Geographical origin of bivalve molluscs in coastal areas using natural radioactivity fingerprinting and multivariate statistical analyses: Andalusian coast as case of study

Santiago Hurtado-Bermúdez[1], José Antonio Jurado-González[2], Juan Luis Santos[3], Carlos Francisco Díaz-Amigo[2], Irene Aparicio[3], José Luis Más[1,4], Esteban Alonso[1,3,*]

[1]Servicio de Radioisótopos, Centro de Investigación, Tecnología e Innovación, Universidad de Sevilla, Av. Reina Mercedes 4B, 41012 Sevilla, Spain

[2]Laboratorio de Control de Calidad de los Recursos Pesqueros, Agencia de Gestión Agraria y Pesquera de Andalucía, Ctra. Punta Umbría-Cartaya, km 12., 21459, El Rompido (Huelva), Spain

[3]Departamento de Química Analítica, Escuela Politécnica Superior, Universidad de Sevilla, C/ Virgen de África 7, 41011 Sevilla, Spain

[4]Departamento de Física Aplicada I, Universidad de Sevilla, Av. Reina Mercedes, 41012 Sevilla, Spain

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*Corresponding author

Address: Esteban Alonso Álvarez

Departamento de Química Analítica

Universidad de Sevilla

C/ Virgen de África, 7

41011 Seville (Spain)

E-mail address: ealonso@us.es

Abstract

The presence of natural and artificial radionuclides in the marine environment produces the accumulation of radionuclides by bivalve molluscs consumed by humans, and therefore it could result in a radiological hazard. In this study, the activity concentrations of ^{210}Po, ^{40}K, ^{210}Pb and ^{234}Th were determined in different types of bivalve molluscs sampled during the period of May 2014–June 2015, along coastal areas from the Andalusian region (South of Spain), through alpha-particle spectrometry and low-level gamma-ray spectrometry.

The activity concentrations of ^{210}Po; ^{40}K; ^{210}Pb and ^{234}Th varied between 40 ± 2 and 515 ± 9 Bq kg^{-1} dry weight (d.w.); 121 ± 7 and 674 ± 34 Bq kg^{-1} d.w.; ND (lower than limit of detection) and 73 ± 10 Bq kg^{-1} d.w.; and ND and 126 ± 27 Bq kg^{-1} d.w., respectively. The committed effective dose to humans was calculated to range from 41–479 μSv year^{-1}. Both radioactivity and dose levels were comparable to previous studies from other countries. Finally, a multivariate statistical analysis of natural radioactivity content allowed the discrimination between bivalve molluscs from Atlantic and Mediterranean coasts.

Keywords: natural radioactivity; bivalve molluscs; geographical origin; fingerprinting; dosimetric evaluation

1. Introduction

In order to meet the soaring demand for seafood, the aquaculture has been on the rise over the past decades and it has shifted the production of bivalve molluscs from captures of wild populations. Aquaculture has led to a decrease in bivalve molluscs prices and a strong increase in their commercialization. The culture of non-fed animal species, including bivalve molluscs (clams, oysters, mussels, etc.), produced 22.7 million tons in 2014, representing 30.8% of world production of all farmed fish species [1]. Europe produced 632,000 tons of bivalves in 2014, and its major producers were Spain (223,000 tons), France (155,000 tons) and Italy (111,000 tons). Other major bivalve world producers include China (12 million tons), Japan (377,000 tons), the Republic of Korea (347,000 tons) and Thailand (210,000 tons) [1]. However, the bivalve molluscs production in Europe has been stagnant because the full capacity production has been reached in traditional locations [2]. This implies an increase in imports by Europe and an unfavorable balance of trade.

Apart from their culinary value, the popularity of bivalve molluscs, which include mussels, oysters and clams, has increased over the past decades due to the presence of proteins, lipids, carbohydrates and bioactive compounds in their meat, which have beneficial effects on human health [3,4]. Bivalve species are mainly filter-feeder with a diet of phytoplankton (diatoms, dinoflagellates, etc.), and additionally trace elements, bacteria or organic material suspended in water [5]. Therefore, due to bivalve species are at a low position in the food chain, there is an increment in the health risk to humans from high exposure to trace elements by consumption, particularly in coastal areas [6,7]. Although many metals are essential biological elements, they are also above a certain concentration threshold. Thus, the concentration of trace elements in bivalves organisms potentially toxic to humans has been the subject of several studies [8–12].

Among all the trace elements present in seawater, most radionuclides, can be bioaccumulated by bivalve molluscs as well as in other foods in diet [13–16]. Since mid of 20th century, two main sources of radioactivity in the marine environment are well-known [17,18]: ^{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 available for uptake by marine organisms depending in part on their chemical nature and their physical state in the seawater. Because some of them are chemical analog of metabolically essential elements, they are finally bioaccumulated in hard and soft tissues of the marine organisms through different mechanisms [19–21]. Consequently, natural and artificial radionuclides get into the human food chain via consumption of marine food. An assessment of radionuclide levels in marine organisms is therefore essential to evaluate the intake of radionuclides by man. The biological effects of the ionizing radiation from radionuclides in humans are generally dependent on the dose received, i.e. the energy absorbed in the body from internal irradiation due to ingestion of radionuclides. A thorough radiation dose assessment determines a baseline benchmark that helps to control any additional dose increment due to nuclear accidents or industrial operations [22,23].

In relation to artificial radionuclides, their release into the atmosphere and the ocean is mainly due to nuclear power plant (NPP) accidents (Chernobyl in 1986, or recently Fukushima-Daiichi in 2011), and nuclear weapon tests (during the 1960s), and therefore the Earth becomes globally contaminated with radioactive debris [24,25]. Several studies revealed that the contribution of anthropogenic radionuclides to the internal radiation dose is lower than the naturally occurring ones [26,27]. Therefore, the focus will be on the determination of natural radionuclides levels in marine organisms.

Among the natural radionuclides ^{226}Ra, ^{222}Rn, ^{210}Pb, and ^{210}Po are members of ^{238}U decay chain. A main source of ^{210}Po ($T_{1/2}$ = 138 days) and ^{210}Pb ($T_{1/2}$ = 22.3 years) in the environment is the emanation of ^{222}Rn from the earth's crust to the atmosphere and their subsequent return to the earth's surface through wet and dry deposition [28,29]. Additionally, ^{210}Po and ^{210}Pb are produced from the radioactive decay of ^{226}Ra dissolved in seawater [30–32]. The other source of ^{210}Po and ^{210}Pb in the environment are the technologically enhanced natural occurring radioactive materials (TENORM). These waste discharges, such as those from phosphate, oil, and gas industries, may enhance radioactivity levels in the coastal marine environment [33–36].

^{210}Po is a hazardous element with high chemical and radiological toxicity. ^{210}Po is an alpha emitter (with an energy of 5.3 MeV), and its radiotoxicity is connected with the fact that the path length of alpha particles from ^{210}Po in tissue is about 40 mm, releasing very locally the radiation dose, and potentially originating a fatal damage to different organs and tissues [37]. Therefore the major contributor to radiation dose received by humans is from ^{210}Po in sea food, such as fish, crustaceans and molluscs [38,39]. Furthermore, ^{210}Pb is a beta emitter and also it is the second highest radiotoxic radionuclide in ^{238}U decay chain [40].

On the other hand, because of its very long half-life ($T_{1/2} = 1.251\times10^{9}$ years) and natural origin, the activity concentration of ^{40}K are generally considered to be natural background levels for marine organisms [41]. The dose attributable to ^{40}K is however mostly due to its beta emission and it is negligible compared to ^{210}Po radiation dose [42]. Finally, the half-life of ^{234}Th is 24.1 days what makes it particularly suited for studying fast biological processes. The radioactive levels of ^{234}Th have been reported by some authors in plankton [43,44]. However, there have been few reports on

bioaccumulation of ^{234}Th in marine organisms from the higher trophic levels such as molluscs [45].

Finally, multivariate data analyses can facilitate the interpretation of the radioactivity concentration results. Principal component analysis (PCA) and hierarchical cluster analysis (HCA) are techniques commonly used in the evaluation of food data, allowing the establishment of similarities and trends in data sets [9,46–52]

With all of this in mind, the main objectives of this study are (1) to assess the activity concentration of different natural isotopes (^{210}Po, ^{40}K, ^{210}Pb and ^{234}Th) on various bivalve species (cockles, peppery furrow shells, mussels, clams and razor shells), (2) to estimate the annual effective ingestion dose to which the public is exposed in terms of health and safety, and (3) to use natural radioactivity concentrations as fingerprints of the origin of the bivalves.

2. Materials and methods

2.1. Sampling and sample preparation

The studied area extends along the Mediterranean Sea, the Gibraltar Strait, and the Atlantic Ocean (Fig. 1) and it corresponds to 17.5% of the approximately 6000 km of coasts in Spain. The studied area are affected by five large cities (Huelva, Bahia de Cadiz, Jerez, Bahia de Algeciras, Malaga and Almeria), in addition to other systems along the coast, such as thermal power plants, ports or chemical industries.

The bivalves molluscs samples were collected from 14 locations during two sampling campaigns in May 2014 and June 2015 (see Fig. 1). Dates of collection, bivalve specie, UTM coordinates and sampling depth are showed in Table S1 in supplementary material. 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) with 5.2–10.3 cm shell length, wedge clams (*Donax trunculus*) with 2.2–3.9 cm shell length, peppery furrow shells (*Scrobicularia plana*) with 3.1–4.3 cm shell length, striped venus clams (*Chamelea gallina*) with 2.1–3.2 cm shell length, warty venus clams (*Venus verrucosa*) with 3.9–6.0 cm shell length, and grooved razor shells (*Solen marginatus*) with 5.8–12.4 cm shell length. Taking into account that, at least, 100 g of dry weight was necessary for each sample to undertake the analytical methods, adult specimens of the same species were pooled together per sampling year. At least, 500 g of wet flesh for each species were analyzed for each sampling campaign.

In the laboratory the bivalves molluscs samples were washed with distilled water to clean them of attached sand/silt. Then, their soft tissues were dissected, weighed, frozen at -20 ºC, and the next day, freeze-dried for 24 h, using a freeze-dryer module; finally the dehydrated sample was weighed, crushed and homogenized.

2.2. Analytical method

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 of polonium. Then, the sample was digested with concentrated HNO_3 and H_2O_2, and if a 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 pore filter. This HCl solution was transferred to a teflon beaker and about 0.1 g of ascorbic acid salt was added as a reducing agent. 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. Alpha spectrum analysis was performed by using Alpha Analyst software. The decay corrections were appropriately applied to the calculation of ^{210}Po and ^{209}Po activities. High chemical yields (>70%) were achieved in the determinations carried out by alpha-particle spectrometry [53].

The radioanalytical method accuracy was validated was validated by the analysis of certified reference materials (CRM) provided by the International Atomic Energy Agency (IAEA-437, IAEA-330 and IAEA-414).

To measure the gamma-ray emitting radionuclides, lyophilized samples were weighted and put into 80 ml sample containers, sealed, and sit for at least 4 weeks prior to the counting in order to reach secular equilibrium between ^{226}Ra, ^{222}Rn and their decay radionuclides (^{214}Pb and ^{214}Bi). ^{210}Pb activity was determined by its gamma emission at 46.5 keV, ^{226}Ra activity was estimated from the 295 and 351 keV γ-rays emitted by its daughter isotope ^{214}Pb. ^{40}K was estimated through 1460.8 keV emission. The absolute efficiencies of the detectors were determined using Canberra LabSOCS software based on Monte Carlo code in order to take into account the effect of self-absorption of low energy gamma-rays within the sample [54]. The spectra were analyzed using Canberra Genie 2000 gamma software v3.2.

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. The main gamma-ray detector was a low-background Canberra high-purity germanium (HPGe)

GR-6022 reverse electrode coaxial detector with 60% relative efficiency, surrounded by a 10 cm thick high-purity lead shield.

The validation of the gamma-ray spectrometry analyses was based on the successful participation on several intercomparison exercises promoted by ICRM working group related to efficiency calibration and coincidence-summing correction [55,56]. It was also determined the Minimum Detectable Activity (MDA) of system ^{40}K, ^{137}Cs, ^{210}Pb, ^{226}Ra, obtaining respectively 33 Bq/kg, 3 Bq/kg, 16 Bq/kg, and 5 Bq/kg.

2.3. Statistical analyses

Statistical analysis was carried out using Statistica 10.0 software for Windows. Correlation, factorial and cluster analysis were carried out in order to establish potential correlations between the activity concentrations of radionuclides and dose, well as relationships between the studied sampling sites.

3. Results and discussion

3.1. Radioactivity concentrations

Average, minimum and maximum activity concentrations of ^{40}K, ^{210}Pb, ^{234}Th, and ^{210}Po in bivalve molluscs in the sampling locations are presented in Table 1. Activity concentrations at each sampling location included all species collected at that location during the two sampling campaigns. Comparing with previous studies on mussels from the Mediterranean Sea, no ^{137}Cs activity was detected in the analyzed bivalve molluscs samples, probably due to low level depositions of the radioactive fallout from the

Chernobyl nuclear accident in the study zone, and also after the Fukushima Daiichi Nuclear Power Plant accident [57].

It is worth to mention that sampling point S1 is the only one involving two different species. Under these conditions, the data dispersion registered at S1 sampling point reflects the combined effect of two different sources of activity concentration variability: natural fluctuations for a certain species and the different capacity of two species of the same animal to concentrate these radionuclides. In this sense, it is a well-known fact that the concentration factors of different species among similar mollusks for actinides and transuranides elements can vary over more than one order of magnitude [26,33,58,59].

^{40}K in bivalve molluscs ranged in average value from 255 to 558 Bq/kg d.w., and they are in the range of values reported for other coastal regions of the Earth [60]. The mean activity concentrations of ^{40}K are similar than the global average value (420 Bq/kg) [42]. Regarding ^{234}Th radionuclide, its activity concentrations ranged from 34 to 93 Bq/kg d.w., and these values are comparable to those reported in the only published study containing ^{234}Th values in marine biota [45], which was focused on samples collected near the Pacific coast of Japan.

The activity concentrations of ^{210}Po in bivalve molluscs samples ranged between 40 ± 2 and 515 ± 9 Bq kg^{-1} dw for two stations. The highest ^{210}Po activity concentration was found in the soft tissues of bivalves collected from Puerto de Benalmádena (S13). The lowest activities were determined in the samples from Punta Umbría (S5). As the accumulation of ^{210}Po in marine organisms is associated with the ingestion of food, it seems that bivalves at the stations located near 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 in the vicinity of the ports.

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. On the other hand, the dependence of results on location reflects easily in Table 1, as discussed below. For example, the activity concentrations of ^{210}Po in *Scrobicularia plana* increases from sampling location S6 to S7 by almost a factor 2, following the address of the circulation of the North Atlantic Surface Water [61] and suggesting the impact of polluted areas such as the Bay of Cadiz [62,63]. Hence, it can be understood that the concentrations of both dissolved and particulate ^{210}Po subsequently decreases as a combined effect of dilution and removal from the water column by scavenging. In this same context, the results also show a drastic increase of ^{210}Po activity concentrations in Mediterranean samples, possibly due to the previously mentioned large impact of the concentration of recreational craft harbors and high-density touristic locations in this geographical area.

The concentration of ^{210}Pb in bivalves ranged between ND (not detected or below Minimum Detectable Activity) and 73 ± 10 Bq kg^{-1} d.w. ^{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 [64]. ^{210}Po and ^{210}Pb activity concentrations measured in this study are comparable with other reported values in the literature for several world regions (see Table 2).

In this study, the $^{210}Po/^{210}Pb$ ratio was calculated due to their different chemical properties. ^{210}Po has its origin mainly through accumulation from the environment, and it is not exclusively supported from the ingrowth of ^{210}Pb. The preferential adsorption of ^{210}Po occurs on organic molecules, while ^{210}Pb is associated with inorganic fine particles [18]. 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 2).

The activity concentrations for each species of bivalve molluscs are shown in Table 3 over two sampling campaigns. ^{40}K activity concentrations were high for all species of bivalves with values close to environmental background, except for clams (*C. Gallina*) with 255 Bq kg^{-1} d.w. on average. ^{234}Th was not found or the values were too low (clams) in all samples, except for mussels (*M. Galloprovincialis*) with 126 Bq kg^{-1} d.w. as the maximum value. A similar pattern emerges for ^{210}Pb. It was not detected in some species of bivalves, and the highest value corresponds to mussels (*M. Galloprovincialis*) with 102 Bq kg^{-1} d.w.

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 306 Bq kg^{-1} d.w. and razor shells (*S. Marginatus*) with 354 Bq kg^{-1} d.w., and the lowest one to cockles (*C. Edule*) with 73 Bq kg^{-1} d.w.

3.2. Radiation dose estimation

Many bivalves are a source of food for many cultures including the Mediterranean diet, and major commercial fisheries for bivalves have long existed worldwide. Therefore, it

is essential to evaluate the radiation dose due to the consumption of seafood in the human diet. Annual ingestion doses due to the consumption of bivalve molluscs were calculated for adults using the following equation [65]:

$$E_d = A \times m \times C_f \qquad (1)$$

where E_d (Sv) is the annual effective ingestion dose of each radionuclide, A is the activity concentration of each radionuclide (Bq/kg 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). The annual intake of molluscs was obtained via the database of food consumption maintained by the Spanish Ministry of Agriculture, Food and Environment (m = 4.55 kg of bivalves of wet tissue per year per capita). The values of the dose coefficients used for ^{210}Po, ^{210}Pb, ^{40}K and ^{234}Th were $1.26 \cdot 10^{-6}$, $6.90 \cdot 10^{-7}$, $6.20 \cdot 10^{-9}$, $3.40 \cdot 10^{-9}$ Sv/Bq, respectively [65].

The annual effective doses resulting from the internal incorporation of ^{210}Po, ^{210}Pb, ^{40}K and ^{234}Th through the consumption of all of the species analyzed in this study are reported in Table 3. The obtained values calculated using the average values for activity concentration were found to range between 69-385 μSv/year. The annual ingestion doses calculated for all of the bivalve molluscs analyzed are comparable with other studies reported in the literature (see Table 2), and are within the normal range of the ingestion exposure due to natural radiation (200–1000 μSv/year) [66]. 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.

3.3. Fingerprinting based on natural radionuclides

Statistical analyses were carried out in order to determinate potential relationships between the studied variables and between the studied areas. A correlation analysis was carried out using the mean of measured activity concentrations of radionuclides, dose, size and ww/dw as variables and sampling points as cases. Table 4 shows the obtained correlations.

High positive correlations (>0.70) were obtained between size, dose and the activity concentrations of ^{210}Po, ^{210}Pb and ^{234}Th, between ^{210}Po and ^{234}Th and between dose and ^{210}Po and ^{234}Th. Size is related to maturity of the specimens; hence the accumulation of lead should increase as the age of the specimen (and its size) does. On the contrary, certain studies show that the accumulation of elements such as Cu and Mn in mollusks soft tissue decreases as the specimen size increases [67]. This apparent contradiction seems to be explained by the different mechanisms and chemical form how these elements are accumulated into the mollusk tissue.

On the other hand, the affinity of Po for the organic fraction of filtered particles (feeding particles) should explain both the significant correlation of size and Po activity concentration, and also that ^{210}Po concentrations are 5-10 times higher than those of ^{210}Pb, which should be mainly adsorbed onto the surface of inorganic particles [38–40,68]. ^{210}Pb and its daughter are easily scavenged from the water by the very abundant particles present near the shoreline where the analyzed species live and feed [69], in such a way that radioactive equilibrium is not reached in these environments and this fact reflects and becomes amplified in the biological material [37].

On the other hand, ^{210}Po has (in relative terms) the highest activity concentrations found, and it is easy to see that its effective dose rate factor per activity concentration unit is much higher than those of the other nuclides. This combination of facts explains the positive, significant correlation with dose. In this way, the concentrations of the highest contributors for effective dose, the size and the dose are positively correlated. The positive correlation with ^{234}Th is harder to explain bearing in mind both the scarce affinity of Th for biota and the scarce relative contribution of this nuclide to annual effective dose [37].

These results were corroborated using factorial analysis. Two factors were obtained with eigenvalues higher than 1 (Factor 1: 3.04; Factor 2: 2.31), explaining the 43 and the 33 % of the total variance, respectively (Table 5). The first factor, participated by size, ^{210}Po and ^{210}Pb, could indicate that the internal variability of data can be explained, on one hand, mainly by variations in size possibly associated to the maturity of the analyzed specimens leading to subsequent variations in ^{210}Po and ^{210}Pb activity concentrations. The second factor, participate positively by ^{234}Th and negatively by ^{40}K groups those variables with a negligible contribution to internal variability of data regarding the calculated effective dose rate.

Potential between the studied sampling points were determined by correlation, factorial and cluster analysis. For this purpose, statistical analysis was carried out considering the contribution of each sampling site to the total activity concentration of radionuclides as variables and radionuclides as cases. Table 6 shows the obtained correlation matrix.

Except in the case of S1 and S7, which it was correlated with the most of the studied sampling points, the main positive correlations (>0.70; $p<0.05$) were obtained between two group of sampling sites: between S1-S6 and between S8-S14. These correlations could be related with the two different areas studied in the present work: Atlantic ocean

(S1 to S7) and Mediterranean Sea (from S8 to S14). These results were corroborated by factor analysis (see Table 7). Two factors with eigenvalues higher than 1 (Factor 1: 6.83; Factor 2: 5.86) were identified. It can be said that stations S1 to S7 are the dominating characters in the first factor, while stations S8 to S14 offer the highest weights in the second factor.

In Fig. 2, the representation of Factor 1 versus Factor 2 allowed an easy evaluation of which stations had a positive contribution in each or in both factors and their degree of contribution. Sampling stations were mainly grouped in two groups, one group formed by stations located on the Mediterranean coast (S1 to S7), and another group formed by the stations located on the Atlantic coast (S8 to S14).

Finally, results from cluster analysis are shown as a dendrogram plot in Fig. 3. Two distinct station clusters, the Mediterranean type and the Atlantic type were recognized in the dendrogram based on all sampling locations. These results also agree with those obtained from PCA. Therefore, radioactivity concentrations in bivalve molluscs in the Andalusian coast give information about molluscs harvested in the Mediterranean and Atlantic zones of the littoral.

4. Conclusion

Therefore, it can be concluded that in this study related to radioactivity concentrations in different types of bivalve 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; ^{40}K; ^{210}Pb and ^{234}Th varied between 40 ± 2 and 515 ± 9 Bq kg^{-1} dry weight (d.w.) ; 121 ± 7 and 674 ± 34 Bq kg^{-1} d.w. ; ND (lower than limit of detection) and 73 ± 10 Bq kg^{-1} d.w. ; and ND and 126 ± 27 Bq kg^{-1} d.w., respectively.

The effective dose assessment to the adult population was performed and the obtained values (41–479 μSv $year^{-1}$) are comparable with other studies in the literature focused in other areas of the world and no significant differences were found. Additionally, the lifetime cancer risk was low compared with the acceptable cancer risk of 10^{-3} for radiological risk.

Finally, natural radioactivity fingerprinting, in combination with multivariate data analyses, can be used in a preliminary way to discriminate bivalve molluscs according to their geographic origins.

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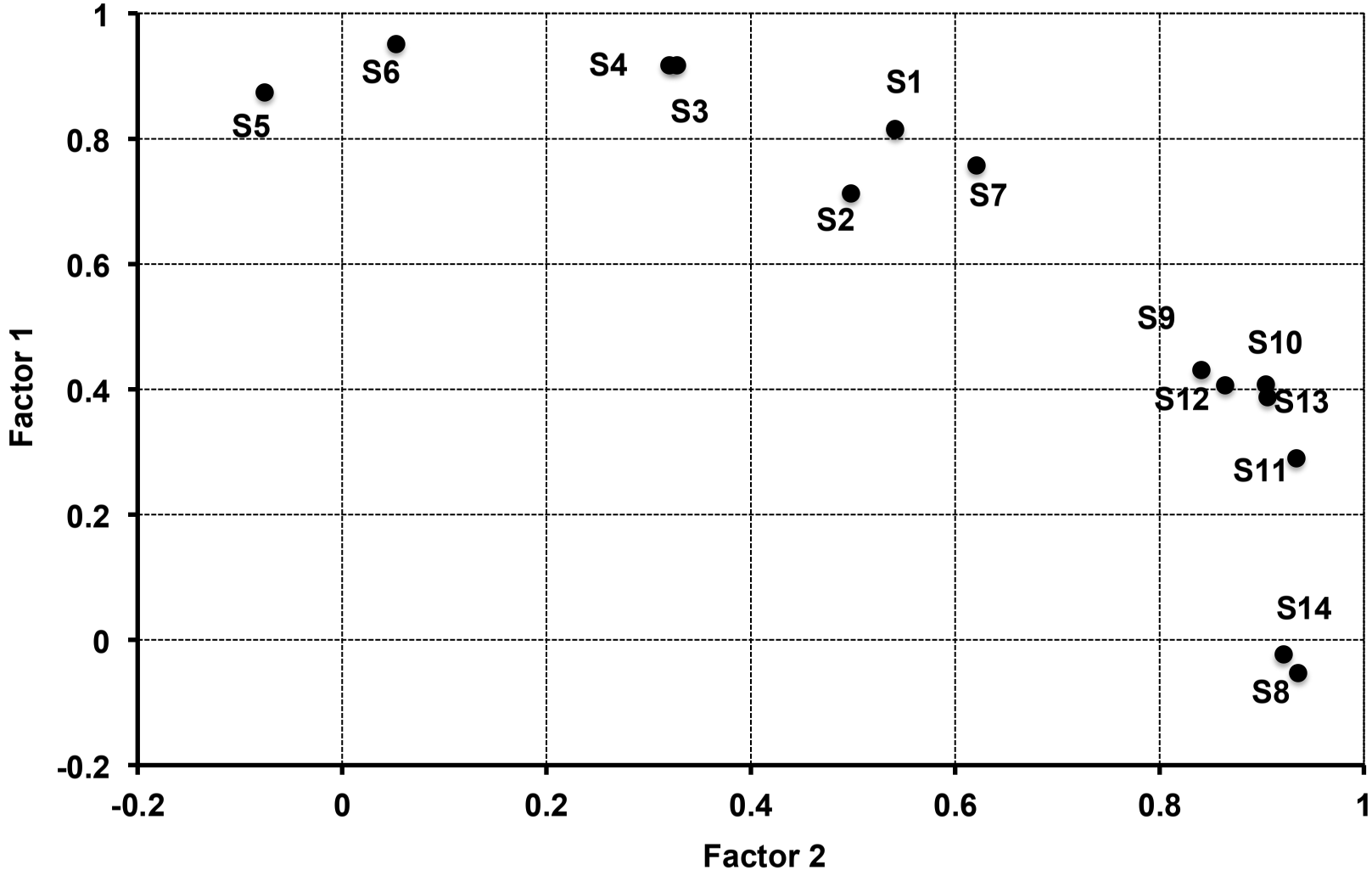
LEGEND OF FIGURES

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

Figure 2. Plot of the variables on the plane Factor 1 versus Factor 2 in the selected sampling stations.

Figure 3. Dendrogram classification of sampling stations after cluster analysis using radioactivity concentrations in bivalve molluscs.


S1
S2
S3
S4
S5
S6
S7
S8
S9
S10
S11
S12
S13
S14
Cerastoderma edule
Mytilus galloprovincialis
Donax trunculus
Scrobicularia plana
Chamelea gallina
Venus verrucosa
Solen marginatus
Sevilla
Málaga
Córdoba
Granada
Jaén
Cádiz
Huelva
Almería
Tánger
Ceuta
Mar de Alborán
Parque Natural Sierra de Andújar
Parque Natural Sierras de Cazorla, Segura y las...
Parque Nacional de Doñana
Parque Nacional de Sierra Nevada
Parque Natural Los Alcornocales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Factor 1
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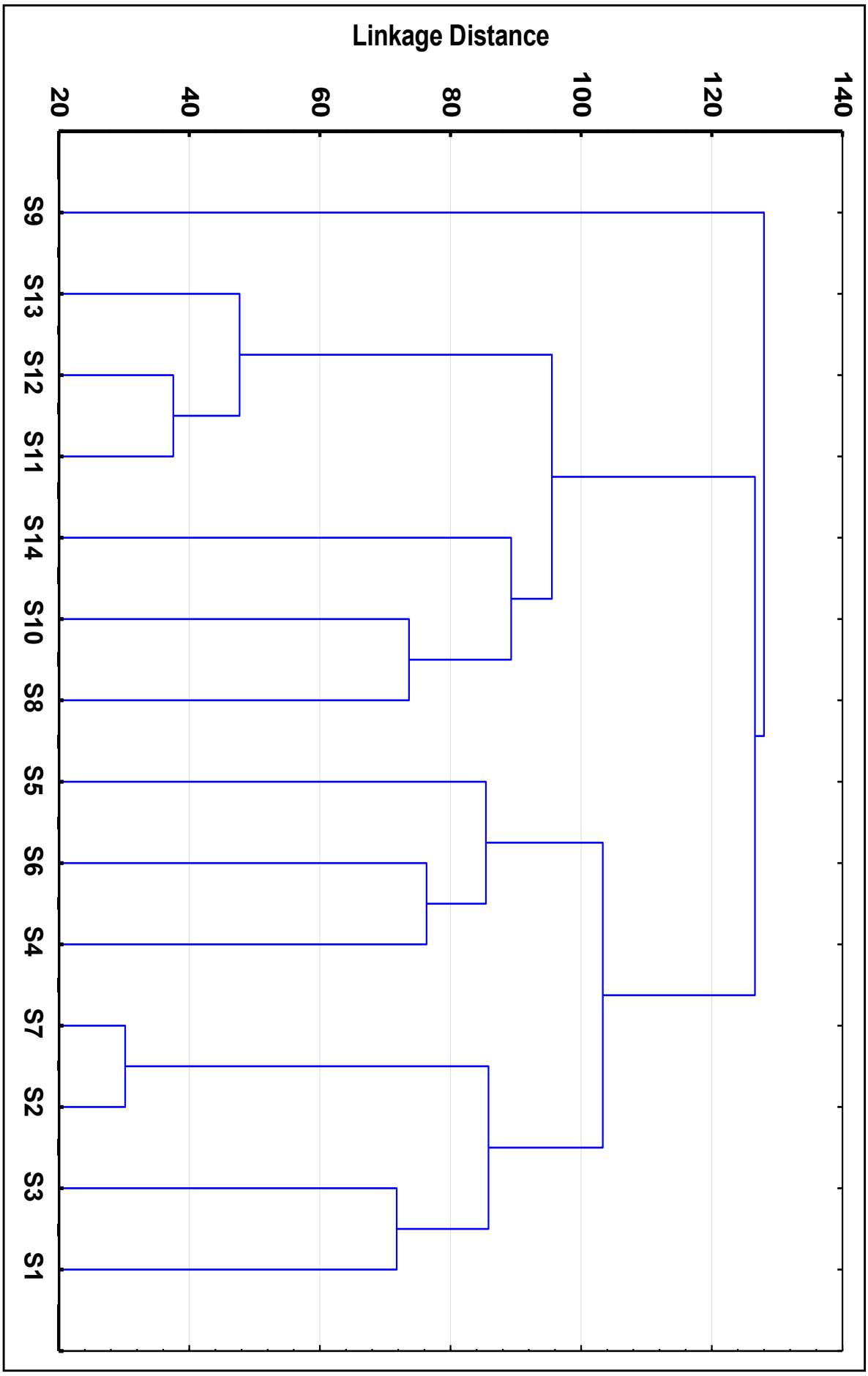
Linkage Distance
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S1

Table 1.

Activity concentrations of radionuclides (Bq/kg d.w.) and annual ingestion dose for bivalve molluscs samples in the study area over two sampling campaigns.

	^{210}Po		^{40}K		^{210}Pb		^{234}Th		ww/dw (%)	E_d (µSv/year)
	min-max	**average**	**min-max**	**average**	**min-max**	**average**	**min-max**	**average**		
S1-Río Guadiana	70-371	214	461-643	552	<16.0	<16.0	<14.0	<14.0	16.6-19.8	69.0-385
S2-Isla Cristina	161-234	196	356-645	496	31.0-47.0	39.0	<14.0	<14.0	17.0-17.1	180.21
S3-Barra del Terrón	108-181	142	399-674	558	<16.0	<16.0	<14.0	<14.0	17.1-18.3	115-163
S4-Desembocadura Río Piedras	44.0-196	116	339-521	430	<16.0	<16.0	<14.0	<14.0	15.5-16.7	41.0-172
S5-Punta Umbría	38.0-94.0	66.0	427-533	468	5.00-31.0	18.0	<14.0	<14.0	16.8-17.4	50.0-86.0
S6-Caño de Sancti Petri	46.0-88.0	67.0	399-577	488	<16.0	<16.0	<14.0	<14.0	18.6-20.9	52.0-99.0
S7-Río Barbate	179-268	222	375-624	498	11.0-44.0	24.0	<14.0	<14.0	18.7-20.0	198-301
S8-Getares	40.0-460	239	290-487	366	25.0-73.0	53.5	24.0-122	64.5	16.5-16.6	77.0-417
S9-Bahía de Algeciras (Ensenada de Getares)	144-404	270	121-419	255	<16.0	<16.0	26.0-42.0	34.0	18.2-19.3	158-390
S10-Bahía de Algeciras (Espigón de San Felipe)	170-196	183	238-553	389	18.0-34.0	26.0	24.0-44.0	34.0	19.9-20.5	205-220
S11-La Línea	124-406	260	275-371	315	17.0-51.0	35.5	<14.0.0	<14.0	16.1-18.8	133-429
S12-Puerto de Marbella	368-472	417	345-497	416	24.0-102	60.0	14.0-72.0	38.5	15.5-16.0	382-389
S13-Puerto de Benalmádena	290-515	407	407-477	440	15.0-46.0	25.5	38.0-88.0	59.5	16.7-19.1	336-479
S14-Caleta de Vélez	302-335	317	294-419	366	17.0-31.0	24.0	60.0-126	93.0	16.8-17.7	295-319

Table 2.

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})
[65]	UK	103–3124	-	-	-
[66]ide	Turkey	52–1344	6–167	3-25	-
[67]	Italy	75–223	2–25	4-62	96–466
[68]	Portugal	102-759	2.6-45	18-51	-
[69]	France	203	20	10-15	-
[64]	Turkey	53-1960	6-135	4-137	-
[40]	Slovenia	51-106	2.7-3.0	17-111	8.5
[70]	Croatia	22-207	2.8-9.3	6-31	53-497
[71]	Turkey	26-280	1-23	8-24	0.2-3.3
[72]	Korea	240	-	-	19-189
This work	Spain (Andalusia)	40-506	17-92	4-16	41-479

Table 3.

Activity concentrations of radionuclides (Bq/kg d.w.) and annual ingestion dose for different species of bivalve molluscs averaging over two sampling campaigns.

	^{210}Po		^{40}K		^{210}Pb		^{234}Th		ww/dw (%)	E_d (μSv/year)
	min-max	average	min-max	average	min-max	average	min-max	average		
Cockles (*C. Edule*)	70.0-76.0	73.0	567-643	605	<16.0	<16.0	<14.0	<14.0	16.6	69.0
Razor shells (*S. Marginatus*)	337-371	354	461-537	499	<16.0	<16.0	<14.0	<14.0	19.8	385
Mussels (*M. Galloprovincialis*)	40.0-515	306	275-645	400	15.0-102	41.2	14.0-126	59.7	17.0	304
Clams (*D. Trunculus*)	18.0-196	108	339-674	485	5.00-31.0	18.0	<14.0	<14.0	17.0	105
Peppery furrow shells (*S. Plana*)	46.0-268	144	375-624	493	11.0-44.0	24.0	<14.0	<14.0	19.6	163
Clams (*C. Gallina*)	144-404	270	121-419	255	<16.0	<16.1	26.0-42.0	34.0	18.8	274
Clams (*V. Verrucosa*)	170-196	183	238-553	389	18.0-34.0	26.0	24.0-44.0	34.0	20.2	213

Table 4.

Correlation matrix of studied variables.

	Size	**ww/dw**	**Dose**	**^{210}Po**	**^{40}K**	**^{210}Pb**	**^{234}Th**
Size	1.00	-0.35	**0.75**	**0.76**	-0.14	**0.75**	**0.70**
ww/dw		1.00	-0.18	-0.27	0.05	-0.42	-0.20
Dose			1.00	**0.99**	-0.39	0.62	**0.71**
^{210}Po				1.00	-0.39	0.62	**0.71**
^{40}K					1.00	-0.25	-0.65
^{210}Pb						1.00	0.53
^{234}Th							1.00

Table 5.

Results of the factorial analysis (considering activity concentrations, size, dose and ww/dw as variables and sampling points as cases). Correlations greater than 0.70 ($p<0.05$) are significant (shown in bold).

	Factor 1	Factor 2
Size	**0.85**	0.31
ww/dw	-0.70	0.27
Dose	0.66	0.64
^{210}Po	**0.71**	0.60
^{40}K	0.02	**-0.85**
^{210}Pb	**0.82**	0.24
^{234}Th	0.47	**0.78**
Eigenvalue	3.05	2.31
Variance	44	33

Table 6.

Correlation matrix of sampling points (considering the contribution of each sampling point to the total activity concentration of each radionuclides as variables and radionuclides as cases). Correlations greater than 0.70 ($p<0.05$) are significant (shown in bold).

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
S1	1.00	**0.78**	**0.97**	**0.97**	0.57	**0.83**	**0.94**	0.39	**0.87**	**0.81**	**0.71**	**0.77**	**0.84**	0.52
S2		1.00	**0.71**	**0.70**	**0.76**	0.57	**0.94**	0.53	0.58	**0.73**	**0.78**	**0.86**	0.65	0.26
S3			1.00	1.00	0.68	**0.94**	**0.86**	0.20	**0.74**	0.67	0.53	0.60	0.69	0.36
S4				1.00	0.68	**0.94**	**0.86**	0.18	**0.74**	0.66	0.52	0.59	0.69	0.35
S5					1.00	**0.77**	0.65	0.05	0.16	0.32	0.26	0.37	0.19	-0.19
S6						1.00	0.69	-0.02	0.51	0.46	0.27	0.34	0.45	0.14
S7							1.00	0.55	**0.81**	**0.86**	**0.84**	**0.90**	**0.84**	0.48
S8								1.00	0.66	**0.86**	**0.91**	**0.82**	**0.77**	**0.81**
S9									1.00	**0.92**	**0.85**	**0.83**	**0.98**	**0.86**
S10										1.00	**0.96**	**0.93**	**0.97**	**0.84**
S11											1.00	**0.98**	**0.93**	**0.78**
S12												1.00	**0.91**	0.67
S13													1.00	**0.87**
S14														1.00

Correlations greater than 0.70 ($p<0.05$) are significant (shown in bold)

Table 7.

Results of factorial analysis in sampling locations. Correlations greater than 0.70 ($p<0.05$) are significant (shown in bold).

	Factor 1	Factor 2
S1	0.54	**0.82**
S2	0.50	**0.71**
S3	0.33	**0.92**
S4	0.32	**0.92**
S5	-0.08	**0.87**
S6	0.05	**0.95**
S7	0.62	**0.76**
S8	**0.94**	-0.05
S9	**0.84**	0.43
S10	**0.90**	0.41
S11	**0.93**	0.29
S12	**0.86**	0.41
S13	**0.91**	0.39
S14	**0.92**	-0.02
Eigenvalue	6.83	5.86
Variance (%)	49	42