Baseline activity concentration of ^{210}Po and ^{210}Pb and dose assessment in bivalve molluscs at the Andalusian coast.

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Highlights

- The first comprehensive study related to radioactivity concentrations in the area.
- Assessment of ^{210}Pb and ^{210}Po in different types of bivalve molluscs.
- The results have been compared with previous studies from other countries.
- The effective dose assessment to the adult population was performed.

Abstract

In this study, the activity concentrations of ^{210}Po and ^{210}Pb were determined in different types of bivalve molluscs sampled during the period of May 2014–June 2015 along the Andalusian littoral. Radioactivity concentrations of ^{210}Po were determined through alpha-particle spectrometry using ^{209}Po as an internal tracer. Radioactivity concentrations of ^{210}Pb were determined through low-level gamma-ray spectrometry. The activity concentrations of ^{210}Po and ^{210}Pb varied between 40 ± 2 and 515 ± 9 Bq kg^{-1} dry weight (d.w.), and ND (lower than limit of detection) and 73 ± 10 Bq kg^{-1} d.w., respectively. The committed effective dose to humans was calculated to range from 39–477 µSv year^{-1}. Radioactivity and dose levels were compared with previous studies from other countries.

Keywords: Baseline assessment; bivalve molluscs; 210Po; 210Pb ; Andalusia; dose

There are two main sources of radioactivity in the marine environment (Shannon and Cherry, 1967): ^{40}K and natural decay series of ^{238}U and ^{232}Th; and artificial radionuclides such as ^{137}Cs, $^{(239+240)}Pu$ or ^{90}Sr. These radionuclides are chemical analog of metabolically essential elements, and are finally bioaccumulated in hard and soft tissues of the marine organisms (Carvalho, 2018; KIlIç and Çotuk, 2011). Consequently, the radionuclides get into the human food chain via consumption of marine food. An assessment of radionuclide levels in marine organisms and radiation doses is therefore essential to evaluate the intake of radionuclides by man (Feroz Khan et al., 2014).

The release of artificial radionuclides into the environment is mainly due to nuclear power plant (NPP) accidents (Chernobyl in 1986, or Fukushima in 2011), and nuclear weapon tests (during the 1960s), and therefore the Earth becomes globally contaminated with radioactive debris (Fathivand and Amidi, 2007). Several studies revealed that the contribution of anthropogenic radionuclides to the radiation dose is lower than the naturally occurring ones (Aarkrog et al., 1997; Connan et al., 2007). Therefore, we focused on the determination of natural radionuclides levels in marine organisms.

Among the natural radionuclides ^{210}Pb, and ^{210}Po are members of ^{238}U decay chain. The sources of ^{210}Po ($T_{1/2}$ = 138 days) and ^{210}Pb ($T_{1/2}$ = 22.3 years) in the environment are the emanation of ^{222}Rn from the earth's crust to the atmosphere and their subsequent fallout through wet and dry deposition (Baskaran, 2011), the radioactive decay of ^{226}Ra dissolved in seawater (Bacon et al., 1976; Carvalho and Fowler, 1993), and also the technologically enhanced natural occurring radioactive materials (TENORM) from phosphate, oil, and gas industries (Carvalho et al., 2010; Shakhashiro et al., 2011; Villa et al., 2009).

^{210}Po is a hazardous element with high chemical and radiological toxicity connected with the fact that the path length of alpha particles of 5.3 MeV in tissue is about 40 mm, releasing very locally the radiation dose, and potentially originating a fatal damage to different organs and tissues (Stewart et al., 2008). Therefore the major contributor to radiation dose received by humans is from ^{210}Po in sea food, such as fish, crustaceans and molluscs (Dahlgaard, 1996; Wildgust et al., 2000). Furthermore, ^{210}Pb is a beta emitter and also it is the second highest radiotoxic radionuclide in ^{238}U decay chain (Štrok and Smodiš, 2011).

Bivalve molluscs have been commonly used as first-order biological indicators of the contaminant levels, thus they are helpful for assessing the contamination and ecotoxicology in the marine environment (Carvalho et al., 2010; Fonollosa et al., 2017; Francioni et al., 2007; Kiliç et al., 2014; Rožmarić et al., 2012; Thébault et al., 2008; Topcuoğlu et al., 2003; Uğur et al., 2011).

With all of this in mind, the main objectives of this study are (1) to assess the activity concentration of ^{210}Po and ^{210}Pb on various bivalve species distributed and consumed in the Andalusian coast, and (2) to estimate the annual effective ingestion dose to which the public is exposed in terms of health and safety.

The littoral of Andalusia extends along the Mediterranean Sea, the Gibraltar Strait, and the Atlantic Ocean (Fig. 1) and it corresponds to 17.5% of the 1,100 km of coasts in Spain. Five of the 10 large urban areas in Andalusia are located in coastal areas, in addition to other systems along the coast, such as thermal power plants, ports or chemical industries.

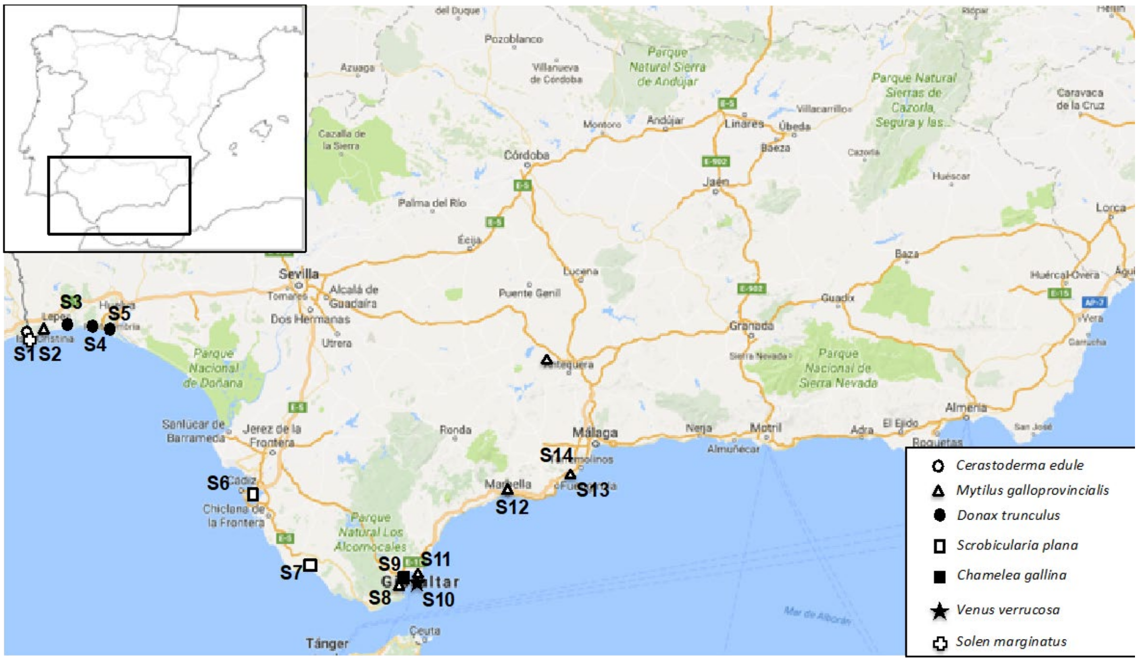

Fig. 1. Map showing the study area and sampling stations.

The bivalves molluscs samples were collected from 14 locations of the Andalusian coast in May 2014 and June 2015 (see Fig. 1). In particular, different bivalves that are usually consumed in this area were collected: cockles (*Cerastoderma edule*) with 2.3–3.1 cm shell length, mussels (*Mytilus galloprovincialis),* wedge clams (*Donax trunculus*), peppery furrow shells (*Scrobicularia plana*), striped venus clams (*Chamelea gallina*), warty venus clams (*Venus verrucosa*), and grooved razor shells (*Solen marginatus*).

In the laboratory the bivalves molluscs samples were washed with distilled water in order to eliminate any sediment residues and other impurities. However, the digestive track was not depurated as it was considered as edible material. Then, their soft tissues, including interstitial fluid, were dissected to remove the flesh using stainless steel scalpel blades to prevent contamination of samples, weighted, frozen at -20 ºC and freeze-dried for 24 h, using a freeze-dryer module; finally the dehydrated sample was weighed, crushed and homogenized.

In order to determine ^{210}Po activity concentration, a known activity of ^{209}Po was added to the lyophilized sample to calculate the chemical recovery. Then, the sample was digested with concentrated HNO_3 and H_2O_2, and if foam was generated during this process, the solution was cooled to a lower temperature. The obtained solution was evaporated slowly to near dryness on a hot plate at 80-90 ºC, and the resulting residue was treated again 2 or 3 times with concentrated HNO_3 and H_2O_2 until all the organic material was digested. Finally, the residue was dissolved in 100 ml of 1 M HCl and the solution was filtered using a 0.45 µm filter. About 0.1 g of ascorbic acid was added as a reducing agent to this HCl solution. The solution was stirred continuously for 4 h at 85-90 ºC and pH 1.5–2.0 in contact with a silver disc, and then ^{210}Po was spontaneously plated onto the disc. The disc was removed and washed with distilled water and acetone, and dried under an infrared lamp. It was then counted using an alpha-spectrometry instrument (Alpha

Analyst, Canberra) containing a Passivated Implanted Planar Silicon (PIPS) detector inside. High chemical yields (>70%) were achieved (Hurtado-Bermudez et al., 2017).

To measure ^{210}Pb activity concentration, non-destructive gamma-ray spectrometry technique was used. Lyophilized samples were weighted and put into 80 ml sample containers, sealed, and ^{210}Pb activity was determined directly by its gamma emission at 46.5 keV. The samples were measured using a low-background Canberra HPGe reverse electrode coaxial detector, and the efficiency was determined using LabSOCS software (Hurtado and Villa, 2010). Each sample was counted for 1–3 days, and activity values were reported as the activity on the date of sampling. Uncertainties reflect one sigma counting statistics.

Both methods were validated in terms of the quantification limit (L_Q), defined as (Currie, 1968):

$$L_Q = \frac{50\{1+\sqrt{1+n_0/12.5}\}}{\varepsilon \cdot t_0 \cdot m \cdot R_c} \quad (1)$$

where n_0 is the total background counts; t_0 the background counting time (in seconds); ε is the counting efficiency; R_c the radiochemical yield (100% for gamma-ray spectrometry); and m is the mass of the sample. The result was 2.0 Bq kg^{-1} for ^{210}Po assuming 1 g of sample, and 16.0 Bq kg^{-1} for ^{210}Pb assuming 15 g of sample.

Additionally, the proposed methods were validated by the analysis of Certified Reference Materials (CRM) provided by the International Atomic Energy Agency (IAEA). IAEA-437 is a reference material designed for the determination of anthropogenic and natural radionuclides in mussel (Mytilus galloprovincialis species) including $^{210}Pb/^{210}Po$ in equilibrium (median value of 4.2 Bq kg^{-1}). IAEA-414, a mixed fish species from eastern Irish Sea, is a reference material certified for $^{210}Pb/^{210}Po$ in equilibrium (median value of 2.1 Bq kg^{-1}).

Following the IUPAC (Thompson et al., 2006) and ISO (ISO/IEC, 2010) recommendations for assessment of performance of laboratories, a z-score methodology was used in the data evaluation. The z-score was calculated as following:

$$z = \frac{Value_{LAB} - Value_{REF}}{\sigma_{REF}} \quad (2)$$

where $Value_{REF}$ is the reference value, $Value_{LAB}$ is our laboratory value, and σ_{REF} is the uncertainty of the sample published by IAEA. The performance in term of accuracy is evaluated as satisfactory if |z-score| ≤ 2, questionable for 2 ≤ |z-score| ≤ 3 and unsatisfactory for |z-score| ≥ 3.

The value of the parameter u (trueness) includes the uncertainty of the assigned value (σ_{LAB}) for bias, and it was calculated from the following equation:

$$u = \frac{|Value_{LAB} - Value_{REF}|}{\sqrt{\sigma_{LAB}^2 + \sigma_{REF}^2}} \quad (3)$$

The calculated u-test value is compared with the critical values listed in the t-statistic tables to determine if the reported result differs significantly from the expected value at a given level of probability. The advantage of u-test is that it takes into consideration the propagation of measurement uncertainties when defining the normalised error, this is especially useful when evaluating results, which may overlap with the reference interval. The limiting value for the u-test parameter was set to 2.58 for level of probability at 99% to determine if a result passes the test ($u < 2.58$).

Finally, the results were evaluated against the acceptance criteria for trueness and precision and assigned the status "Acceptable", "Warning" or "Not Acceptable" accordingly.

The result is assigned "Acceptable" status for trueness if:

$$|Value_{LAB} - Value_{REF}| \leq 2.58 \cdot \sqrt{\sigma_{LAB}^2 + \sigma_{REF}^2} \quad (4)$$

And additionally the result is assigned "Acceptable" status for precision if:

$$P = \sqrt{\left(\frac{\sigma_{LAB}}{Value_{LAB}}\right)^2 + \left(\frac{\sigma_{REF}}{Value_{REF}}\right)^2} \, x100\% \quad (5)$$

Applying the above reported equation the result is assigned "Acceptable" status if P is < 20% for alpha-particle spectrometry, and P is < 30% for gamma-ray spectrometry due to the high uncertainties associated to this method because of low-energy and low-probability gamma-ray emission of ^{210}Pb. A result must obtain "Acceptable" status in both criteria to be assigned final status of "Acceptable".

In view of the above, the statistical tests were applied to the results obtained for the determination of ^{210}Pb and ^{210}Po in the IAEA CRMs. Five aliquots of approximately 1 g and 55 g were analyzed for the determination of ^{210}Po and ^{210}Pb presented in each CRM respectively, and results are shown in Table 1. The z-score and u values obtained are inside the acceptable range for trueness of the proposed method. All the results obtained an "Acceptable" status referring to precision and trueness. The analysis of the IAEA-437 samples gives a median value of 4.5 Bq kg^{-1} for ^{210}Po and 4.9 Bq kg^{-1} for ^{210}Pb, very close to the reference material reported value and within its 95% confidence interval. Lastly for IAEA-414 samples the obtained median value is within the reported 95% confidence interval. The observed deviations are in the order of the precision values associated to environmental materials, and overall, we conclude that the proposed method is adequate to analyse ^{210}Po and ^{210}Pb in seafood samples.

Table 1. Results obtained for two IAEA reference materials for five aliquots (N=5). Uncertainties (σ) are expressed at k=1.

ID	Radionuclide	A_{LAB} Bq kg^{-1}	σ (k=2)	A_{REF} Bq kg^{-1}	σ (k=2)	z-score	u	Trueness	Precision P (%)
IAEA-437 (mussel)	^{210}Po	4.5	0.3	4.2	0.7	0.4	0.4	Acceptable	18
IAEA-437 (mussel)	^{210}Pb	4.9	1.1	4.2	0.7	1	0.5	Acceptable	28
IAEA-414 (fish)	^{210}Po	2.4	0.3	2.1	0.3	1	0.7	Acceptable	11
IAEA-414 (fish)	^{210}Pb	2.7	0.7	2.1	0.3	2	0.8	Acceptable	29

Average, minimum and maximum activity concentrations of ^{210}Pb and ^{210}Po in bivalve molluscs in the sampling locations are presented for 2014 in Table 2, and for 2015 in Table 3.

Table 2. Activity concentrations of radionuclides (Bq/kg d.w.) and annual ingestion dose for bivalve molluscs samples in the study area during 2014.

	bivalve specie	^{210}Po		^{210}Pb		ww/dw (%)	E_d (µSv/year)
		Bq/kg	uncertainty	Bq/kg	uncertainty		
S1-Río Guadiana	Cerastoderma edule	73	3	<16.0		16.6	69
S2-Isla Cristina	Mytilus galloprovincialis	167	6	39	8	17.1	180
S3-Barra del Terrón	Donax trunculus	112	4	<16.0		18.3	115
S4-Desembocadura Río Piedras	Donax trunculus	46	2	<16.0		15.5	41
S5-Punta Umbría	Donax trunculus	40	2	18	13	17.4	50
S6-Caño de Sancti Petri	Scrobicularia plana	48	2	<16.0		18.6	52
S7-Río Barbate	Scrobicularia plana	187	8	17	6	18.7	198
S8-Getares	Mytilus galloprovincialis	41	1	75	8	16.5	77
S9-Bahía de Algeciras	Chamelea gallina	149	5	<16.0		19.3	158
S10-Bahía de Algeciras	Venus verrucosa	179	9	26	8	20.5	220
S11-La Línea	Mytilus galloprovincialis	129	5	37	12	16.1	133
S12-Puerto de Marbella	Mytilus galloprovincialis	382	14	92	10	16.0	382
S13-Puerto de Benalmádena	Mytilus galloprovincialis	308	18	20	5	19.1	336
S14-Caleta de Vélez	Mytilus galloprovincialis	314	12	24	7	17.7	319

The activity concentrations of ^{210}Po in bivalve molluscs samples ranged between 40 ± 2 and 383 ± 14 Bq kg^{-1} d.w. for 2014, and 85 ± 3 and 506 ± 9 Bq kg^{-1} d.w. for 2015. The highest ^{210}Po activity concentration was found in bivalves collected from ports, Puerto de Marbella (S12) and Puerto de Benalmádena (S13), during both years. The lowest activities were determined in the samples from Punta Umbría (S5) and Caño de Sancti Petri (S6) in the Atlantic coast. As the accumulation of ^{210}Po in marine organisms is associated with the ingestion of food, it seems that bivalves at the stations located at the ports (S12 and S13) have on the one hand more phytoplankton available as food, and on the other hand more organic particulate matter from sewage discharges accumulates inside the ports. The activity concentrations of ^{210}Po in bivalve molluscs samples during summer 2014 and summer 2015 are shown in Fig. 2. There is an overall average increment of the activity concentrations in summer 2015. Probably, there was an annual change of some environmental parameters, such as the amount of suspended particulate matter or the volume of the existing plankton, that implies higher values for activity concentrations of ^{210}Po in bivalve molluscs during summer 2015.

Table 3. Activity concentrations of radionuclides (Bq/kg d.w.) and annual ingestion dose for bivalve molluscs samples in the study area during 2015.

	bivalve specie	**^{210}Po**		**^{210}Pb**		**ww/dw (%)**	**E_d (µSv/year)**
		Bq/kg	**uncertainty**	**Bq/kg**	**uncertainty**		
S1-Río Guadiana	Solen marginatus	354	17	<16.0		19.8	385
S2-Isla Cristina	Mytilus galloprovincialis	224	10	<16.0		17.0	210
S3-Barra del Terrón	Donax trunculus	172	9	<16.0		17.1	163
S4-Desembocadura Río Piedras	Donax trunculus	186	10	<16.0		16.7	172
S5-Punta Umbría	Donax trunculus	91	3	<16.0		16.8	86
S6-Caño de Sancti Petri	Scrobicularia plana	85	3	<16.0		20.9	99
S7-Río Barbate	Scrobicularia plana	256	12	31	13	20.0	301
S8-Getares	Mytilus galloprovincialis	436	24	37	12	16.6	417
S9-Bahía de Algeciras	Chamelea gallina	390	14	<16.0		18.2	390
S10-Bahía de Algeciras	Venus verrucosa	187	9	<16.0		19.9	205
S11-La Línea	Mytilus galloprovincialis	397	15	34	17	18.8	429
S12-Puerto de Marbella	Mytilus galloprovincialis	451	21	28	4	15.5	389
S13-Puerto de Benalmádena	Mytilus galloprovincialis	506	9	30	14	16.7	479
S14-Caleta de Vélez	Mytilus galloprovincialis	320	15	<16.0		16.8	295

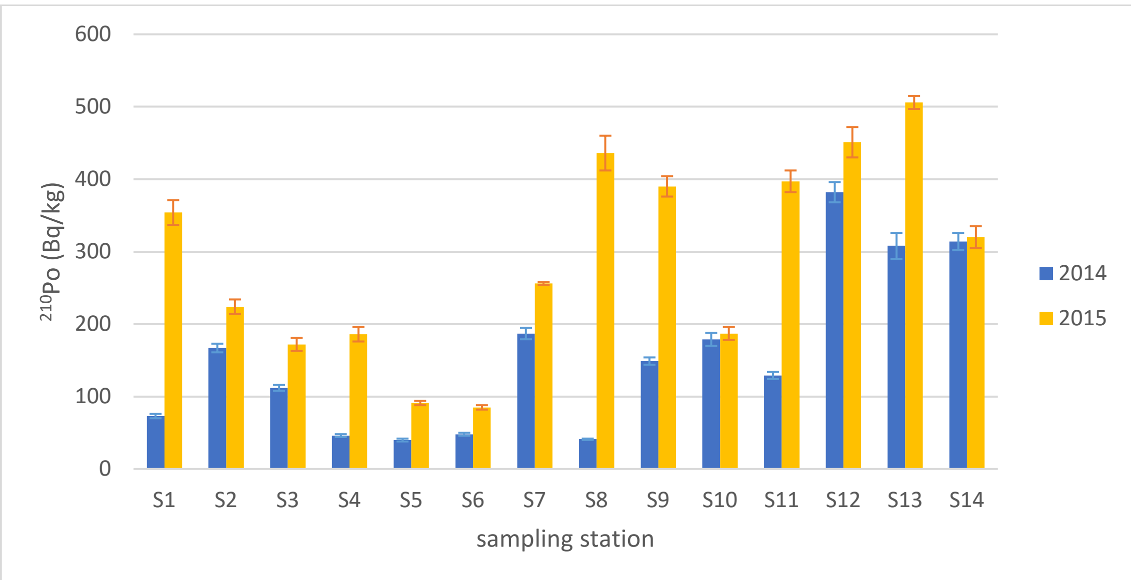

Fig. 2. Concentrations of ^{210}Po (Bq kg^{-1} dw) in bivalve molluscs sampled during summer 2014 and summer 2015 from different locations at Andalusian coast.

The concentration of ^{210}Pb in bivalves ranged between ND (not detected or below Minimum Detectable Activity) and 92 ± 10 Bq kg^{-1} d.w. in 2014, and ND and 37 ± 12 Bq kg^{-1} d.w. in 2015. ^{210}Pb activity concentrations were relatively low probably due to the fact that the sampling stations are under the influence of Mediterranean climate with cool wet winters and hot and dry summers. Because a high concentrations of ^{210}Pb in molluscs is usually linked to high atmospheric deposition of ^{210}Pb during the wet season, a low activity concentration of ^{210}Pb is expected for samples collected during summer (Uğur et al., 2011). On the other hand, ^{210}Pb activity concentrations are higher at Mediterranean coast than at the Atlantic coast of Andalusia (see Fig. 3).

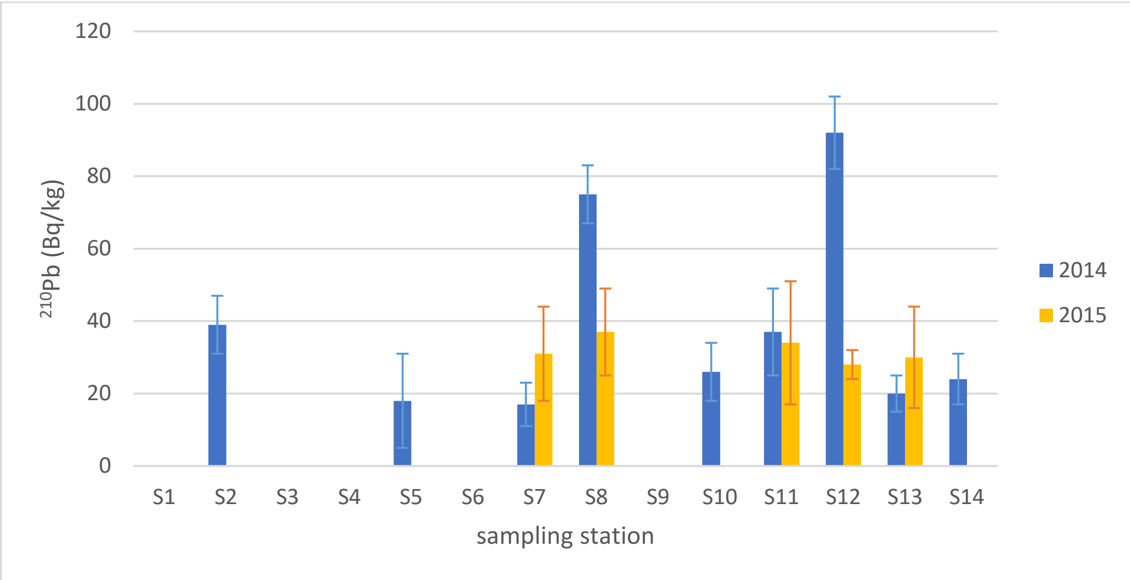

Fig. 3. Concentrations of ^{210}Pb (Bq kg^{-1} d.w.) in bivalve molluscs sampled during summer 2014 and summer 2015 from different locations at Andalusian coast.

^{210}Po and ^{210}Pb activity concentrations measured in this study are comparable with other reported values in the literature (see Table 4). In this study, the ^{210}Po/^{210}Pb ratio was found to range from 4 to 16 with a mean value of 8, which shows that the ^{210}Po majority in the bivalves is unsupported. The range of ^{210}Po/^{210}Pb ratio is similar to those found by several studies (see Table 4).

Table 4. Comparison of ^{210}Po and ^{210}Pb activity concentrations, ^{210}Po/^{210}Pb ratio, and annual ingestion dose in bivalves collected from various studies.

References	Country	^{210}Po (Bq kg^{-1} dw)	^{210}Pb (Bq kg^{-1} dw)	^{210}Po/^{210}Pb	E_d (µSv year^{-1})
(McDonald et al., 1996)	UK	103–3124	-	-	-
(Uğur et al., 2002)ide	Turkey	52–1344	6–167	3-25	-
(Desideri et al., 2011)	Italy	75–223	2–25	4-62	96–466
(Carvalho et al., 2011)	Portugal	102-759	2.6-45	18-51	-
(Charmasson et al., 2011)	France	203	20	10-15	-
(Uğur et al., 2011)	Turkey	53-1960	6-135	4-137	-
(Štrok and Smodiš, 2011)	Slovenia	51-106	2.7-3.0	17-111	8.5
(Rožmarić et al., 2012)	Croatia	22-207	2.8-9.3	6-31	53-497
(Kiliç et al., 2014)	Turkey	26-280	1-23	8-24	0.2-3.3
(Kim et al., 2017)	Korea	240	-	-	19-189

This work	Spain (Andalusia)	40-506	17-92	4-16	41-479

The activity concentrations for each species of bivalve molluscs are shown in Table 3 and 4 for both years. ^{210}Pb was not found or the values were too low (clams) in all samples, except for mussels (*M. Galloprovincialis*) with 92 Bq kg^{-1} d.w. as the maximum value.

Significant variation of ^{210}Po activity concentrations were observed within different species of bivalves, which may be due to difference in the size, age, metabolism, feeding habit and the environment of the specific bivalves species. The highest value in average corresponds to mussels (*M. Galloprovincialis*) with 506 Bq kg^{-1} d.w., and the lowest one to cockles (*D. trunculus*) with 40 Bq kg^{-1} d.w. and peppery furrow shells (*S. plana*) with 48 Bq kg^{-1} d.w.

Table 5. Activity concentrations of radionuclides (Bq/kg d.w.) and annual ingestion dose for different species of bivalve molluscs.

	^{210}Po		**^{210}Pb**		**ww/dw (%)**	**E_d (µSv/year)**
	min-max	**average**	**min-max**	**average**		
Cockles (*C. Edule*)	70.0-76.0	73.0	<16.0	<16.0	16.6	66.0
Razor shells (*S. Marginatus*)	337-371	354	<16.0	<16.0	19.8	382
Mussels (*M. Galloprovincialis*)	40.0-515	306	15.0-102	41.2	17.0	302
Clams (*D. Trunculus*)	40.0-196	108	5.00-31.0	18.0	17.0	102
Peppery furrow shells (*S. Plana*)	48.0-268	144	11.0-44.0	24.0	19.6	160
Clams (*C. Gallina*)	144-404	270	<16.0	<16.1	18.8	271
Clams (*V. Verrucosa*)	170-196	183	18.0-34.0	26.0	20.2	210

Annual ingestion doses due to the consumption of bivalves molluscs were calculated for adults using the following equation (IAEA, 2014):

$$E_d = A \times m \times C_f \quad (6)$$

where E_d (Sv) is the annual effective ingestion dose of each radionuclide, A is the activity concentration of each radionuclide (Bq kg^{-1} w.w.) in the bivalve molluscs samples, m (kg) is the estimation of annual intake of each bivalve mollusc specie, and C_f is the dose coefficient for adults (Sv Bq^{-1}). The annual intake of molluscs was obtained via the database of food consumption maintained by the Spanish Ministry of Agriculture, Food and Environment (m = 3.5 kg of bivalves of wet tissue per year per capita). The values of the dose coefficients used for ^{210}Po and ^{210}Pb were $1.26 \cdot 10^{-6}$ and $6.90 \cdot 10^{-7}$ Sv Bq^{-1}, respectively (IAEA, 2014).

The annual effective doses resulting from the internal incorporation of ^{210}Po and ^{210}Pb through the consumption of all of the species analyzed in this study are reported in Table 5. The obtained values were found to range between 66-382 µSv year^{-1}. The annual ingestion doses calculated for all of the bivalve molluscs analyzed are comparable with other studies reported in the literature (see Table 4), and are within the normal range of the ingestion exposure due to natural radiation (200–1000 μSv year^{-1}) (UNSCEAR, 2011). However, depending on the country and the annual intake of bivalves molluscs consumed in the diet, the annual effective ingestion dose varies significantly. The average consumption of bivalve molluscs in each country should also be taken into account in the comparison of annual effective doses.

Therefore, it can be concluded that in this first comprehensive study related to radioactivity concentrations in the Andalusian littoral in different types of bivalves molluscs sampled during the period of May 2014–June 2015, the levels of ^{210}Po, ^{40}K, ^{210}Pb and ^{234}Th are comparable with previous studies from other countries. The activity concentrations of ^{210}Po and ^{210}Pb varied between 40 ± 2 and 515 ± 9 Bq kg^{-1} dry weight (d.w.) ; and ND (lower than limit of detection) and 73 ± 10 Bq kg^{-1} d.w., respectively.

The effective dose assessment to the adult population was performed and the obtained values (39–477 μSv year^{-1}) are comparable with other studies in the literature focused in other areas of the world and no significant differences were found.

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