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Determination of Natural Radionuclides (Ra-226, Pb-210, Po-210, Ra-228 and K-40) and Cs-137 in Fish Consumed in the City of São Paulo

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1. Introduction

Fish is a food rich in proteins and nutrients necessary for human health, being of excellent nutritional quality. Its consumption has increased in Brazil [1], however it can also present risks if there is any type of contamination. In the marine environment, several natural and artificial radionuclides can be discharged with varied levels of concentration.

Natural radionuclides can be enhanced in the marine environment due to the activities related to the oil, phosphate and fertilizer industries [2,3]. An example of this is ^{226}Ra and ^{228}Ra releases into the ocean in large volumes of water from the oil exploration industry [4].

The ^{137}Cs is one of the main artificial radionuclides released into the marine environment, as a result of nuclear weapon tests, nuclear reprocessing, nuclear accidents, marine dumping and river runoff [5]. The estimated atmospheric and sea discharge of this radionuclide into the environment in the accident at the Fukushima Daiichi Nuclear Power Plant was in the range of 7 to 20 PBq and 1 to 6 PBq, respectively [6].

The aim of this study is to quantify the activity concentration of the natural radionuclides (^{226}Ra, ^{210}Pb, ^{210}Po, ^{228}Ra and ^{40}K) and artificial radionuclide ^{137}Cs in the muscle of marine fish species most consumed in the city of São Paulo. The concentration of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{40}K and ^{137}Cs were measured by gamma spectrometry, using an HPGe detector; ^{210}Po was measured by alpha spectrometry.

2. Methodology

The fish samples were purchased in two supermarkets with the largest sale of fish in the city of São Paulo. The marine fish species were chosen taking into account their consumption in the city of São Paulo from the study carried out by the SOS Mata Atlântica Foundation, through the Atlantic Coast Program, which analyzed the most available fish species in different types of supermarkets [7]. The six fish species analyzed were bluefish (*pomatomus saltatrix*), tuna (*thunnus spp.*), Smooth hounds nei (*mustelus spp.)*, croaker (*argyrosomus regius*), hake (*merluccius merluccius*) and sardine (*sardina pilchardus*). About 1,100 kg of muscle from samples were dried by calcination at 450 ^{0}C resulting in about 45 g of ash, the calcination process took 48 hours per sample depending on the species. For the determination of ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{40}K and ^{137}Cs, the fish ashes were packed in polyethylene flask and sealed for about four weeks prior to the measurement, in order to ensure that equilibrium had been reached (between ^{226}Ra and its decay products of short half-life). The activity concentration of the fish samples was measured by gamma spectrometry with Hyper Pure Germanium detector HPGe, GX4020 with 47% relative efficiency with associated electronics and coupled to a microcomputer. For the determination of ^{226}Ra it is assumed that it is in equilibrium with ^{214}Pb and ^{214}Bi. Its activity is determined by the line of its ^{214}Pb decay products, which emits gamma energies of 295.2 keV and 351.9 keV, and ^{214}Bi, which emits gamma energies of 609.3 keV and 1120.3 keV, respectively. ^{228}Ra was determined by measuring gamma energies of 911.07 keV and 969.11 keV for ^{228}Ac. ^{210}Pb was determined directly through its 46.5 keV line. The content of ^{40}K was determined by measuring its 1460 keV gamma rays. The artificial radionuclide ^{137}Cs was determined by measuring the gamma energy of 661. 6 keV. The gamma spectra were obtained by the multichannel emulator program Maestro [8] and were analyzed with the WinnerGamma program on the InterWinner platform [9]. The counting time was determined using the model proposed by Nisti et al. [10]. The background radiation was estimated by measuring ultrapure water. The determination of the minimum detectable concentration (MDC) was made using the model proposed by Currie [11]. The performance of the gamma-ray spectrometry measurements was evaluated by participating in the Proficiency Test (PT) organized by Instituto de Radioproteção e Dosimetria (IRD), which is available on a routine basis.

The determination of ^{210}Po in fish samples was performed by alpha spectrometry. The samples were initially dried in an oven with forced circulation at a controlled temperature, not higher than 80ºC, to avoid losses of ^{210}Po by volatilization. Approximately 1g of each sample (dry weight) was used; prior to the analysis, 100μL of ^{209}Po tracer of known activity (0.6483 Bq g^{-1}) was added. For the acid dissolution of the sample, 10 mL of concentrated HNO_3 and hydrogen peroxide were added, under heating at 80ºC to avoid loss by volatilization of polonium isotopes. The solution was evaporated carefully to near dryness. This procedure was repeated until complete dissolution of the sample. The final solution was conditioned with concentrated HCl to eliminate nitrates. The final residue was dissolved in 0.5M HCl and filtered in Millipore 0.1 μm; 20% hydroxylamine hydrochloride was added to the solution. The pH was adjusted to 1.5 and the polonium was spontaneously plated on the silver disc at 80ºC for 4h, with agitation of the solution. The prepared sources were counted in a Camberra Alpha Analyst surface barrier detector for 150.000 seconds.

3. Results and Discussion

The results of the activity concentration obtained for ^{226}Ra, ^{210}Pb, ^{210}Po, ^{228}Ra, ^{40}K and ^{137}Cs are presented in Table I, together with data from the literature.

Table I. Activity concentration of ^{226}Ra, ^{210}Pb, ^{210}Po, ^{228}Ra, ^{40}K and ^{137}Cs (Bq kg^{-1} wet weight)

Fish species (No. of samples)	Ra-226	Pb-210	Po-210	Ra-228	K-40	Cs-137
Bluefish (2)	0.06 - 0.10	<0.37 - 0.38	0.24 - 0.34	0.16 - 0.20	81.6 - 96.8	<0.05
Nisti et al., 2019 [12]	<0.19	<0.76		<0.32		0.11±0.02
Carvalho, 1995* [13]		0.42±0.01	9.4±0.3			
Görür et al., 2012 [14]	0.19 - 0.45				35.04 - 112.00	0.06 - 0.62
Tuna (4)	0.06 - 0.09	<0.42 - 0.72	0.33 - 0.51	<0.22 - 0.27	103- 123	0.07 - 0.11
[12]	0.15±0.05	<0.96		0.31±0.12		0.13±0.04
[14]	0.26-0.35				92.97 - 113.95	1.23 - 1.53
Smooth hounds nei (3)	0.07 - 0.10	<0.37 - 0.54	0.15 - 0.19	0.15 - 0.24	72.3 - 104.0	0.04 - 0.12
[12]	0.23±0.08	<1.3		0.37±0.18		<0.19
Cunha et al., 1993 [15]						0.3
Croaker (4)	<0.11 - 0.13	0.41 - 0.58	0.14 - 0.18	0.12 - 0.31	73.2 - 112.0	<0.04 - 0.09
[12]	0.58±0.14	<2.2		0.71±0.30		<0.33

Godoy et al., 2003 [16]**						0.03 - 1.6
[15]						0.3
Hake (4)	0.04 - 0.18	<0.29 - 0.69	0.10 - 0.16	0.09 - 0.28	42.6 - 127.0	<0.04 - 0.07
[12]	<0.17	<0.63		<0.31		<0.08
[13]*		0.15±0.01	6.7±0.3			
[15]						0.1
Sardine (2)	0.08 - 0.13	<0.46 - 0.56	0.40	0.12 - 0.25	79.9 - 135.0	<0.06
[12]	0.24±0.08	<0.95		0.27±0.09		<0.11
[13]*		1.00±0.02	66±2			
[15]						0.1

*Mean value

**Godoy et al., 2003 [16] - results for croaker and hake

The Brazilian regulatory guide Posição Regulatória 3.01/006 from 2011 entitled "Medidas de Proteção e Critérios de Intervenção em Situações de Emergência" established the recommended action levels for food control [17]. According to this standard, the concentration of ^{137}Cs in food cannot exceed the value of 1 kBq kg^{-1}. All the results obtained for this radionuclide are well below this limit.

The activity concentration observed for the radionuclides ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{137}Cs in all the species analyzed were low and close to the detection limits of the gamma spectrometry. The ^{40}K presented concentrations ranging from 42.6±6.0 Bq kg^{-1} to 135±19 Bq kg^{-1}. The ^{210}Po concentrations ranged from 0.10±0.03 Bq kg^{-1} to 0.51±0.09 Bq kg^{-1}. Carvalho (1995) [13] measured ^{210}Po concentration in fish from the north-eastern Atlantic Ocean of Portugal, obtaining 66±2 Bq kg^{-1} in sardine, of 6.7±0.3 Bq kg^{-1} in hake and 9.4±0.3 Bq kg^{-1} in bluefish. These results are several orders of magnitude higher than our results.

In general, the results obtained for the studied radionuclides in all the species analyzed are in good agreement with literature values.

4. Conclusions

The results obtained in this study is useful to verify the quality of the fish consumed in the city of São Paulo. All the results obtained for the species studied are below the limits adopted by the Brazilian Standards and therefore their consumption offers no risk due to the ingestion of radionuclides. However, to ensure the quality of the marine fish consumed by the population, it is suggested to measure a larger number of fishes in order to get a more representative sampling.

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References

[1] M.X. Pereira Filho et al. O mercado de peixes da piscicultura no Brasil: estudo do segmento de supermercados / autores, Palmas, TO: Embrapa Pesca e Aquicultura (2020).

[2] IAEA, International Atomic Energy Agency. "Sediment distribution coefficients and concentration

factors for biota in the marine environment", *TECHNICAL REPORTS SERIES No. 422*, Vienna (2004).

[3] M.S. Baxter, Environmental radioactivity: A perspective on industrial contributions, IAEA Bulletin 2 (1993) 33.

[4] NRPA, Radioactivity in the Marine Environment 2007, "Results from the Norwegian National Monitoring Programme (RAME)", *StrålevernRapport 2009:15, Østerås: Norwegian Radiation Protection Authority* (2009).

[5] IAEA, International Atomic Energy Agency. Worldwide marine radioactivity studies (WOMARS) radionuclide levels in oceans and seas, *TECDOC-1429*, Vienna (2005).

[6] IAEA, International Atomic Energy Agency. The Fukushima Daiichi accident, *Technical vol. 4 - Radiological consequences*, Vienna (2015).

[7] F. Estrella, G. Raposo, J. Pascoli, J. G. Gonzalez, F. S. Motta, R. L. De Moura Relatório Técnico Comercialização de pescado nas cidades de São Paulo e Rio de Janeiro (2014) Available at: https://www.sosma.org.br/wp-content/uploads/2014/09/ESTUDO-PESCADO-2014_Relatorio-Final.pdf Access in 12 mar 2021.

[8] Maestro Software, Maestro for Windows (Emulation software for Gamma Spectroscopy). Model A65-B1Version 3.04, EG&G ORTEC (1995).

[9] InterwinnerTM 6.0, MCA Emulation, Data Acquisition and Analysis software for Gamma and Alpha Spectroscopy, IW-B32 2004. ORTEC. Oak Ridge, TN, USA (2004).

[10] M.B. Nisti, A.J.G. Santos, B.R.S. Pecequilo, M.F. Máduar, M.M. Alencar, S.R.D. Moreira, "Fast methodology for time counting optimization in gamma-ray spectrometry based on preset minimum detectable amounts", *Journal Radioanalytical Nuclear Chemistry*, vol. 281, pp. 283–286 (2009).

[11] L.A. Currie, "Limits for qualitative detection and quantitative determination", *Anal. Chem.,* vol. 40, pp. 586-593 (1968).

[12] M.B. Nisti, C. H. R. Saueia, B. Castilho, B. P. Mazzilli, "Assessment of Sr-90, Cs-137, Natural Radionuclides and Metals in Marine Fish Species Consumed in the City of São Paulo Brazil". *Special Publications. VI ed.: Royal Society of Chemistry*, p. 161-166 (2019).

[13] F.P. Carvalho, ^{210}Po and ^{210}Pb intake by the Portuguese population: The contribution of seafood in the dietary intake of 210Po and 210Pb, Health Phys. 69 (1995) 469–480.

[14] F. Korkmaz Görür, R. Keser, N. Akçay, S. Dizman, Radioactivity and heavy metal concentrations of some commercial fish species consumed in the Black Sea Region of Turkey, *Chemosphere*, vol. 87, pp. 356–361 (2012).

[15] I.I.L. Cunha, C.S. Munita, P.P. Paiva, A. Teixeira. Sci Total Environ. 139/140:431-5 (1993).

[16] J.M. Godoy, Z.L. Carvalho, F. C. Fernandes, O.M. Danelon, A.C.M. Ferreira, L.A. Roldão. J Environ Radioact., 70, 193 (2003).

[17] Comissão Nacional de Energia Nuclear – CNEN, "Medidas de Proteção e Critérios de Intervenção em Situações de Emergência", *Posição Regulatória 3.01/006* (2011).