^{210}Po IN THE DIET AT SEVILLE (SPAIN) AND ITS CONTRIBUTION TO THE DOSE BY INGESTION

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The activity concentrations of ^{210}Po have been determined in a total of 24 representative diet samples from Seville (south of Spain), inferring from the obtained values the annual intakes of ^{210}Po by ingestion of the affected population and the corresponding committed effective doses. The annual intakes of ^{210}Po and, consequently, the corresponding doses of this radionuclide show a high variability in correspondence with the variability in the composition of the analysed samples over time, and their magnitude is comparable with the estimated ones in other regions/countries of the world with similar diet habits (countries where the marine products have a considerable weight in the diets). Committed effective doses by ingestion higher than 0.1 mSv y^{-1} have been estimated exclusively for ^{210}Po , reflecting the importance of this radionuclide and this route of incorporation in the magnitude of the total doses received by the affected population from natural sources.

INTRODUCTION

Consumption of food is usually the most important route by which natural and artificial radionuclides can enter into the human body. An assessment of radionuclide levels in different foods and diets is therefore important to estimate the intake of radionuclides by man.

A large fraction of the radiation exposure experienced by individuals through ingestion of food is from the naturally occurring radionuclide ^{210}Po ⁽¹⁾, which is one of the most radiotoxic natural radioactive isotopes known by man due to its high specific activity and its emission of high linear energy transfer (LET) alpha radiation⁽²⁾. ^{210}Pb ($T_{1/2} = 22.3 \text{ y}$) is the parent nuclide of ^{210}Po and is formed by the decay of radon (^{222}Rn) in the uranium series. Radon gas exists in atmospheric air, originated from exhalation from the ground, and moves with continental air masses, being its formed daughters (e.g. ^{210}Pb and ^{210}Po) wet and dry deposited onto terrestrial surface (vegetation, soils, waters) and surface of the seas where they can be incorporated into the food chain. Hence, man is exposed to radioactive polonium by natural processes, mainly from the oral intake of foodstuff.

United Nations Scientific Committee on the Effect of Atomic Radiation (UNSCEAR)⁽¹⁾ quotes a worldwide average annual intake of 58 Bq of ^{210}Po from the diet and a value for annual ^{210}Po intake from the typical European diet of 40 Bq . Nevertheless, the commented worldwide average value was created from many values that are on both sides of the average, being therefore not unexpected that values from one city are much different from the average reflected in the UNSCEAR report. Previous dietary studies indicate

that the intake of this radionuclide may vary considerably because of differences in concentration among classes of food in the diet composition⁽³⁾.

Particularly, it is well known that high intakes of ^{210}Po are experienced by population with diets high in seafood⁽⁴⁾. In fact, the distribution and behaviour of the alpha-emitter ^{210}Po in the marine environment have been under study for many years primarily due to its enhanced bioaccumulation, its strong affinity for binding with certain internal tissues and its importance as a contributor to the natural radiation dose received by marine biota as well as humans consuming seafood⁽⁵⁾.

Up to the knowledge of the authors, no information on the levels of this natural radionuclide exists in the diet of the Spanish population, and the assignation of the average annual value indicated by UNSCEAR can be quite inaccurate: the annual intake of ^{210}Po from the Spanish diet can be quite different (higher) because the consumption of seafood by the Spanish population is significant, particularly in comparison with other European countries. To cover partially this deficiency, in this paper, the annual intakes of ^{210}Po estimated for the population of Seville (Spain) are presented for a total of 6 years (2007–12), based on the experimental determination of the ^{210}Po activity concentrations in representative diet samples. In addition, and for comparison purposes, the annual intakes of U are also presented. On the basis of this information, the committed effective doses by ingestion of the mentioned two elements (Po and U) in the affected population are presented.

In this study, the interest was not only to evaluate the magnitude of the Po and U intakes but also to

evaluate its variability along time, because it will give an important information about the possible variability of the concentrations of these radioelements in key human compartments (blood, urine, faces) under normal conditions, and, consequently, how difficult can be the establishment of natural background values in internal dosimetric studies.

MATERIALS AND METHODS

Samples: Composition and place of collection

Representative Spanish diet samples were collected from a cafeteria/restaurant located in Seville (Spain) in the vicinity of the authors' laboratory where daily breakfast, lunch and dinner menus are offered, mainly for the university community. Every 3 months (one composite sample per 3 months, four composite samples per year), a composite diet sample was formed for a week from Monday to Friday including the breakfast (coffee/tea, toasts, fruit), the lunch (starter, main dish, beverage, bread) and the dinner (main dish and beverage) of each day, trying in this way to reproduce with certain fidelity the type and amount of food ingested by an adult during 5 days. This composite sample excludes the water and other beverages consumed out of the three main daily meals.

Immediately after the collection, the bones, skins and other non-edible parts are removed, and the composite sample is homogenised by grinding and mixing of all the materials collected. The resulting mixture is allowed to dry in an oven at 50°C for at least 1 week until it reaches the total desiccation, and the obtained product is again ground and mixed to ensure a complete homogenisation.

Initially, just before the homogenisation, the weight (wet) of each composite sample was about 7 kg, while after the homogenisation and desiccation processes, around 80 % of the initial wet weight was lost (1.5 kg dry weight per sample). Considering that the composite sample represents the expected amount of food ingested by an adult during 5 days of a week (Monday to Friday), it can be estimated a daily intake of 1.4 kg wet weight diet by the affected population.

Radiometric technique

The activity concentrations of ^{210}Po and U-isotopes in the diets have been determined by applying the high-resolution alpha-particle spectrometric technique. The application of this technique implies the previous isolation and deposition in thin layers of the radioelements of interest in order to avoid interferences in the measurements.

In particular, an alpha-particle spectrometric system, Alpha-Analyst from Canberra Co., formed of a total of eight independent chambers working in

parallel, each one equipped with a PIPS type silicon detector (450 mm² active area), has been employed. The radioelements of interest previously isolated from its original matrix are deposited forming thin layers (after the application of the radiochemical procedure detailed in the following sub-section) onto metallic disks of stainless steel in the case of U or copper in the case of Po, forming the sources to be measured.

The measurements were performed with a fixed-distance source detector of 1.2 cm, corresponding to a geometric efficiency of around 25 %. With this efficiency and for the range of radiochemical recoveries obtained for U and Po after the application of the radiochemical procedure for their isolation and conditioning for the measurements, typical minimum detectable activities in the order of 10⁻¹ mBq were reached. The software Genie 2000 (Canberra Co.) was used for the analyses of the alpha spectra.

Radiochemical procedure and sources preparation

The radiochemical procedure starts in each case by taking an amount between 1 and 4 g of the previously treated sample (homogenisation and drying) and by adding known amounts of ^{209}Po and ^{232}U . Afterwards, the sample is acid digested by using a microwave oven system, model Multiwave 3000, Anton Paars, equipped with a rotor with eight closed glasses XF100 that allow the work to be carried out under controlled pressure until 260°C without loss of any volatile element during the digestion process. With this end, 300–400 µg of each dried sample was mixed with 6 ml of 65 % nitric acid, 1 ml of oxygen peroxide and 1 ml of 37 % hydrochloric acid in separate Teflon containers, being heated in the microwave by ramping to 800 W power over 10 min and then heated at this power for 10 min. The resulting solution was transferred to a glass beaker, evaporated to 10 ml and diluted with distilled water to 50 ml.

Afterwards, the 50 ml solution is conditioned to a basic pH with ammonia after the addition of few milligrams of FeCl₃, and the formed iron hydroxide precipitate is allowed to settle overnight under mild heating. The supernatant is then discarded, and the precipitate containing the radionuclides of interest is dissolved in few millilitres of 8 M HNO₃ just before proceeding to isolate sequentially the radionuclides under study (^{210}Po and U-isotopes). This isolation process is performed by applying a liquid-liquid extraction procedure in the 8 M HNO₃ solution with TBP and xylene as it is properly detailed in ⁽⁶⁾.

Finally, and for the preparation of the sources suitable for alpha-spectrometric determinations, each liquid fraction containing the polonium and the uranium in isolated form is evaporated to near dryness and conditioned in order to proceed either with the selective self-deposition of polonium onto

copper planchets⁽⁷⁾ or with the electrodeposition of uranium onto stainless-steel planchets⁽⁸⁾.

Validation of the whole procedure

In order to validate the procedure applied for the determination of ²¹⁰Po activity concentrations in diet, the procedure has been applied for two International Atomic Energy Agency (IAEA) reference materials with similar matrix: IAEA-414 (fish muscle) and IAEA-437 (mussels).

As a validation parameter, the so-called Z-score has been used. Following the criteria applied in the different IAEA intercomparison exercises⁽⁹⁾, the measured value can be considered satisfactory if $|Z\text{-score}| \leq 2$, questionable if $2 \leq |Z\text{-score}| \leq 3$ and not satisfactory if $|Z\text{-score}| \geq 3$.

In this sense, and by observing the set of values obtained in this validation exercise (see Table 1), it can be considered that the results obtained by applying the methodology used in this work are satisfactory.

Dose calculation

From the activity concentrations determined in the four diet samples analysed per year (A_{1i} , A_{2i} , A_{3i} , A_{4i}), it is possible to obtain an average annual activity concentration of the radionuclide of interest for each year i , A_i .

Then, the annual intake of this radionuclide in the year i , AI_i , can be immediately calculated by applying the expression:

$$AI_i = A_i \times C \times T$$

where AI_i and A_i are the annual intake (Bq y^{-1}) and the average activity concentration of the radionuclide evaluated in the year i ($\text{Bq wet weight}^{-1}$), respectively; C is the amount of sample ingested per day ($C = 1.4 \text{ kg wet weight d}^{-1}$) and $T = 365 \text{ d y}^{-1}$.

The corresponding committed effective dose of the radionuclide of interest by ingestion associated to the year i , D_i , can be then easily determined through the expression:

$$D_i = AI_i \times h_{\text{ing}}$$

where h_{ing} is the committed effective dose per unit of activity of the ingested radionuclide under evaluation (Sv Bq^{-1})⁽¹⁰⁾.

In this work, the values of D_i for ²¹⁰Po and U-isotopes for the years 2007–12 have been determined based on the experimental determinations performed in quarterly representative samples collected each year.

RESULTS AND DISCUSSION

In Table 2, the ²¹⁰Po activity concentrations (mBq kg^{-1}) determined in the 24 diet samples in this study are compiled. Analysing the obtained results, it is possible to observe first that the uncertainties in the determinations performed, and arising only from the analytical and measuring method, cover a quite ample range of values, from $<3\%$ until 30% , with a high number of samples with uncertainties of 10% or higher. These uncertainties are negligible in comparison with other unquantifiable uncertainties arising from sample composition, being not unexpected that the activity concentration of ²¹⁰Po in the diet samples analysed is quite variable over time, covering a very ample range that goes from 75 to more than 5000 mBq kg^{-1} . The non-homogeneous composition among the samples analysed is the main reason for this variability. Each sample diet reflects the menus offered by the restaurant at the time of collection, which are quite variable depending on the season of the year and suffers also variations from one year to another at the same season.

A high variability was found also in the determination of ²³⁸U activity concentrations in the same diets (variations higher than one order of magnitude), for the same reasons given for polonium. However, the U activity concentrations found are clearly lower than the Po concentrations, not exceeding in any sample the value of 30 mBq kg^{-1} .

From the activity concentrations determined in the analysed samples, and by assuming a daily consumption/intake of 1.4 kg of diet (wet weight), it has been possible to estimate an average value of the ²¹⁰Po intake for the period of 2007–12, and for each year, which can be associated to the Sevillian population. These annual intake values are compiled in Table 3 and, as it can easily be observed, are also quite variable.

The ample range of values obtained for the annual intake of ²¹⁰Po by the people of south of Spain goes from 90 to 755 Bq y^{-1} (with the average value of 375 Bq y^{-1} for the 6-year period sampled), being interesting first of all to remark that in spite of the amplitude of the mentioned range, all the annual values obtained are higher than the worldwide reference average annual intake of 58 Bq of ²¹⁰Po in the diet quoted by UNSCEAR⁽¹⁾ and, in particular, all of them are higher than the value given in the same publication for the annual ²¹⁰Po intake in the typical European diet, which is of 40 Bq ; even in some cases,

Table 1. Results obtained from the validation of the radiochemical procedure applied for Po determination in organic matrixes.

Sample	Matrix	Reference value (Bq kg^{-1})	Measured value (Bq kg^{-1})	Z-score
IAEA_414	Fish	2.22 ± 0.67	2.59 ± 0.32	1.67
IAEA_437	Mussels	4.6 ± 0.9	4.1 ± 0.4	-1.07

Table 2. ^{210}Po activity concentrations (mBq kg^{-1} wet weight) in the 24 diet samples analysed.

Period of sampling	^{210}Po (mBq kg^{-1})	Period of sampling	^{210}Po (mBq kg^{-1})
1st Quarter 2007	94 ± 11	1st Quarter 2010	893 ± 47
2nd Quarter 2007	120 ± 12	2nd Quarter 2010	759 ± 43
3rd Quarter 2007	129 ± 18	3rd Quarter 2010	2038 ± 97
4th Quarter 2007	372 ± 19	4th Quarter 2010	1812 ± 79
1st Quarter 2008	5113 ± 30	1st Quarter 2011	545 ± 43
2nd Quarter 2008	180 ± 37	2nd Quarter 2011	413 ± 34
3rd Quarter 2008	203 ± 37	3rd Quarter 2011	465 ± 43
4th Quarter 2008	421 ± 25	4th Quarter 2011	1193 ± 73
1st Quarter 2009	235 ± 22	1st Quarter 2012	336 ± 43
2nd Quarter 2009	74 ± 22	2nd Quarter 2012	437 ± 57
3rd Quarter 2009	891 ± 65	3rd Quarter 2012	218 ± 17
4th Quarter 2009	615 ± 51	4th Quarter 2012	506 ± 24

Table 3. Annual ^{210}Po intakes (Bq y^{-1}) by ingestion of the population from south of Spain estimated from the analyses performed in this work.

Year	^{210}Po annual intake (Bq y^{-1})
2007	90
2008	755
2009	230
2010	670
2011	350
2012	195
Average	375

the annual intake of ^{210}Po determined is one order of magnitude higher.

The worldwide and European reference values given by UNSCEAR should be taken with precaution, in its comparison with the data obtained in the present study, because those are reflecting only average intake values. As it can be easily deduced from the data compiled in Table 4, the annual intake of ^{210}Po in different countries/regions around the world is quite variable depending on the particular characteristics of the diets in those countries/regions. This high variability is not reflected at all in the previously commented reference or average UNSCEAR values.

By analysing more in depth the data compiled in Table 4, it is possible to observe that the lower values of the annual ^{210}Po intakes are found in countries (Argentina, Brazil, former Soviet Union and UK) where the marine food plays a minor role in diets. The reference worldwide value given by UNSCEAR is in agreement with these values, reflecting a diet poor in marine compounds. On the contrary, the annual ^{210}Po intake determined in the present study is comparable with the ones found on other countries like Portugal and Japan where the marine food is an essential part of the diet. In fact, as an example, the

Table 4. Average annual ^{210}Po intakes (Bq y^{-1}) by ingestion estimated in different countries/regions over the world.

Country	^{210}Po annual intake (Bq y^{-1})	Reference
Argentina	20	(11)
Brazil	10–30	(11)
UK	30	(12)
India (vegetarian)	50	(13)
Former Soviet Union	60	(11)
Poland	20–110	(14)
Italy	125	(15)
Japan	225	(16)
Portugal	400	(17)
India (non-vegetarian)	600	(13)
Marshall Islands	800	(18)
Lappland (North Sweden)	900	(14)
North Canada	1200	(14)

determination of the annual ^{210}Po intake in the Portuguese people estimated that 67 % of the intake is associated to the ingestion of marine products⁽¹⁷⁾. The ^{210}Po activity concentrations in marine food are clearly higher than the ones found in other products with terrestrial origin (meat, vegetables, fruits, etc.), having for that reason this component of the diet an important weight in the magnitude of the annual ^{210}Po intakes associated to the population in different regions of the world.

Special mention deserves the very high ^{210}Po annual intakes determined in three outliers reflected in Table 4. The explanation of these extreme values in the case of the Marshall Islands can be related with the fact that more than 90 % of the food forming the diet in this islands have a marine origin, while in the case of the population of north Canada and Lappland, it is related with the simplicity of the food chain (lichen/mosses–reindeer–man) where a bio-accumulation of ^{210}Po occurs⁽¹⁹⁾.

Table 5. Committed effective doses by ingestion of ^{210}Po and ^{234}U ($\mu\text{Sv y}^{-1}$) estimated for two age groups (12–17 y olds and adults) of the population of south of Spain, based on the determinations performed in representative diets.

Period of sampling	^{210}Po		^{234}U	
	12–17 y olds	Adults	12–17 y olds	Adults
2007	145	110	N.M.	N.M.
2008	1210	910	0.5	0.75
2009	370	280	0.5	0.75
2010	1070	835	0.7	1.05
2011	560	400	0.2	0.3
2012	310	235	0.2	0.3

From the annual ^{210}Po and ^{238}U intakes determined in this study, it has been possible to determine the associated committed effective dose of these radionuclides by ingestion. The set of values obtained for the ^{210}Po intake by ingestion in the population aged from 12 until 17 y and adults is compiled in Table 5. The committed effective doses for the population younger than 12 y have not been calculated, because the diet samples collected from the restaurant cannot be considered representative of its intake.

By observing the data from Table 5, it is evident to conclude that for the affected adult population, the committed effective doses by ingestion of ^{210}Po are clearly higher than that of ^{238}U (in general, two orders of magnitude), in part due to higher activity concentrations found in the diets for this radionuclide, but mostly to the higher committed effective dose per unit of activity for ^{210}Po due to its radiotoxicity⁽²⁰⁾. All the determined committed effective doses by ingestion of ^{210}Po are higher than 0.1 mSv y^{-1} , and even 40 % are higher than 0.5 mSv y^{-1} . These committed effective doses cannot be considered anecdotic (for the 12–17-y-old population, the values are even a factor around 1.5 higher than for adults) and will represent a non-negligible fraction of the total dose received by the population of the south Spain through different routes (including external radiation) from natural sources. This point highlights the importance from a dosimetric point of view of the ^{210}Po incorporated into the human body from natural sources, reinforced by the fact that other ways of incorporation of this radionuclide such as the inhalation have not been taken into account in this study.

Finally, it is interesting to mention that a clear derivation of the high temporal variability observed in the intakes of ^{210}Po by the Spanish population, due to variations in the ^{210}Po content in the diet, is the variability in the amount of ^{210}Po incorporated into the human body and, consequently, in the amount of ^{210}Po that associated to key compartments like blood, urine and faeces. This last point should be taken into consideration in hypothetic emergency situations

where incorporation of anthropogenic amounts of this radionuclide can be involved, due to the difficulty to define with enough accuracy a reference or baseline level of ^{210}Po with natural origin, for example, in the urine or in the blood, which could allow the evaluation or discrimination between the natural and the anthropogenic ^{210}Po present in them⁽²¹⁾. A detailed knowledge about the diet habits of the person under study is essential to a better understanding and interpretation of the ^{210}Po levels found in compartments like urine and blood.

CONCLUSIONS

The annual intakes of ^{210}Po through ingestion by the population of Seville (Spain) has been estimated by analysing a total of 24 representative diet samples collected in the period of 2007–12. The obtained results show a high temporal variability of these intakes associated to the non-uniform composition of the diet over time, and that the magnitude of these intakes is comparable with the estimated ones in countries with similar diet habits, particularly with the countries where marine products have an important weight in the composition of the food ingested by the people. The committed effective doses associated to ingestion exclusively of ^{210}Po are higher than 0.1 mSv y^{-1} for the affected adult population, reflecting the important weight of the mentioned radionuclide and the ingestion route of the total dose received from natural sources.

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