted with the addition of HCl 1.5 M; U was preferentially removed into the aqueous phase. The solution containing thorium was evaporated to dryness, redissolved in 10 mL 8N  $\text{HNO}_3$  and further purified using BIO-RAD AG 1-X8 (100–200 mesh) anion exchange resin. The U and Th solutions were subsequently evaporated near dryness and electroplated independently onto 2.2-cm diameter stainless steel planchets. Polonium-210, uranium and thorium activities were determined using PIPS detectors in a CANBERRA alpha-analyst system, model PD-450.18AM. Backgrounds in the corresponding windows were: 0.0011 ± 0.0010 cpm for  $^{210}\text{Po}$ ; 0.0006 ± 0.0002 cpm for  $^{238}\text{U}$ ; 0.0004 ± 0.0001 cpm for  $^{235}\text{U}$ ; 0.0004 ± 0.0001 cpm for  $^{234}\text{U}$ ; 0.00035 ± 0.00004 cpm for  $^{232}\text{Th}$  and 0.0005 ± 0.0002 cpm for the  $^{230}\text{Th}$  window.

#### 2.4. Metals

Samples were digested with diluted  $\text{HNO}_3$  (2%). The solution was filtered and the non-soluble fraction discarded. Concentrations of Fe, Al, Mg, Cd, Hg, Pb, As, Cr and Zn were determined using an inductively coupled plasma mass spectrometry (ICP-MS) Agilent, model 7500 ce.

#### 2.5. Statistical data analysis

A hierarchical cluster analysis of the data was conducted using SPSS™ version 12.0 for Windows. This procedure allows the identification of relatively homogeneous groups of cases (or variables) based on selected characteristics, using an algorithm that starts

with each case (or variable) in a separate cluster. Dendrograms were used to assess the cohesiveness of the clusters formed and provide information about the appropriate number of clusters.

### 3. Results

#### 3.1. DCP samples for animal consumption – samples 1–12

Radionuclide activities ( $^{238}\text{U}$ ,  $^{234}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ ) are listed in Table 2. In general, uranium isotopes and  $^{234}\text{Th}$  were present in similar activities in all the DCP samples, with the exception of sample 8 which contained activities almost double than the other samples (average of 1–12: 1363 ± 576 Bq kg $^{-1}$  of  $^{238}\text{U}$ , 1237 ± 642 Bq kg $^{-1}$  of  $^{234}\text{U}$ , and 1025 ± 397 Bq kg $^{-1}$  of  $^{234}\text{Th}$ ).  $^{230}\text{Th}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  specific activities were significantly more heterogeneous.

Thorium-232 had an average specific activity of 22 ± 34 Bq kg $^{-1}$  with activities of  $^{228}\text{Th}$  and  $^{228}\text{Ra}$  close to detection limits, below 10 Bq kg $^{-1}$  of  $^{228}\text{Th}$  and ~2 Bq kg $^{-1}$  of  $^{228}\text{Ra}$ . Potassium-40 generally ranged from 10 to 30 Bq kg $^{-1}$  of  $^{40}\text{K}$  with a high value of 60 Bq kg $^{-1}$  in sample 8 (Table 3).

#### 3.2. TCP samples for human consumption – samples 13–16

TCP samples were characterized by significantly different radionuclides activities relative to the DCP samples (Table 2). TCP samples contained less than 25 Bq kg $^{-1}$  in all cases, with mean activities of  $^{238}\text{U}$  and  $^{234}\text{U}$  of 12 ± 10 and 11 ± 9 Bq kg $^{-1}$ , respectively. Thorium-230 activities ranged from 10.3 ± 0.3 to 53 ± 6 Bq kg $^{-1}$  while  $^{226}\text{Ra}$  activities were all below 25 Bq kg $^{-1}$ . Concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  did not exceed 10 Bq kg $^{-1}$ . The radioactive daughters of  $^{232}\text{Th}$  (less than 3.2 ± 0.2 Bq kg $^{-1}$ ) and  $^{235}\text{U}$  (average of 0.5 ± 0.4 Bq kg $^{-1}$ ),  $^{228}\text{Th}$ ,  $^{228}\text{Ra}$  and  $^{231}\text{Pa}$ , were below detection.

#### 3.3. Metal concentrations

Concentrations of Mg, Al, Fe, Zn, Cr, As, Cd, Hg and Pb in DCP and TCP samples are shown in Table 4. Magnesium, aluminium, and iron were the most abundant, with mean values of 2.4 ± 2.9, 1.0 ± 1.1, and 1.1 ± 0.8 mg g $^{-1}$ . Zinc had concentrations of only 0.2 ± 0.3 mg g $^{-1}$ , while mean values of Cr, As, Cd and Hg were 82 ± 59, 1.6 ± 1.3, 2.3 ± 2.1 and <0.025 µg g $^{-1}$ , respectively. All Hg concentrations were below the detection limit (0.025 µg g $^{-1}$ ) except for sample 10, with 0.045 µg g $^{-1}$ .

**Table 3**

Radionuclide concentrations of the  $^{232}\text{Th}$  and  $^{235}\text{U}$  decay series and  $^{40}\text{K}$  in DCP and TCP samples for animal and human consumption commercialized in Catalonia (Spain) in 2006.

Sample code	$^{232}\text{Th}$ (Bq kg $^{-1}$ )	$^{228}\text{Th}$ (Bq kg $^{-1}$ )	$^{228}\text{Ra}$ (Bq kg $^{-1}$ )	$^{235}\text{U}$ (Bq kg $^{-1}$ )	$^{231}\text{Pa}$ (Bq kg $^{-1}$ )	$^{40}\text{K}$ (Bq kg $^{-1}$ )
DCP for animal consumption						
1	1.5 ± 0.5	<4.2	1.9 ± 0.4	47 ± 1	<28	<6.1
2	1.1 ± 0.1	<4.1	2.0 ± 0.3	53 ± 1	<29	<5.9
3	0.7 ± 0.2	<4.3	<1.4	51 ± 1	<28	<5.4
4	2.5 ± 0.4	<4.5	2.0 ± 0.8	81 ± 3	16 ± 2	<6.5
5	53 ± 3	7.8 ± 0.2	<1.4	72 ± 5	105 ± 3	26.7 ± 0.4
6	27 ± 2	8.2 ± 1.3	<1.1	79 ± 3	132 ± 1	23 ± 1
7	111 ± 4	2.4 ± 0.7	<1.2	69 ± 5	105 ± 6	23 ± 2
8	27 ± 6	<2.8	<1.6	168 ± 6	196 ± 25	58 ± 1
9	0.9 ± 0.5	<3.9	<1.3	41 ± 1	<26	<5.7
10	3.6 ± 0.3	<3.8	1.9 ± 0.1	45 ± 1	<26	<5.7
11	9 ± 2	3.2 ± 0.7	2.4 ± 0.1	63 ± 1	83 ± 3	21 ± 1
12		<3.9	<1.7	49 ± 1	47 ± 11	15.3 ± 0.1
MCP for human consumption						
13	0.41 ± 0.05	<3	<1.5	1.0 ± 0.1	<19	<5.7
14	3.2 ± 0.2	<6.4	<2.3	0.6 ± 0.1	<40	7 ± 3
15	<0.76	<5.2	<2.5	0.3 ± 0.1	<32	<9.5
16	<0.76	<5.2	<2.5	0.2 ± 0.1	<32	<10

**Table 4**

Metal content in DCP and TCP samples for animal and human consumption commercialized in Catalonia in 2006.

Sample code	Mg (mg g $^{-1}$ )	Al (mg g $^{-1}$ )	Fe (mg g $^{-1}$ )	Zn (mg g $^{-1}$ )	Cr (μg g $^{-1}$ )	As (μg g $^{-1}$ )	Cd (μg g $^{-1}$ )	Hg (μg g $^{-1}$ )	Pb (μg g $^{-1}$ )
DCP for domestic animals									
1	0.18	0.19	0.41	0.16	49	2.4	0.62	<0.025	4.9
2	0.2	0.2	0.43	0.057	43	1.6	0.53	<0.025	4.7
3	0.16	0.18	0.39	0.26	57	3.9	0.55	<0.025	4.9
4	0.26	0.24	0.46	0.12	47	2.4	0.44	<0.025	4.5
5	2	2.8	1.8	0.12	156	0.22	4.1	<0.025	1.2
6	2.1	2.7	1.9	0.11	166	0.21	2.8	<0.025	0.76
7	5.3	2	1.9	0.41	67	0.99	2.8	<0.025	0.39
8	10.2	3.2	2.4	1.05	127	0.57	6.5	<0.025	0.29
9	0.27	0.26	0.44	0.07	43	2.4	1.3	<0.025	3.9
10	0.23	0.34	0.48	0.1	46	2.3	0.48	0.045	4.4
11	4.2	0.65	1.9	0.28	166	3.6	5.2	<0.025	1.5
12	3.6	0.74	1.9	0.19	163	1.4	4.2	<0.025	0.9
TCP for humans									
13	0.91	0.2	0.32	<0.01	2.7	0.058	<0.05	<0.025	0.22
14	4.6	0.44	0.55	0.014	22	0.49	0.15	<0.025	0.39

TCP samples for human consumption (samples 13 and 14) had lower metal concentrations compared to DCP samples, especially Cr and Cd.

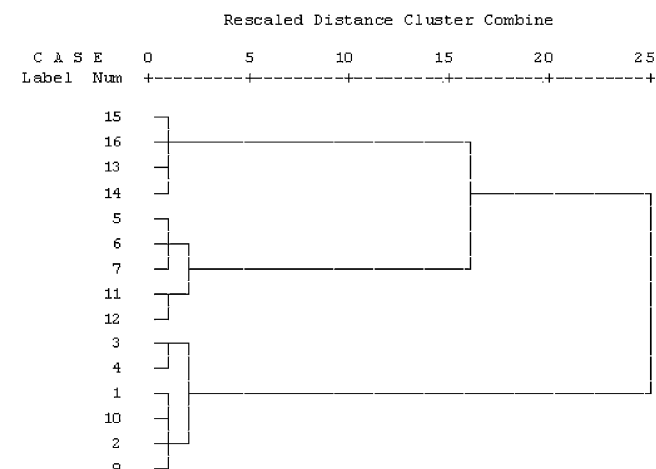
### 3.4. DCP and TCP radionuclides data analysis

The broader results of some of the  $^{238}\text{U}$ -series radionuclides were analyzed through a hierarchical cluster analysis, allowing a statistical identification of relatively homogeneous sample groups based on radionuclide activities (e.g.  $^{238}\text{U}$ ,  $^{234}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ ) (Fig. 1). Excluding sample 8, radionuclide contents in DCP and TCP samples were classified into three main different groups:

- (i) Group A: samples 1–4, 9 and 10.
- (ii) Group B: samples 5–7, 11 and 12.
- (iii) Group C: samples 13–16.

Samples of group A (Table 5) were characterized by high concentration values of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  (with mean activities of  $2108 \pm 146$  and  $852 \pm 286$  Bq kg $^{-1}$ ) and low activities of  $^{230}\text{Th}$  ( $48 \pm 22$  Bq kg $^{-1}$ ). In contrast, samples of group B had low specific activities of both  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  ( $<100$  Bq kg $^{-1}$ ), whereas they contained high activities of  $^{230}\text{Th}$  ( $1203 \pm 1022$  Bq kg $^{-1}$ ). Group C was characterized for its low uranium, thorium, radium, lead and polonium radionuclide concentrations ( $<25$  Bq kg $^{-1}$ ). It is important to note that there was relatively large heterogeneity within group B. The differences were

Dendrogram using Average Linkage (Between Groups)



**Fig. 1.** Hierarchical cluster analysis of DCP samples for human and animal consumption. Variables considered were specific concentrations of  $^{238}\text{U}$ ,  $^{234}\text{Th}$ ,  $^{234}\text{U}$ ,  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . Clusters were named as group A (samples 1–4, 9 and 10), group B (samples 5–7, 11 and 12) and group C (samples 13–16). Sample 8 was considered as an outlier.

**Table 5**  
Average radionuclide concentrations in groups A, B and C of DCP and TCP samples. Group A: samples 1–4, 9 and 10; group B: samples 5–7, 11 and 12; group C: TCP samples for human consumption (13–16).

Group code	$^{238}\text{U}$ (Bq kg $^{-1}$ )	$^{234}\text{Th}$ (Bq kg $^{-1}$ )	$^{234}\text{U}$ (Bq kg $^{-1}$ )	$^{230}\text{Th}$ (Bq kg $^{-1}$ )	$^{226}\text{Ra}$ (Bq kg $^{-1}$ )	$^{210}\text{Pb}$ (Bq kg $^{-1}$ )	$^{210}\text{Po}$ (Bq kg $^{-1}$ )
A	1138 ± 109	909 ± 76	906 ± 97	48 ± 22	96 ± 23	2108 ± 146	852 ± 286
B	1279 ± 183	923 ± 165	1254 ± 219	1203 ± 1022	15 ± 4	65 ± 79	20 ± 7
C	12 ± 10	<12	11 ± 9	31 ± 21	9 ± 7	5 ± 3	7 ± 2

Group A									
$^{238}\text{U}$	1								
$^{234}\text{Th}$	0,80 ± 0,13	1							
$^{234}\text{U}$	0,80 ± 0,14	1,00 ± 0,14	1						
$^{230}\text{Th}$	0,04 ± 0,46	0,05 ± 0,46	0,05 ± 0,46	1					
$^{226}\text{Ra}$	0,08 ± 0,25	0,11 ± 0,25	0,11 ± 0,26	2,00 ± 0,51	1				
$^{210}\text{Pb}$	1,85 ± 0,12	2,32 ± 0,11	2,33 ± 0,13	43,62 ± 0,45	21,9 ± 0,2	1			
$^{210}\text{Po}$	0,75 ± 0,35	0,94 ± 0,20	0,94 ± 0,11	17,63 ± 0,56	8,8 ± 0,4	0,40 ± 0,34	1		
	$^{238}\text{U}$	$^{234}\text{Th}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$		
Group B									
$^{238}\text{U}$	1								
$^{234}\text{Th}$	0,72 ± 0,23	1							
$^{234}\text{U}$	0,98 ± 0,23	1,36 ± 0,23	1						
$^{230}\text{Th}$	0,80 ± 1,01	1,11 ± 1,02	0,81 ± 1,02	1					
$^{226}\text{Ra}$	0,01 ± 0,29	0,02 ± 0,31	0,01 ± 0,31	0,01 ± 1,03	1				
$^{210}\text{Pb}$	0,05 ± 0,14	0,07 ± 1,23	0,05 ± 1,23	0,06 ± 1,58	4,4 ± 1,2	1			
$^{210}\text{Po}$	0,02 ± 0,39	0,02 ± 0,31	0,02 ± 0,17	0,02 ± 1,06	1,3 ± 0,4	0,30 ± 1,27	1		
	$^{238}\text{U}$	$^{234}\text{Th}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{226}\text{Ra}$	$^{210}\text{Pb}$	$^{210}\text{Po}$		

**Fig. 2.** Activity ratios of the U-238 decay series isotopes in groups A and B samples. Isotopes in the Y-axis correspond to the ratio numerator.

mainly due to samples 11 and 12, which had lower activities of  $^{230}\text{Th}$  compared to the rest of the samples from group B. Sample 8 also had low specific concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ , similar to group B, but rather high specific concentrations of the other radionuclides. Thus this sample was considered to be an outlier in our clustering analysis. Isotopic ratios are shown in Fig. 2, determined using average values compiled in Table 5.

#### 4. Discussion

The different radionuclide activities in DCP samples could be derived from two causes: (i) the geological characteristics of the phosphate rock; and (ii) the industrial manufacturing processes used for its production.

##### 4.1. Geologic characteristics of DCP and TCP source rocks

Unfortunately, very little information regarding the origin and industrial process of the phosphate-based products were provided (Table 1). Samples 1–9 were produced using phosphate rocks from either Morocco or the Negev Dessert, Israel. Samples 5–8, and 11 and 12 were produced using phosphoric acid, suggesting extraction via sulphuric acid (see below).

This information allowed us to make some assumptions regarding our samples. For example, samples 1–9 were likely produced from sedimentary phosphate rocks, typical of the Morocco or the Negev Dessert. This is supported by the radionuclide activities. All DCP samples used as a poultry feed supplement contained elevated concentrations of nuclides in the  $^{238}\text{U}$  decay chain ( $\sim 10^3$  Bq kg $^{-1}$ ) and low activities in  $^{232}\text{Th}$  decay series isotopes. If DCP samples came from the digestion of igneous rocks, the proportion  $^{238}\text{U}/^{232}\text{Th}$  would be reversed. Furthermore, although  $^{238}\text{U}$  and its decay chain

daughters may vary from 1500 Bq kg $^{-1}$  in Morocco to 5000 Bq kg $^{-1}$  in Tanzania [15,16], the activities of the DCP samples were of a similar order of magnitude. No information was available for samples 10–16, but the high  $^{238}\text{U}$  activities of samples 12 and 13 ( $\sim 10^3$  Bq kg $^{-1}$ ) relative to  $^{232}\text{Th}$ , suggests a sedimentary origin of the raw material.

##### 4.2. Radionuclide distributions due to industrial manufacturing processes used for DCP and TCP production

DCP and TCP are produced by the wet acid digestion of phosphate rock by either sulphuric or hydrochloric acid. When using sulphuric acid the resulting slurry is filtered to separate the product, phosphoric acid, from the insoluble by-product, phosphogypsum. The phosphoric acid is then further processed for the production of fertilizer ingredients and animal feed ingredients, such as DCP and TCP [1]. The use of hydrochloric acid for digestion of phosphoric rock is less widespread, but it is the dominant method for production of DCP in Spain. The phosphate rock is partially dissolved in hydrochloric acid. Whereas the undissolved fraction is eliminated in the form of slag, in the dissolved fraction  $\text{CaCO}_3$  is added in order to adjust the pH to  $\sim 2$ . This results in the precipitation of DCP and subsequent separation by vacuum filtration [12]. According to Gáfvert et al. [12] two sludges are formed: one mainly consisting of undissolved phosphate rock,  $\text{SiO}_2$  and fluoride compounds such as  $\text{CaF}_2$  and the other, composed of  $\text{Mg}(\text{OH})_2$ .

Prior to industrial processing, the  $^{238}\text{U}$  decay series within phosphate rocks is essentially in radioactive equilibrium [4,17–20]. Deviations from secular equilibrium occur during the wet phosphoric acid treatment of the rock, as the various radionuclides are partitioned into various phases according to their solubility (which in turn depends on variables such as pH, temperature, and



O<sub>2</sub> availability). Unfortunately, although a considerable amount of compositional data exists for phosphogypsum, there is little information available on the fractionation and distribution of radionuclides within phosphate products [11].

The isotopic ratios (Fig. 2) confirm that radionuclide fractionation occurred during the production of DCP. <sup>230</sup>Th/<sup>238</sup>U, <sup>226</sup>Ra/<sup>238</sup>U and <sup>210</sup>Pb/<sup>238</sup>U were for the most part, far from unity, suggesting different reaction mechanisms of the elements during the treatment of the phosphate rock in DCP and TCP production. The following discussion mainly focused on specific chemical behaviours of various U-series radioactive daughters that may occur during phosphate rock processing and is used to identify the method by which the DCP and TCP samples were produced in this study.

#### 4.2.1. Uranium

Uranium is generally soluble in any acid, although it strongly depends on redox conditions [6,21]. All analyzed samples of DCP for animal consumption contained relatively high activities of both <sup>238</sup>U and <sup>234</sup>U, ranging from 999 and 1450 Bq kg<sup>-1</sup> and 784 and 1436 Bq kg<sup>-1</sup>, respectively (excluding sample 8). However, uranium isotopic ratios for group A and B samples differed ( $p < 0.08$  for <sup>238</sup>U and 0.03 for <sup>234</sup>U) (Fig. 2). Whereas the <sup>234</sup>U/<sup>238</sup>U ratio was close to unity in samples from group B, they were below unity in group A. It has been suggested that <sup>234</sup>U/<sup>238</sup>U disequilibria may occur in phosphate rock due to the preferential leaching of <sup>234</sup>U relative to <sup>238</sup>U mostly in particle sizes <1 μm during weathering processes [18]. In our case, however, these differences were likely due to the oxidation conditions produced by the acids during the digestion of the phosphate rock [6,12].

When phosphate rock is digested with sulphuric acid, only a small percentage of uranium (5–10%) fractionates into the solid phosphogypsum phase [10,16]. In other words, U tends to favour the dissolved phosphoric acid phase during sulphuric acid processing as the U<sup>4+</sup> present in the phosphate rock oxidizes to U<sup>6+</sup> (which is more soluble, and hence more mobile) during the acidification process. The dissolved uranium is then largely incorporated into the acid phase as uranyl phosphate, sulphate or fluoride complexes [6,11]. Under reducing conditions, U<sup>6+</sup> reduces to U<sup>4+</sup> and then precipitates with phosphogypsum, since U<sup>4+</sup> has very similar ionic radii to Ca<sup>2+</sup> [21]. Reduction conditions depend on the amounts of Fe<sup>2+</sup> [21,22]. Moreover, the oxidation state of uranium is not exactly the same in all sedimentary phosphate ores. Indeed, Rajković et al. [23] concluded that for phosphate rock from the USA in which uranium is present mainly as U<sup>4+</sup>, 60–80% of the uranium passes into the acid using the wet method and the remaining 20–40% precipitates together with phosphogypsum. In contrast, uranium in phosphate from Africa is predominantly in the form U<sup>6+</sup>, and thus its fraction in the acid can reach 90%. Another factor affecting uranium solubility is pH. At pH < 5, the uranyl ion (UO<sub>2</sub><sup>2+</sup>) and uranyl fluoride complexes dominate, but minimum uranium solubility occurs between a pH of ~5–8.5 [6], resulting in most of the U precipitating with the final product (in this case, DCP). Thus, uranium in the phosphogypsum was considerably lower (~5%), and a high percentage of the uranium contained in the raw material was found in the final DCP products [11,19].

During hydrochloric acid production of DCP, Gäfvvert et al. [12] found that DCP contains about 75% of the total uranium from the initial phosphate rock. This is because uranium in contact with hydrochloric acid leads to soluble U<sup>4+</sup> and U<sup>3+</sup> and both are soluble under acidic conditions [24]. While small differences in the uranium content of DCP were found; this is likely due to the fact that sulphuric acid dissolves uranium more slowly than HCl [24].

#### 4.2.2. Thorium

<sup>230</sup>Th concentrations were significantly different between groups A and B (Fig. 2): whereas in group A the <sup>230</sup>Th/<sup>238</sup>U ratios

were very low ( $0.04 \pm 0.46$ ), they were above unity ( $1.50 \pm 0.26$ ) in group B (excluding samples #11 and #12). Group A samples did not contain significant concentrations of <sup>230</sup>Th ( $77 \pm 22$  Bq kg<sup>-1</sup>), in agreement with Gäfvvert et al. [12], who reported that only 1% of the <sup>230</sup>Th from the phosphate precipitates together with DCP. Although thorium is very soluble with hydrochloric acid [24], it has also a high affinity for particulate and colloidal surfaces [6,25]. It thus concentrates in the sludge. Thorium may also be complexed by fluoride ions to form ThF<sub>4</sub>, which co-precipitates with CaF<sub>2</sub> during HCl processing [12]. Samples from group A contained relatively large concentrations of <sup>234</sup>Th. This is due to the fact that while thorium is not significantly present in the final product just after its production, the time lapse between DCP production and its commercialization (and analysis) is long enough for <sup>234</sup>Th to grow back into secular equilibrium with <sup>238</sup>U (<sup>234</sup>Th half life is 24 days). This was not the case for <sup>230</sup>Th due to its much longer half life ( $7 \times 10^4$  years).

Concentrations of <sup>230</sup>Th in samples 5–8 ranged from 1453 to 4512 Bq kg<sup>-1</sup>. This suggests that samples from group B were produced via sulphuric wet acid digestion, in which both thorium and uranium distribute primarily into the acid phase [20,26]. Its presence in DCP was due to the fact that total Th in solution decreases as pH is increased to 5, as solid Th(OH)<sub>4</sub> forms [6]. Hence, it is likely that thorium precipitated once lime was added to the phosphoric acid to produce DCP. Samples 11 and 12 contained measurable <sup>230</sup>Th activities, although in significantly lower concentrations than the rest of the samples from group B. This might be due to subtle variations in the production process used in these particular samples.

The above analysis suggests that group A was produced via hydrochloric acid digestion, while group B samples were derived from sulphuric acid. However, it should be noted that different patterns within each production process, particularly to the longer and more complex processing associated with sulphuric acid likely exists as samples from group B were significantly more heterogeneous.

#### 4.2.3. Radium

Unlike uranium and thorium, radium geochemistry was less clear. The fractionation of radium and its progeny is evident from the corresponding isotopic ratios (Fig. 2). The <sup>226</sup>Ra/<sup>238</sup>U ratios were far below unity in both groups ( $0.08 \pm 0.25$  and  $0.01 \pm 0.29$  for groups A and B, respectively), as only a small fraction of the radium found in the rock was maintained in the final product. Radium is a divalent element, such as Ba, Sr and Ca, and thus follows similar chemical pathways [6,19]. When hydrochloric acid is used for the phosphate rock digestion some radium co-precipitates in the sludge with CaF<sub>2</sub> in the form of RaF<sub>2</sub>. The remaining radium remains in solution in the form of RaCl<sub>2</sub>. The concentration of <sup>226</sup>Ra in the various products should thus be proportional to the concentration of calcium chloride [12].

Radium concentrations in Group B samples were even lower than in group A samples. Several studies have demonstrated that radium partitions into phosphogypsum when the phosphate rock is digested with sulphuric acid, leading to little amounts of <sup>226</sup>Ra (<2%) in DCP [1,17,27]. Ra-226 appears to be closely associated with the finer hemihydrate particles than the larger dehydrate particles, similar to fine phosphogypsum grains [6,27]. The exact reasons why <sup>226</sup>Ra is mostly found in phosphogypsum remains enigmatic, but it is likely due to a combination of several mechanisms [11]: radium may (i) be strongly sorbed by phosphogypsum surfaces [28]; (ii) co-precipitate as some yet unknown phase or solid solution with CaSO<sub>4</sub>·nH<sub>2</sub>O [1]; (iii) be included in radiobarite (Ra-bearing BaSO<sub>4</sub>) or (Ba,Sr)SO<sub>4</sub> solid solutions [22] or (iv) even remain within phosphate rock particles which have survived the sulphuric acid attack [6].

#### 4.2.4. Lead

Lead to uranium ratios generally followed reverse trends than the  $^{230}\text{Th}/^{238}\text{U}$  ratios discussed above, with the exception of samples 11 and 12 (Fig. 2).  $^{210}\text{Pb}/^{238}\text{U}$  ratios were above unity in group A samples ( $1.85 \pm 0.12$ ), but were very low in samples from group B ( $0.05 \pm 0.14$ ). Group A distributions are explained through the fact that Pb, like Th, is more particle reactive than U. Thus lead activities increase when DCP precipitates due to its adsorption onto smaller size particles [18]. During hydrochloric acid digestion,  $^{210}\text{Pb}$  forms a  $\text{PbCl}_2^{-4}$  complex [24] that does not precipitate until the final step in DCP production. However, Gäfvert et al. [12] reported that  $^{210}\text{Pb}$  concentrations in DCP was only 13% of the total  $^{210}\text{Pb}$  inflow. They suggested that  $^{210}\text{Pb}$  is uniformly distributed between the various products and wastes of the DCP production. Differences between the results obtained in this study and those found in Gäfvert et al. [12] might be due to varying steps within the production process. In their study, after chemical digestion of the rock, the pH is adjusted to  $\sim 2$  and the DCP is precipitated from solution, which is subsequently used for the production of calcium chlorine. Before the solution is transported elsewhere, the pH is readjusted to  $\sim 10$ , resulting in a second sludge which contains more than 30% of the total inflow of  $^{210}\text{Pb}$  [12]. In a similar industrial process also using HCl, monocalcium phosphate is formed and the pH is adjusted with  $\text{CaCO}_3$  after chemical digestion of the rock. This results in direct production of DCP with no further steps [29]. Therefore  $^{210}\text{Pb}$  is not removed, and remains in the final products.

All group B samples presented low  $^{210}\text{Pb}$  concentrations and corresponding  $^{210}\text{Pb}/^{238}\text{U}$  ratios were well below unity (Fig. 2). Some studies suggest that when phosphate rock is digested with sulphuric acid,  $^{210}\text{Pb}$  may: (i) appear primarily in the acid stream together with Th [1,6], since lead solubility is low except in acidic environments [30]; or (ii) distribute uniformly in the product and in phosphogypsum [26]. Our results suggested that  $^{210}\text{Pb}$  was not present in phosphoric acid [10,11,19,31]. Lead speciation and solubility may also be controlled by pH, temperature and redox conditions. In particular, Rutherford et al. [6] stated that lead carbonate and lead sulphate are quite insoluble and often control the solubility of lead in oxidizing environments. Furthermore, under reducing conditions Pb is likely to precipitate as  $\text{PbS}$ . Adsorption onto clays and organic materials may maintain low Pb concentrations in solution (i.e. Pb may be absorbed onto the small particles of the sludge). Regarding the effect of temperature, Burriel-Martí et al. [24] reported that lead is dissolved in the form of  $\text{Pb}(\text{HSO}_4)_2$  only at high temperatures of sulphuric acid digestion.

#### 4.2.5. Polonium

The  $^{210}\text{Po}/^{238}\text{U}$  ratio followed a pattern similar to that of the  $^{210}\text{Pb}/^{238}\text{U}$  ratio, although  $^{210}\text{Po}$  concentrations were lower. Gäfvert et al. [12] reported that for the HCl process, only 30% of the total input of  $^{210}\text{Po}$  co-precipitates with the DCP. The reasons are that polonium either co-precipitates with  $\text{Mg}(\text{OH})_2$  and is collected in the sludge [12] or forms  $\text{PoCl}_2$  and remains dissolved into the waste solution. As it can be shown in Fig. 2, the  $^{210}\text{Po}/^{210}\text{Pb}$  ratio in Group A samples were always  $< 1$ , around 0.5. This suggests that in Group A  $^{210}\text{Po}$  were mostly derived from  $^{210}\text{Pb}$  decay since production, although not enough time had passed for  $^{210}\text{Po}$  to reach secular equilibrium with  $^{210}\text{Pb}$  at the time of analysis.

In contrast, samples from group B (digested with sulphuric acid) contained low specific activities of  $^{210}\text{Po}$ , ranging from 0 to  $29 \text{ Bq kg}^{-1}$ . Most of the  $^{210}\text{Po}$  found in the original phosphate rock may have been partitioned, together with  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$ , into the phosphogypsum during wet acid production [6,11,19,22,31]. These values agree with Hurst and Arnold [21], who reported that 99% of the  $^{210}\text{Po}$  appears in the phosphogypsum phase. Therefore, the  $^{210}\text{Po}$  found in DCP samples from this group would also come from  $^{210}\text{Pb}$  decay since production.

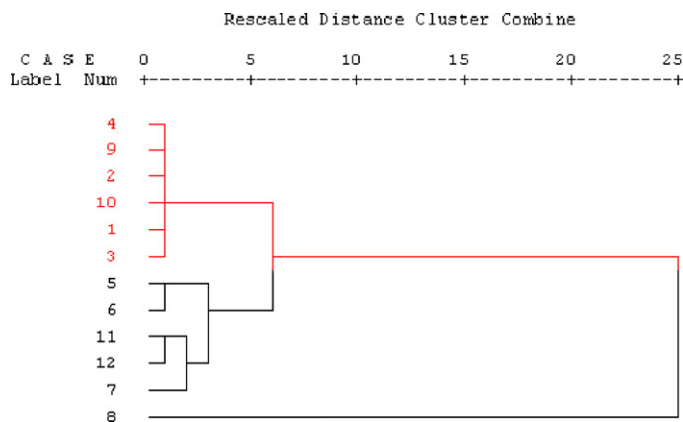


Fig. 3. Hierarchical cluster analysis of DCP samples for animal consumption. Variables considered were specific concentrations of Mg, Al, Fe, Zn, Cr, As, Cd and Pb.

#### 4.2.6. Other isotopes

Although the  $^{238}\text{U}$  decay series radionuclides are the most abundant in sedimentary phosphate rocks, radionuclides of the  $^{235}\text{U}$  and  $^{232}\text{Th}$  decay series may also help when interpreting our results. Indeed,  $^{235}\text{U}$  distributions followed those of  $^{238}\text{U}$  and  $^{234}\text{U}$ , but activities were one order of magnitude lower; the same occurred for  $^{232}\text{Th}$ , which chemically behaves like  $^{230}\text{Th}$ . Protactinium-231 was quantifiable only in samples produced via sulphuric acid digestion, agreeing with Beddow et al. [32] who reported that  $^{234}\text{Pa}$  was retained in the sulphuric acid solution as it is rich in fluorides and phosphates. In contrast, when DCP is produced via HCl, which contains lower fluoride and phosphates,  $^{231}\text{Pa}$  may co-precipitate with the waste slag.

It is also important to note the chemical behaviour of potassium. Phosphate ores are usually poor in  $^{40}\text{K}$  [14], generally ranging from below detection to  $200 \text{ Bq kg}^{-1}$  for both sedimentary and magmatic ores [5,15,19,33]. According to Burriel-Martí et al. [24] potassium is not soluble in any acid, so concentration increases in acidic solutions do not occur. In our study, there were clear differences in  $^{40}\text{K}$  activities between samples from group A with  $^{40}\text{K}$  activities below  $10 \text{ Bq kg}^{-1}$  and samples within group B, characterized by specific  $^{40}\text{K}$  activities of  $15\text{--}57 \text{ Bq kg}^{-1}$ . This suggests that  $^{40}\text{K}$  might be slightly more soluble in sulphuric acid than in hydrochloric acid. Costa-Garangou [29] reported that residual muds analyzed from a phosphate industry where DCP was produced via hydrochloric acid contained higher values of  $^{40}\text{K}$  compared to the raw material, up to  $820 \pm 51 \text{ Bq kg}^{-1}$ . Indeed, Gäfvert et al. [12] reported that  $^{40}\text{K}$  concentrations were enhanced in sands and clays that are removed prior to delivery of phosphate rock to the processing plant.

#### 4.3. Metal contents in DCP samples

The hierarchical cluster analysis of the metal contents in DCP and TCP samples for animal consumption commercialized in Catalonia (Fig. 3) also suggested different chemical processing mechanisms. Metals, like radionuclides, fractionate either in the acid or in wastes of the wet acid digestion of the phosphate rock. For example, high concentrations of Mg, Al and Fe, as well as Cr and Cd, corresponded to samples with high concentrations of  $^{230}\text{Th}$  ( $\sim 10^3 \text{ Bq kg}^{-1}$ ) and low values of  $^{210}\text{Pb}$  (group B). Higher values of As and Pb with the group of samples with high concentrations of  $^{210}\text{Pb}$  ( $\sim 2 \times 10^3 \text{ Bq kg}^{-1}$ ) (group A). The exceptions were samples 11 and 12, which contain higher concentrations of As and lower concentrations of Al compared to the other samples of the same group. This again demonstrated the heterogeneity of group B samples relative to group A.

**Table 6**

Specific concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  ( $\text{Bq kg}^{-1}$  dry weight) in Diets I, II and III. For each diet, samples of breast ( $n=2$ ), thigh ( $n=2$ ), liver ( $n=2$ ), kidney ( $n=2$ ), bone ( $n=2$ ) and excrements ( $n=3$ ) as well as samples of whole animal ( $n=3$ ) at age 21 days were analyzed.

	Diet I (2.5% TCP)		Diet II (5% DCP)		Diet III (2.5% DCP)	
	$^{210}\text{Pb}$	$^{210}\text{Po}$	$^{210}\text{Pb}$	$^{210}\text{Po}$	$^{210}\text{Pb}$	$^{210}\text{Po}$
Chicken fodder	$1.0 \pm 0.3$	$0.9 \pm 0.4$	$101 \pm 4$	$74 \pm 8$	$51 \pm 2$	$37 \pm 2$
Breast	$0.6 \pm 0.5$	<0.2	$0.2 \pm 0.2$	$1.4 \pm 0.1$	$0.3 \pm 0.4$	$0.9 \pm 0.4$
Thigh	<0.06	$0.1 \pm 0.2$	<0.1	$1.0 \pm 0.2$	<0.2	$0.9 \pm 0.9$
Liver	$0.3 \pm 0.4$	$0.4 \pm 0.2$	$1.2 \pm 0.6$	$11 \pm 3$	$0.50 \pm 0.07$	$13.6 \pm 0.4$
Kidney	<0.05	$1.20 \pm 0.02$	$3.0 \pm 0.3$	$28.3 \pm 0.3$	$3.10 \pm 0.02$	$26 \pm 4$
Bone	$0.3 \pm 0.3$	<0.1	$12.6 \pm 0.4$	$2.63 \pm 0.03$	$11 \pm 2$	$1.5 \pm 0.8$
Excrements	$5.0 \pm 1.1$	$4.5 \pm 0.7$	$369 \pm 26$	$230 \pm 3$	$176 \pm 16$	$112 \pm 21$

Our results agree with Beddow et al. [32], who suggested that Hg and Pb distribute primarily into phosphogypsum and thus do not reach the final phosphate products (DCP). Other studies report that Al, Fe and Mg, together with P, F and Si, are also found in the phosphogypsum, especially when the phosphate rock has a sedimentary origin [6]. As a matter of fact, heavy metals are presumed to be stabilised and encapsulated in calcium sulphate and calcium hydroxyapatite [32]. Therefore phosphogypsum displays higher relative and absolute concentrations of metals contained in the mobile fraction than phosphate rock [34,35].

When phosphate rock is treated with hydrochloric acid even lower values of Mg, Fe and Al are found in group A samples compared to group B. This is in agreement with El-Shall and Abdel-Aal [36], who reported that as much as 89% of Mg, Fe and Al are eliminated during its co-precipitation with calcium fluoride.

Overall, the wet acid digestion of the phosphate rock using either hydrochloric acid or sulphuric acid explains the different elemental distributions between groups A and B. However, differences in metal concentrations of group C (meant for human consumption) were a result of Spanish law RD 465/2003 [37] (transposed from 2002/32 CE Directive [38]) and JECFA [39]. The stricter limits for As, Cd, Hg and Pb in human foodstuff additives therefore requires better purification of the final P products, thus leading to even further reduced radionuclide activities.

#### 4.4. Radiological risk assessment due to DCP consumption

A radiological risk assessment was conducted to estimate the dose that humans would receive due to the ingestion of poultry meat (in particular chicken meat) previously fed with certain quantities of DCP in their diets.

Three different diets were prepared with different contents of TCP and DCP. Diet I was used as a blank, and had only 2.5% TCP by weight (sample 13); Diet II had fodder with 5% DCP by weight, of DCP characteristic of group A samples; and Diet III contained a 2.5% DCP by weight of group A, again, similar to group A. It is important to note that typical percentages of DCP in poultry fodder are around 1.4%. Three groups of 9 chickens were divided into 9 cages (3 chickens in each cage) and fed over 2 weeks with the three different diets (Diets I, II and III). A total of 48 samples were collected, freeze-dried and analyzed. For each diet, samples were divided into the following: 3 samples of whole chicken; 2 pools of 6 samples of thigh, breast, bone, liver and kidneys (each pool corresponding to one cage); and 3 excreta samples corresponding to the 3 cages. Lead-210 and  $^{210}\text{Po}$  were chosen to analyze in all samples, since they are the two radionuclides of the  $^{238}\text{U}$  decay series that mostly contribute to radioactive exposure, or dose, by ingestion. Their high effective dose coefficients ( $h(g)$ ) of  $6.9 \times 10^{-7} \text{ Sv Bq}^{-1}$  (for  $^{210}\text{Pb}$ ) and  $1.2 \times 10^{-6} \text{ Sv Bq}^{-1}$  (for  $^{210}\text{Po}$ ), result in relative effective doses of 19 and 63% of the nuclides within the  $^{238}\text{U}$  decay series, assuming secular equilibrium [40].

The specific concentrations in chicken fodders were 1, 101 and 51  $\text{Bq kg}^{-1}$  for  $^{210}\text{Pb}$  and 0.9, 74 and 37  $\text{Bq kg}^{-1}$  for  $^{210}\text{Po}$  in Diets

I, II and III, respectively (Table 6). Results clearly show that most  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  is eliminated through animal excreta and only a small fraction is accumulated in the edible parts (breast and thigh). Observable concentrations of  $^{210}\text{Pb}$  were only determined in bones, while only slightly enhanced activities of  $^{210}\text{Po}$  were measured in liver and kidneys. Our results agree with Linsalata [41] who reported values of  $16.7 \text{ mBq kg}^{-1}$  (fresh weight, corresponding to  $\sim 0.06 \text{ Bq kg}^{-1}$  dry weight) of  $^{210}\text{Pb}$  in poultry muscle. Results were also similar to the ones reported in UNSCEAR [40] as reference values of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in food.

From the obtained concentrations in chicken, the dose to human could be calculated as [42]:

$$E = M \cdot C \cdot h(g) \quad (1)$$

where  $M$  is the annual average quantity of poultry meat consumed per person in Catalonia, Spain (25 kg wet weight) [43],  $C$  is the specific concentration of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in edible parts as determined in this work ( $\text{Bq kg}^{-1}$  dry weight) and  $h(g)$  refers to the effective dose coefficients for  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  ( $\text{Sv Bq}^{-1}$ ) [44].

Calculated annual radiological doses due to ingestion of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in chicken meat previously fed with Diets I, II and III were:  $2 \pm 2$ ,  $11 \pm 2$  and  $9.4 \pm 0.3 \mu\text{Sv y}^{-1}$ , respectively (Table 7). These doses are negligible compared to the average dose of  $2400 \mu\text{Sv y}^{-1}$  received per person due to natural sources (surface soils, air, food and water supplies). Izak-Biran et al. [8] estimated the dose to human from chicken consumption is about  $40 \mu\text{Sv y}^{-1}$ . This larger dose compared to our estimate relies on the fact that they assumed similar activities of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the breast and thighs of chicken, while in the present paper it is shown that  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  were not in equilibrium in poultry meat. Our estimates were also lower than Arruda-Neto et al. [9], who assumed that 2% of DCP containing 200 ppm of  $^{238}\text{U}$  was included in chicken diet. However, theoretical assumptions were made to predict the uranium food-to-animal transfer, which resulted in activities of  $8.68 \text{ Bq kg}^{-1}$  of  $^{238}\text{U}$  in poultry meat. This lead to a much higher annual dose ( $\sim 0.5 \text{ mSv y}^{-1}$  per person). In the present study,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  were specifically determined in DCP samples as well as in chicken tissues, allowing us to predict a more realistic dose to humans.

**Table 7**

Annual dose to a Catalan adult through the ingestion of chicken fed with fodder containing different types and concentrations of DCP or TCP. Concentrations of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  are the main values obtained from their accumulation in breast and thigh (see Table 6). The annual chicken meat consumption is 25 kg per person. See text for details.

Diet	Radionuclide	Dose ( $\mu\text{Sv y}^{-1}$ )	Total dose ( $\mu\text{Sv y}^{-1}$ )
TCP 2.5%	$^{210}\text{Pb}$	$1.6 \pm 2.3$	$2 \pm 2$
	$^{210}\text{Po}$	$0.6 \pm 0.9$	
DCP 5%	$^{210}\text{Pb}$	$0.4 \pm 0.5$	$11 \pm 2$
	$^{210}\text{Po}$	$11 \pm 2$	
DCP 2.5%	$^{210}\text{Pb}$	$1.2 \pm 0.2$	$9.4 \pm 0.3$
	$^{210}\text{Po}$	$8.2 \pm 0.3$	



## 5. Conclusions

The concentrations of the naturally occurring  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{232}\text{Th}$  decay series in DCP and TCP samples indicated that the radioactive equilibrium in the phosphate rock was disrupted during industrial chemical processing. Samples corresponding to TCP used in human additives were characterized by low radioactivities ( $<50\text{ Bq kg}^{-1}$  of the analyzed radionuclides). Samples of DCP used for animal consumption contained higher activities, and were classified into two sub groups. Group A samples were characterized by low  $^{230}\text{Th}$  activities ( $<150\text{ Bq kg}^{-1}$ ), but high activities of  $^{210}\text{Pb}$  ( $\sim 2 \times 10^3\text{ Bq kg}^{-1}$ ),  $^{210}\text{Po}$  ( $\sim 800\text{ Bq kg}^{-1}$ ) and slightly elevated values of  $^{226}\text{Ra}$  ( $10^2\text{ Bq kg}^{-1}$ ). In contrast, samples from group B had high activities of  $^{230}\text{Th}$  ( $10^3\text{ Bq kg}^{-1}$ ) but low activities of  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  ( $<30\text{ Bq kg}^{-1}$ ). These differences were due to the chemical behaviour of the various elements during the production process: group A samples were produced by wet-acid digestion of the phosphate rock via hydrochloric acid, whereas group B samples were obtained through phosphate rock digestion with sulphuric acid. The two different chemical processes for the production of the DCP samples are corroborated through the analysis of metal concentrations. Whereas hydrochloric acid digestion lead to high Pb and As concentrations in the final product, the sulphuric acid treatment of the rock generally produced high concentrations of Cd and others (Mg, Al, Fe, Cr). The legal limits for Hg, Cd, Pb and As in food additives for human consumption (i.e. TCP) required further purification that in turns lead to lower concentrations of radionuclides from the  $^{238}\text{U}$  decay chain in these sample types.

Our experiments with poultry fed with different contents of DCP and TCP allowed us to determine the degree of accumulation of radionuclides in chicken tissues. The estimated dose to humans via consumption of chicken meat ranged between 2 and  $11\ \mu\text{Sv y}^{-1}$ , suggesting the absence of any actual radiological risk to man associated with the consumption of radioactive containing DCP fed to animals.

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