Fluxes of the ^{238}U-Series Isotopes in the Industrial Production of Dicalcium Phosphate and the Radiological Impact due to the Incorporation to Poultry Diets

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INTRODUCTION

Phosphate rock is used as a source for the production of feed supplements, such as in the form of dicalcium phosphate (DCP), which is a supply of calcium and phosphorus for domestic animals. Due to the replacement of calcium by uranium in the apatite structure during the formation of sedimentary phosphate rocks, elevated quantities of ^{238}U and its decay chain daughters ($>10^3$ Bq·kg^{-1}) are found in this geological formation (Guilbert and Park, 1986). This is the case of Morocco and Florida ores, both being used as raw materials in the phosphate industry (UNSCEAR, 1988). Phosphate rock is normally wet-acid digested with either sulphuric acid (H_2SO_4) or hydrochloric acid (HCl). The former one is by far the most widespread and leads to phosphate acid as the main product and phosphogypsum as a by-product; whereas the later is used to directly obtain dicalcium phosphate as a final product (Gäfvert, 2002). It is well known that the various members of the ^{238}U decay chain series, including ^{238}U, ^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po, are in approximate radioactive equilibrium in phosphate rock and no disruption occurs but if chemical partitioning (Menzel, 1968; Roessler *et al.*, 1979; Metzger *et al.*, 1980). However, during the wet acid process, the radioactive equilibrium between the Uranium-series radionuclides is broken and may be partitioned into various phases according to their solubility, thus as a function of other variables (i.e pH, temperature, red-ox conditions). Therefore, potential accumulation of some of them in the final product, by-products and/or wastes is to be expected, largely depending on the processes of industrial production. The presence of Naturally Occurring Radioactive Materials (NORM) in the products and by-products of the phosphate industry may somehow increase the potential for exposure to population through either the ingestion of chicken previously fed with food containing some dicalcium phosphate as an additive or the exposure to wastes highly enhanced with ^{238}U decay chain radionuclides. Of major concern are the radionuclides ^{210}Pb and ^{210}Po, since they would contribute the most in radiological dose due to ingestion. At present time, implementation of regulation at national level is not yet in place. Therefore, we carried out a comprehensive study aiming to evaluate: i) the concentration of radionuclides of the ^{238}U -series in DCP samples in Spain; ii) the fate of the radionuclides during the production process via wet acid digestion; and iii) the accumulation of radiologically relevant isotopes in chicken fed with certain quantities of DCP and the potential radiological impact to humans by ingestion.

MATERIALS AND METHODS

Samples

Analysed material consisted on DCP samples and industrial products and by-products, as well as chicken tissues and excrements.

Dicalcium phosphate
16 DCP samples for both animal and human consumption commercialized in Catalonia during the first semester of 2006 were analysed. Gathering of the samples was carried out by the *Agència Catalana de Seguretat Alimentària.*

DCP production process
22 samples in the DCP production process where collected and analyzed. Samples include the raw material, the solid and liquid wastes produced during the treatment of the rock and the middle-step products.

Chicken tissues
42 chickens gathered in three groups were fed with three different diets. Diet A included a 2.5% of DCP for human consumption (<10 Bq·kg^{-1} of ^{210}Pb and ^{210}Po); diets B and C included DCP for animal consumption (with $\sim 2 \cdot 10^3$ Bq·kg^{-1} of ^{210}Pb and ^{210}Po) at 5% and 2.5% respectively. After 21 days chickens were slaughtered and representative samples of breast, thigh, kidneys, liver and bones were collected and ice-dried. Excrements were also periodically collected to evaluate the radionuclide output fluxes.

Sample quantification

Alpha and gamma spectrometry techniques were used to quantify **non-organic samples**. For **organic samples**, only ^{210}Pb and ^{210}Po were analyzed.

Uranium and thorium isotopes and ^{210}Pb and ^{210}Po were quantified through alpha spectrometry after radiochemical purification (Martinez-Aguirre et al., 1997; Sanchez-Cabeza *et al.*, 1998). **For the pair ^{210}Pb-^{210}Po, polonium is the isotope that is actually measured,** and concentrations of ^{210}Pb at sampling time are calculated by using appropriate ingrowth and decay corrections.

Concentrations of ^{226}Ra and ^{40}K were determined by using a coaxial HPGe detector (GMX. EG&G Ortec) equipped with an iron, copper and lead shielding. For radionuclide quantification in DCP samples, between 500 and 1000 g of dry homogenized sample were placed into a 500 cm^3 Marinelli geometry. The rest of inorganic samples were placed in a 100 cm^3 geometry. Geometries were sealed and stored for three weeks before its quantification to reach secular equilibrium between ^{226}Ra and its short-lived daughters.

Data analysis

A hierarchical cluster analysis of the data was carried out using SPSS 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 are used to assess the cohesiveness of the clusters formed and provide information about the appropriate number of clusters.

RESULTS AND CONCLUSIONS

Dicalcium phosphate

A hierarchical cluster analysis (Figure 1) of the ^{238}U and its decay chain daughter's concentrations resulted in three different groups of DCP samples, named as group A, B and C. Variables considered for the sample clustering are specific concentrations of ^{238}U (^{234}Th), ^{226}Ra, ^{210}Pb and ^{210}Po.
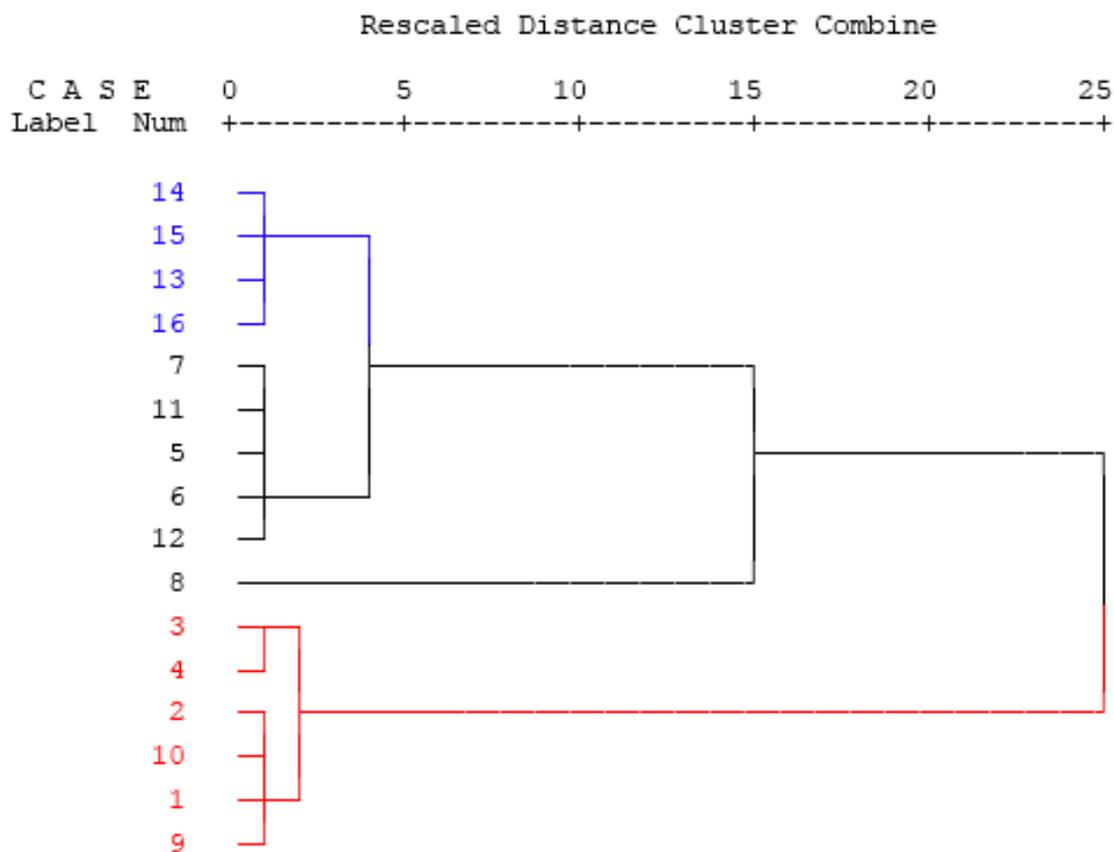
Figure 1: Hierarchical cluster analysis of DCP samples for human and animal consumption. Variables considered are specific concentrations of ^{238}U (^{234}Th), ^{226}Ra, ^{210}Pb and ^{210}Po.

Group A (samples #1, #2, #3, #4, #9 and #10) corresponded to samples with high concentrations of ^{238}U (~1000 Bq·kg^{-1}), ^{226}Ra (~100 Bq·kg^{-1}), ^{210}Pb (2000 Bq·kg^{-1}) and ^{210}Po (800 Bq·kg^{-1}). Group B (samples #5, #6, #7, #8, #11 and #12) was characterized by high concentrations of ^{238}U (1000 Bq·kg^{-1}) and ^{230}Th (~1000 Bq·kg^{-1}) but rather low values of ^{210}Pb and ^{210}Po (< 30 Bq·kg^{-1}). Finally, group C (samples #13, #14, #15 and #16) had very low values of all ^{238}U decay chain daughters (<50 Bq·kg^{-1}). Indeed, samples of Group C consisted of MCP for human consumption. Regarding group A and B, in all cases were DCP samples for animal consumption, and differences between both groups rely on the chemical partitioning of ^{238}U elements due to different chemical behaviours when the phosphate rock is digested with hydrochloric acid or sulphuric acid. Whereas uranium radioisotopes are generally soluble (90-95%) in any acid, thorium, radium, lead and polonium might behave differently. Thorium is soluble both in hydrochloric acid and sulphuric acid but its high affinity for particulate and colloid surfaces leads to a thorium reduction in the DCP when rock is digested via hydrochloric acid. During this process thorium complexes with fluoride ions forming ThF$_4$ and eventually co-precipitate with the CaF$_2$ in the slag (Gäfvert *et al.*, 2001). On the contrary, when using sulphuric acid, thorium might remain in the phosphoric acid and is finally precipitated to the final product, DCP (Saueia and Mazzilli, 2006). Radium might be less present in samples processed via sulphuric acid since it precipitates together with the phosphogypsum and is eliminated in a proportion of 90 to 100% (Rutherford *et al.*, 1994). In samples processed via hydrochloric acid, ^{226}Ra might precipitate in the sludge with one of the reaction products (CaF$_2$) in the form of RaF$_2$, whereas another fraction remains in solution in the form of RaCl$_2$ (Gäfvert *et al.*, 2001). However, still a little fraction of ^{226}Ra might be present in DCP. Lead dissolves in concentrated HCl, forming a PbCl$_4^{2-}$ complex precipitating with DCP, but it precipitates in a 90-100% together with phosphogypsum if phosphate rock is digested with sulphuric acid (Hull and Burnett, 1996). Po-210 co-precipitates either with the Mg(OH)$_2$ when the raw material is processed via hydrochloric acid, or with the phosphogypsum if treated with sulphuric acid. (Hull and Burnett, 1996). Therefore, most of the ^{210}Po found in DCP is derived from the ^{210}Pb decay, although not having yet reached the secular equilibrium at the time of analysis. This lead to the conclusion that Group A samples might correspond to samples produced through the hydrochloric acid digestion of the phosphate rock, whereas group B samples might be produced after digestion of the rock with sulphuric acid.

Dicalcium Phosphate production process

To more accurately quantify the radionuclide partitioning in a factory in Spain, where phosphate rock is wet acid digested with hydrochloric acid (type group A samples), ^{238}U-series radionuclides are being studied during the DCP industrial process. These are of major concern in terms of radiological impact to population due to the relatively high contents of two of the radionuclides that might pose a relevant dose due to its ingestion (i.e. ^{210}Pb and ^{210}Po). Moreover, it is of our interest to quantify radionuclides content in by-products that eventually could be of radiological relevance in terms of external exposure to workers an/or population. The phosphate rock is imported from Morocco, initially accounting for 1625±32 Bq·kg^{-1} of ^{238}U; 1511±14 Bq·kg^{-1} of ^{226}Ra, 1714±156 Bq·kg^{-1} of ^{210}Pb and 1748±56 Bq·kg^{-1} of ^{210}Po. The secular equilibrium prevailing in the phosphate rock is already disrupted once the rock is digested with hydrochloric acid. In terms of radionuclide fluxes, in a normal daily production of 300 Tm of DCP, lead clearly follows the DCP production line, whereas thorium and polonium are eliminated together with the sludges. In terms of radionuclide specific concentrations, accumulation of noticeable levels of some ^{238}U -series radionuclides is observed in several by-products such as muds (i.e. ~10^4 Bq·kg^{-1} dw of both ^{230}Th and ^{210}Po) as well as in the final

product, DCP (1530±25 Bq·kg^{-1} of ^{238}U and 1940±141 Bq·kg^{-1} of ^{210}Pb).

Results are comparable to those reported by Gäfvert *et al.* (2001), who found 99% of the ^{230}Th that enters the process is found in the sludge due to the high affinity for particulate or colloid surfaces and more than 60% is of ^{238}U is measured in the final product. On the contrary, their study reported that lead was more uniformly distributed between the various products and wastes and that 30% of the ^{210}Po was coprecipitated with the DCP. This might be due slightly differences between both production processes.

Future regulations foreseen to be mandatory by 2009 in Spain shall allow making educated decisions on the need and/or convenience of adapting the production process to minimize the levels of specific radionuclides in both liquid and solid wastes. At present, liquid wastes are discharged to a major river, while muds are stored in a solid waste facility.

Accumulation in chicken tissues

Given the radionuclide contents in DCP, concern refers to ^{210}Po and, to a lesser extern, ^{210}Pb as they are the radionuclides which mostly contribute to human dose through ingestion Therefore, specific concentrations of both radionuclides were determined in kidneys, liver, bones, thigh, breast and excrements of 21 days age farm chickens. Specific concentrations in dry weight (dw) in chicken fed with diet B were slightly higher in liver (1.2 ± 0.6 and 11.0 ± 2.9 Bq·kg^{-1} for ^{210}Pb and ^{210}Po, respectively) and kidneys (3.0 ± 0.3 and 28.3 ± 0.3 Bq·kg^{-1} for ^{210}Pb and ^{210}Po, respectively). Accumulation of ^{210}Pb and ^{210}Po in edible parts (breast and thigh) was very low (<0.5 Bq·kg^{-1} for ^{210}Pb and ~1 Bq·kg^{-1} for ^{210}Po). However, most (98-99%) of the ingested radionuclides were found in chicken excrements, agreeing with Reid *et al.* (1977) which obtained a similar response in their study of uranium intake by poultry. It must be noted that specific concentrations of ^{210}Pb and ^{210}Po in chicken tissues were proportional to the intaken quantity depending on their diet. Whereas diet B lead to doubled specific concentrations in chicken tissues than diet C; animals fed with diet A hardly accumulated any (<1 Bq·kg^{-1} dw).

Having determined radionuclide contents in chicken tissues, estimated doses to humans due to poultry meat ingestion are obtained through the following formula:

$$E = M \cdot \sum_j C_j \cdot h(g)_j \cdot f_j$$

where *M* is the chicken meat consumed annually by humans in dw, *C* the concentrations of ^{210}Pb and ^{210}Po in Bq·kg^{-1} dw, *h(g)* the committed effective dose per unit intake and *f* the fractional nuclide absorption to human body. Total dose due to ingestion of chicken meat is the sum of doses due to both, ^{210}Pb and ^{210}Po intake.

Table 1: Estimation of the annual dose to an adult through the ingestion of poultry meat fed with different types of dicalcium phosphate. Concentrations of ^{210}Pb and ^{210}Po are the average values in breast and thigh. The annual chicken meat consumption is 25 kg per person (7.5 kg dw).

Diet	Radionuclide	M (Bq·kg⁻¹)	C (Bq·kg⁻¹)			h(g) (Sv·Bq⁻¹)	f	Dose (μSv·y⁻¹)			Total dose (μSv·y⁻¹)		
A	^{210}Pb		0.31	±	0.44	$6.90 \cdot 10^{-07}$	0.2	0.32	±	0.45	0.6	±	1.7
	^{210}Po		0.07	±	0.37	$1.20 \cdot 10^{-06}$	0.5	0.31	±	1.68			
B	^{210}Pb	7.5	0.07	±	0.10	$6.90 \cdot 10^{-07}$	0.2	0.08	±	0.11	5.5	±	1.0
	^{210}Po		1.20	±	0.23	$1.20 \cdot 10^{-06}$	0.5	5.41	±	1.02			
C	^{210}Pb		0.23	±	0.01	$6.90 \cdot 10^{-07}$	0.2	0.24	±	0.01	4.3	±	0.1
	^{210}Po		0.91	±	0.03	$1.20 \cdot 10^{-06}$	0.5	4.09	±	0.12			

Results shown in Table 1 underscore the higher contribution of ^{210}Po (>90%) due to chicken meat ingestion other than ^{210}Pb. It furthermore highlights that even in animals fed with 5% in weight of DCP with relatively high concentrations of ^{210}Pb and ^{210}Po in their diets (~$2 \cdot 10^3$ Bq·kg⁻¹ and 10^3 Bq·kg⁻¹, respectively), the dose to human would not exceed 5.5 μSv·y⁻¹. In a similar study, Izak-Biran *et al.* (1989) reported a dose per person of 0.04 mSv·y⁻¹ assuming that ^{210}Pb and ^{210}Po were in equilibrium in chicken meat. To the contrary, the present study shows that assimilation of ^{210}Pb and ^{210}Po to the chicken tissues is different. A final conclusion is that although the calculated dose of 5.5 μSv·y⁻¹ would be larger than when DCP is virtually free of radionuclides, it however points to the absence of actual radiological risk to man associated to the consumption of current DCP as an additive in food for animals.

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