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Determination of ^{210}Po in calcium supplements and the possible related dose assessment to the consumers

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A B S T R A C T

The aim of this pioneer study was to investigate the most popular calcium supplements as a potential additional source of polonium ^{210}Po in human diet. The analyzed calcium pharmaceutics contained organic or inorganic calcium compounds; some from natural sources as mussels' shells, fish extracts, or sedimentary rocks. The objectives of this research were to investigate the naturally occurring ^{210}Po activity concentrations in calcium supplements, find the correlations between ^{210}Po concentration in medicament and calcium chemical form, and calculate the effective radiation dose connected to analyzed calcium supplement consumption.

As results showed, ^{210}Po concentrations in natural origin calcium supplements (especially sedimentary rocks) were higher than the other analyzed. Also the results of ^{210}Po analysis obtained for inorganic forms of calcium supplements were higher. The highest ^{210}Po activity concentrations were determined in mineral tablets made from sedimentary rocks: dolomite and chalk – 3.88 ± 0.22 and 3.36 ± 0.10 mBq g^{-1} respectively; while the lowest in organic calcium compounds: calcium lactate and calcium gluconate – 0.07 ± 0.02 and 0.17 ± 0.01 mBq g^{-1}.

The annual effective radiation doses from supplements intake were estimated as well. The highest annual radiation dose from ^{210}Po taken with 1 tablet of calcium supplement per day was connected to sample made from chalk – 2.5 ± 0.07 μSv $year^{-1}$, while the highest annual radiation dose from ^{210}Po taken with 1 g of pure calcium per day was connected to dolomite – 12.7 ± 0.70 μSv $year^{-1}$.

1. Introduction

Polonium-210 is a radio-ecologically interesting natural element to investigate due to its high radiotoxic characteristics. It appears at the end of the decay-chain of Uranium-238 where the long lived Lead-210 (22.3 years) decays to Bismuth-210, and finally Polonium-210. This radionuclide is introduced into the biosphere through various routes of terrestrial and marine radioecological pathways and as an α-emitter, is an important component of Man's natural radiation background (Persson and Holm, 2011). Among alpha radioactive elements occurring in the environment, polonium plays an important role because ^{210}Po belongs to the most radiotoxic nuclides to human beings. It has a relatively long half-life time ($T_{1/2} = 138.376$ days) and high specific activity (1.66×10^{14} Bq g^{-1}) (Heiserman, 1997). Although the melting point of polonium is 254 °C and its boiling point is 962 °C, Po generally evaporates at much lower temperatures. About 50% of it is vaporized at 50 °C and become airborne within 45 h as a radioactive aerosol (Gjelsvik et al., 2012; Henricsson and Persson, 2012). This radioactive element is, together with radon, the natural radioactive material delivering the highest natural dose to living organisms (Holm et al., 2010). ^{210}Po is not dangerous in the environment per se, but is toxic if actually taken into the body (Donaldson, 2006).

Atmospheric fallout of ^{210}Po results in the contamination of plants and the top layer of soil (Henricsson and Persson, 2012). Most of the natural radioactivity content in wild leafy plants is ^{210}Po as the result of the direct deposition of ^{222}Rn daughters from atmospheric precipitation (Hill, 1960; Persson and Holm, 2011). Thus ^{210}Po in soils may originate either as a product of the radioactive decay of radionuclides of ^{238}U series present in the soil (supported) or the result of the precipitation of radon decay products from the atmosphere (unsupported) (Henricsson and Persson, 2012). Atmospheric deposition is also the main source of ^{210}Po in the ocean waters; t There are, however, only minor latitudinal or temporal gradients (Aarkrog et al., 1997; Carvalho, 2011). Uptake of cationic ^{210}Po onto particles (fractionated towards organic phases) and into

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phyto- and zooplankton results in removal of ^{210}Po from the more productive, shallower marine regions (Fowler, 2011). The concentrations of ^{210}Po in marine biota are related to species rather than to geographical regions. Typical activity concentration values for species within the larger groups of fish are in the order of 2.4–220 Bq kg^{-1} wet, for molluscs and crustacean the corresponding values of ^{210}Po concentrations are 13–152 Bq kg^{-1} wet and 6–96 Bq kg^{-1} wet respectively (Aarkrog et al., 1997; Stepnowski and Skwarzec, 2000; Raja and Hameed, 2010; Carvalho, 2011; Strok and Smodis, 2011).

Polonium is transferred to man mainly by dietary intake and much less by inhalation of contaminated aerosols. The fraction of polonium taken up is 20–80% (Henricsson et al., 2012). ^{210}Po ingested with food contributes significantly to the internal radiation dose to man. The data on its concentrations in daily foods showed their concentrations depend on the climate, geological- and agricultural conditions (Henricsson and Persson, 2012). Accumulations of ^{210}Po in marine food chains contribute considerably more (about 80%) to the total ^{210}Po ingestion than food of terrestrial origin (Carvalho, 1995; Skwarzec, 1997; Strok and Smodis, 2011); for example, the annual effective ingestion doses due to ^{210}Po in fish were: 0.75 μSv year^{-1} in Syria, 18.63 μSv year^{-1} in Poland, 19.44 μSv year^{-1} in India, 32.82 μSv year^{-1} in Slovenia, 50 μSv year^{-1} in Japan, 24–77 μSv year^{-1} in Lebanon and 117 μSv year^{-1} in Portugal (Carvalho, 1995; Pietrzak-Flis et al., 1997; Strok and Smodic, 2011; Henricsson and Persson, 2012; Aoun et al., 2015).

Calcium is one of the most essential elements in living organisms, especially vertebrates; the most abundant metal by mass in many animals; used in mineralization of bone, teeth and shells, very important in cell physiology. Adult human body contains about 1.2 kg of Ca and 99% of this amount is located in bones and teeth (Ziółko, 2006). Long-term calcium deficiency can lead to rickets and poor blood clotting, affect bone and tooth formation; while over-retention can cause hypercalcemia, impaired kidney function and decreased absorption of other minerals (Ross et al., 2011). Recommendations of Dietary Reference Intakes for calcium are: children – 0.8–1.2 g, adults – 1 g, pregnant – 1.2–1.5 g, postmenopausal – 1.5 g, over 65 years old – 1.2–1.5 g (Ross et al., 2011). Some research showed much lower calcium intake (540–619 mg) among Polish inhabitants that covered 58–60% of the recommended values (Dybkowska et al., 2004). Thus calcium has become extremely popular to supplement, especially amongst older women, in the hope that it will prevent osteoporosis, a serious condition affecting at least 30% of Polish women and 8% of men after 50 years of age (Czerwiński et al., 2015). Media are full of calcium compounds adverts what leads to uncontrolled calcium consumption. New research showed Ca supplementation can have a small effect in improving bone mineral density. This is of no meaningful benefit to health in children, but in women the risk of vertebral fractures may be reduced (Shea et al., 2004; Winzenberg et al., 2006). Several sources suggested a correlation between high calcium intake (2 g per day) and prostate cancer (Giovanucci et al., 1998). Excessive consumption of calcium carbonate antacids/dietary supplements over a period of weeks/months can cause symptoms ranging from hypercalcemia to fatal renal failure (Beall et al., 2006). The other fact is excessive calcium supplementation can be detrimental to cardiovascular health, especially in men (Michaëlsson et al., 2013; Xiao et al., 2013).

The idea behind this study was to investigate ^{210}Po activity concentrations in popular calcium supplements in Poland. It was completely new examination of food additives. Geological material is rich of uranium, ^{210}Po as its daughter product widely occurs in the environment. Some marine organisms are rich in polonium. And some questions occurred. How much polonium do calcium supplements contain? Are natural origin calcium supplements richer in ^{210}Po in comparison to highly processed supplements? If yes, are calcium supplements of natural origin a potential source of polonium? Are inorganic calcium compounds richer in Po than organic? What is the annual effective radiation dose from ^{210}Po consumed with calcium supplements? Which supplements are safer in case of potential annual effective radiation dose from ^{210}Po? Is there any risk of increase of annual effective radiation dose connected to calcium supplements consumption connected to ^{210}Po?

2. Materials and methods

In this study, 17 different calcium supplements available in Poland were analyzed. These calcium pharmaceutics were bought in commercial pharmacies and contained different organic or inorganic calcium compounds. Some of them were, as described by their producers, natural origin: mussels' shells, mineral fish extracts, or sedimentary rocks. Analyzed samples were from 4 to 35 g and contained from 375 to 6000 mg of pure elementary Ca (Table 1).

The polonium analysis covered the samples mineralization, electrodeposition and ^{210}Po activity measurements (Skwarzec, 1995, 2010). From each analyzed compound 3 subsamples were prepared and before radiochemical analysis, to each 10 mBq of ^{209}Po was added as a yield tracer. Further, 65% HNO_3 was added and the samples were kept cold for 3 days. Then they were slowly warmed until the HNO_3 was completely decomposed and evaporated (about 1 week). Further 35% HCl were added and the samples were warmed again. At this stage, if necessary, only concentrated HCl was added to remove carbonates (on the basis of the supplement composition) and change insoluble calcium carbonate into soluble calcium chloride. Whole procedure took about 3 weeks. When the light clear solvent solution was reached, the samples were ready for polonium electrodeposition that took 4 h at 90 °C on silver discs (Skwarzec, 1995, 2010). The activities of polonium isotopes (^{209}Po and ^{210}Po) were measured in alpha spectrometer (Alpha Analyst S470, Canberra-Packard). Activity measurement of a single sample took 1–3 days and ^{210}Po activities in analyzed samples were corrected for decay to the day of polonium electrodeposition (time of separation ^{210}Po from ^{210}Pb). The results showed, the subsamples were homogenous and the differences among ^{210}Po activities in every compound subsamples were less than 4%.

The accuracy and precision of the radiochemical method were evaluated using IAEA reference materials (IAEA-384, IAEA-385, IAEA-414) and estimated at less than 4%. The polonium yield in the analyzed samples of calcium supplements ranged from 90 to 99%. The results of ^{210}Po concentration were given with standard deviation (SD) calculated for 95% confidence intervals. Statistic tests showed there was positively skewed non-normal distribution of the data and the results showed statistically significant differences. That is why all statistical procedures were based on non-parametric tests, mainly U-test (Mann–Whitney) (Mazerski, 2009).

3. Results and discussion

3.1. Activity concentrations in calcium supplements

The results of ^{210}Po analysis in calcium supplements were much differentiated and the average values of ^{210}Po activity concentrations were presented in Table 1. The highest ^{210}Po activity concentrations were measured in mineral tablets made from sedimentary rocks, sample Ca7 (dolomite) and sample Ca16 (chalk) – 3.88 ± 0.22 and 3.36 ± 0.10 mBq g^{-1} respectively. The lowest ^{210}Po activities were determined in organic calcium compounds,