
A study of the bioavailability of ^{90}Sr , ^{137}Cs , and $^{239+240}\text{Pu}$ in soils at two locations of Spain affected by different radionuclide contamination events

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Abstract. It is well known that the bioavailability of artificial radionuclides such as ^{90}Sr , ^{137}Cs and $^{239+240}\text{Pu}$ in contaminated soils depends on the source term origin of the contamination. Although the behaviour of the mentioned radionuclides in the soil is also influenced by the time passed from the contamination event and the characteristics of the contamination receiving soils. The objective of the present work is to analyse the different bioavailability and possible chemical-physical associations of ^{90}Sr , ^{137}Cs , and $^{239+240}\text{Pu}$ in soils located in different Spanish ecosystems (Almeria and Cáceres provinces) by application of a sequential extraction procedure based on the NIST standard sequential extraction protocol. The resulting fractions obtained are: a) water soluble and exchangeable, b) associated to organic matter, and c) residual fraction. They will be studied jointly with the polluting sources (deposit of nuclear fallout-50s and 60s, Palomares accident in 1966 and the cesium release by Acerinox in 1998) in each ecosystem to interpret the observed behaviour of radionuclides.

1. INTRODUCTION

The bioavailability of artificial radionuclides in soils depends on the characteristics of the source, time passed from the contamination event and climatic conditions. The main sources of man-made radionuclides in different localities of Spain are: (a) global fallout in the 50s and 60s; (b) the Palomares accident in 1966, in which plutonium and americium were released; and (c) the radiocaesium release by Acerinox in 1998. Chernobyl fallout was not taken into consideration because in Spain it was negligible compared to global fallout [1]. To analyze the effect on the bioavailability of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ of the various sources we selected two ecosystems affected by each to a different degree – Bazagona and Palomares, located in Cáceres and Almería provinces respectively, and separated by more than 650 km (see fig. 1). Bazagona was presumed to be affected only by global fallout. At this location a profile of soil was also collected to estimate the inventory of the deposited ^{137}Cs and ^{90}Sr , which would confirm its origin. The soil of Palomares was presumed to be in principle affected by all three sources – global fallout, the Palomares accident, and the Acerinox release. Indeed, it was one of the few places in Spain affected by the last event, as can be seen in fig. 1. In both ecosystems, surface soil (0-5 cm) was collected and the bioavailability of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ was determined by means of a sequential extraction procedure based on the NIST standard extraction protocol [2]. Three fractions have been considered: exchangeable (extracted with MgCl_2), bound to organic matter (extracted with NaClO), and residual (extracted with $\text{HF} + \text{HNO}_3$).

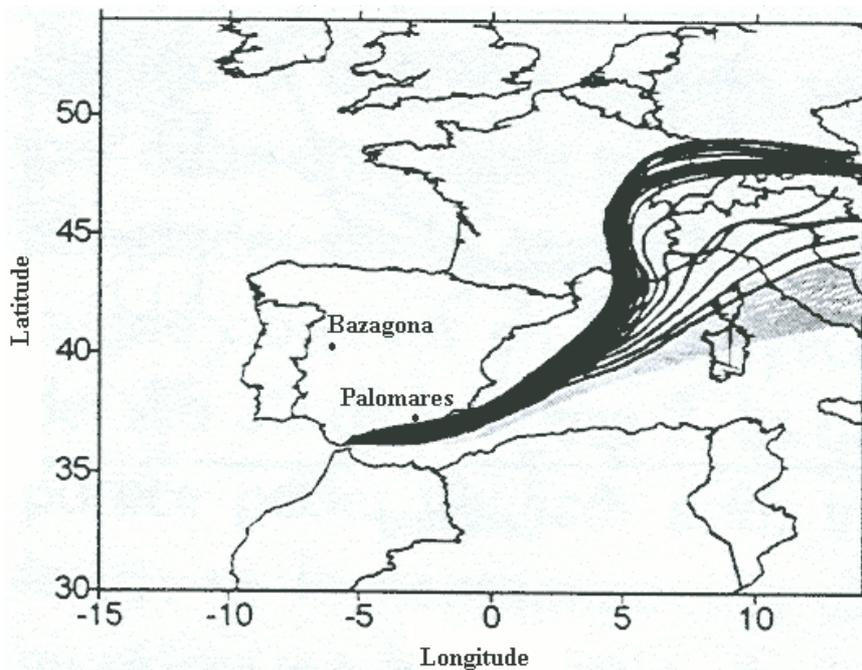


Figure 1. Wind trajectories after the Acerinox release of ^{137}Cs [3].

2. MATERIALS AND METHODS

2.1 Sequential extraction

The sequential extraction procedure is based on the NIST standard sequential extraction protocol [2]. Three fractions have been obtained:

- Exchangeable, extracted with MgCl_2 0.4M with a liquid-soil ratio of 15:1 at room temperature for 4 h.
- Bound to organic matter, extracted with NaClO 5% at pH 8.5 with a liquid-soil ratio of 15:1 at room temperature for 2 h.
- Residue: this was acid digested with HNO_3 and HF .

After each extraction, the liquid phase was separated from the solid phase by vacuum filtration through Whatman 42 filter paper and then through a $0.47\ \mu\text{m}$ membrane filter. The filter was then calcined at $400\ ^\circ\text{C}$ and added to the residue before the following extraction.

2.2 Radionuclide determination

All fractions were evaporated to dryness and the residues were put into 71 mm diameter, 30 mm deep, Petri dishes for gamma spectrometric assay. This was carried out using an n-type germanium detector with a 25% relative efficiency, a 1.87 keV resolution for the 1332 keV ^{60}Co peak, and a peak-to-Compton ratio of 57.5:1. The detector was coupled to a Compton effect suppressing device [4], which permits a better determination of the ^{137}Cs activity level since it reduces the contribution of the equipment's background that is largely due to the Compton scattering of photons from ^{40}K present in the samples. The reduction is by a factor of 2 in the 661.6 keV energy region of the ^{137}Cs emission.

After their gamma spectrometric analysis, the soil samples were calcined at 600 C to eliminate the organic matter prior to the ^{90}Sr radiochemical separation [5]. A second stage included acid digestion and precipitation of strontium and barium as nitrates. This precipitate was dissolved in distilled water, and iron and other multivalent elements precipitated out as hydroxides. With these elements removed from the solution, strontium was then precipitated out at pH 8 as SrCO_3 onto a 5 cm diameter striated planchet. The recovery was determined by gravimetry. Once ^{90}Sr - ^{90}Y equilibrium had been reached, the sample was measured in a low background gas flow proportional counter (Canberra model 2401).

The procedure used for the determination of plutonium is based on an optimization of various methods proposed by other authors [6, 7]. The soil samples were calcined at 600 C, and acid digested with HF and HNO_3 . For the extraction, Fe was added to the solution, and the plutonium was coprecipitated with iron hydroxide. The iron and plutonium were reduced by adding hydrazine, with which plutonium passes to Pu (III). The plutonium valence was adjusted to IV by adding HNO_3 and NaNO_2 , followed by separation in a column with Dowex 1x8 resin or AG 1x2 [6]. The samples were passed through in HNO_3 8M to retain the plutonium and thorium. Thorium was eluted from the column with concentrated HCl, and plutonium with a combination of dilute HCl and hydroxylamine. The alpha sources were prepared by coprecipitation with NdF_3 [8] and electrodeposition [6]. The alpha spectrometric analyses were carried out using silicon detectors with a mean efficiency of 23.2%, and a resolution of 38.7 keV for a source-detector distance of 6 mm.

3. RESULTS AND DISCUSSION

Table 1 lists the activity levels of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ from the total fraction of the soils from Bazagona and Palomares. As can be seen, the greatest difference between the two soils was in the $^{239+240}\text{Pu}$ content because of the plutonium released in the Palomares accident in 1996. The ^{90}Sr contents were similar, suggesting that global fallout is their common origin. The ^{137}Cs content was higher in Bazagona than in Palomares, suggesting that the release of radiocaesium from Acerinox might not have made a significant contribution to the ^{137}Cs deposited in the soil because the direction of the wind was as shown in fig. 1, and the activity level of ^{137}Cs in the air of Palomares (890 mBq/m^3) was lower than in some locations of France (200-2430 Bq/m^3) and Italy (140-1700 Bq/m^3) [3].

Table 1. Activity levels of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$, in Bq/kg d.w., detected in surface soil (0-5 cm) in Bazagona and Palomares.

Location	^{137}Cs (Bq/kg)	^{90}Sr (Bq/kg)	$^{239+240}\text{Pu}$ (Bq/kg)
Bazagona	21.7 ± 1.6	1.00 ± 0.14	0.210 ± 0.016
Palomares	8.2 ± 0.3	1.16 ± 0.22	11400 ± 1200

In order to verify the global fallout origin, in Bazagona the soil profile of ^{137}Cs and ^{90}Sr was also determined (fig. 2). The maximum activity for ^{137}Cs was detected in the surface layer, but for ^{90}Sr was deeper due to the different mobility of caesium and strontium in soil [9, 10]. To estimate the total inventory deposited in the soil, we fitted the experimental data to an exponential function that decreases with depth:

$$I(z) = I_{\infty} (1 - e^{-\alpha z}) \quad (1)$$

where $I(z)$ is the cumulative inventory in Bq/m^2 down to depth z , I_{∞} is the total inventory to infinite depth in Bq/m^2 , α is the reciprocal of the relaxation length in cm^{-1} , and z is the linear depth. The results of the fit for ^{137}Cs and ^{90}Sr in the Bazagona soil were:

$$I(^{137}\text{Cs}) = (6.725 \pm 0.024) (1 - e^{-(0.202 \pm 0.03)z}) \quad \chi^2 = 0.0014 \quad (2)$$

$$I(^{90}\text{Sr}) = (6 \pm 4) (1 - e^{-(0.015 \pm 0.011)z}) \quad \chi^2 = 0.0082 \quad (3)$$

Considering the total inventory in the soil, the $^{137}\text{Cs}/^{90}\text{Sr}$ ratio is (1.1 ± 0.7) . Given the associated uncertainty, this ratio is coherent with the value of 1.66 for global fallout at the latitude of Spain [9, 11].

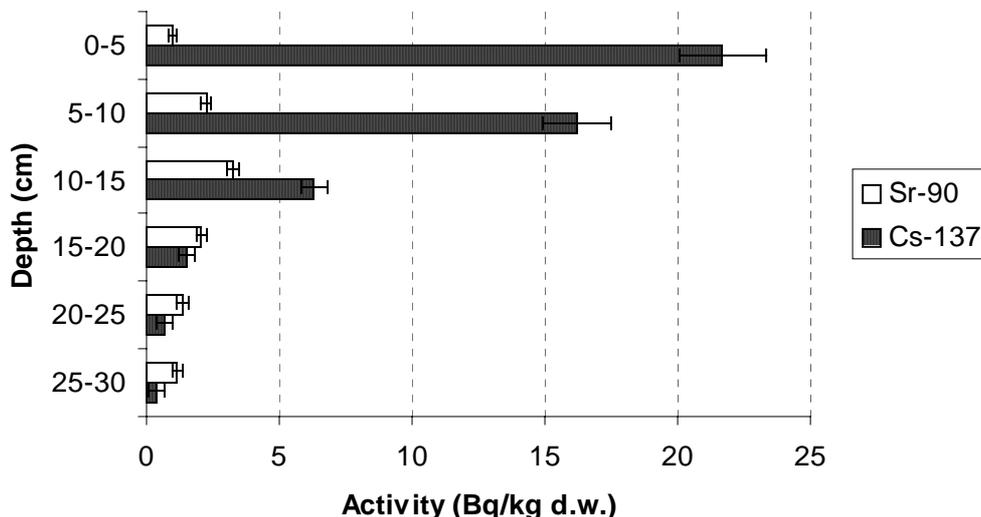


Figure 2. ^{137}Cs and ^{90}Sr activity levels, in Bq/kg d.w., in the profile of soil from Bazagona.

Table 2 lists the percentages of the total activity of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ detected in each fraction considered in the sequential extraction procedure. The results of the speciation for ^{137}Cs and ^{90}Sr are the same for both soils – most is found in the residual fraction, the percentages in the fractions extracted with MgCl_2 and NaClO being beneath the detection limit of 0.028 and 0.020 Bq for ^{137}Cs and ^{90}Sr respectively. This suggested that the ^{137}Cs source was the same for the two soils. The percentage of ^{137}Cs bound to the organic matter fraction is coherent with the low percentage of radiocaesium that binds to humic and fulvic acids, which are a significant component of the organic matter of soil [12, 13]. For $^{239+240}\text{Pu}$, the exchangeable fraction was the least important in both soils. Whereas in Bazagona these isotopes were mainly bound to organic matter, as found by other authors [12, 13, 14], in Palomares they were mainly detected in the residual fraction. This different association is probably due to the chemical form of plutonium incorporated to each soil. In Palomares, the plutonium was spread as the result of conventional chemical explosions destroying the two H-bombs, whereas that of global fallout was spread mainly as the result of nuclear explosions with far higher temperatures involved.

Table 2. Percentages of ^{137}Cs , ^{90}Sr , and $^{239+240}\text{Pu}$ detected in exchangeable (extracted with MgCl_2), bound to organic matter (extracted with NaClO), and residual fractions in surface soil from Bazagona and Palomares. DL = detection limit.

Fraction	Bazagona			Palomares		
	^{137}Cs	^{90}Sr	$^{239+240}\text{Pu}$	^{137}Cs	^{90}Sr	$^{239+240}\text{Pu}$
MgCl_2	DL	DL	0.92 ± 0.19	DL	DL	$(9.4 \pm 1.7) \cdot 10^{-3}$
NaClO	DL	DL	61 ± 4	DL	DL	0.36 ± 0.05
Residue	98 ± 5	116 ± 25	38 ± 5	100 ± 6	81 ± 28	100 ± 11

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