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Temporal Evolution of Natural and Man-Made Radioactivity Levels in Milk Samples: Dosimetry Implications

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Atmospheric nuclear weapons tests, especially those of the late 1950s and early 1960s, released great amounts of man-made radioactive materials into the environment. As fallout, they became incorporated into waters, soils, and vegetation, and from these passed into the different levels of the trophic chain (Unscear, 1982). The ingestion of contaminated foods is hence one of the routes of uptake of potentially dangerous radionuclides for man, and, of these foods, dairy products are of particular significance because of their importance in human diets. Of the radioactive fallout contaminants, there currently still persist those of relatively long half-lives, such as ^{137}Cs and ^{90}Sr whose physical half-lives are 30.07 and 28.78 years, respectively. There have therefore been frequent studies of the concentration of these radionuclides and of their temporal evolution in milk, as well as of their transfer along different pathways (Shukla et al., 1994), (Mück, 2003). The present study centered mainly on analyzing the temporal evolution over the period 1990-1999 of the ^{40}K, ^{137}Cs, and ^{90}Sr activity levels in samples of cow and goat milk collected in two zones of the region of Extremadura, Spain. These zones have been almost exclusively affected by historic fallout from atmospheric nuclear blasts. The objectives were, on the one hand, to analyze the importance on these levels of such factors as the type of animal producing the milk, the Mediterranean climate of the zones, and how that climate conditions dairy farming management practices, and, on the other, to attempt to identify, superposed on the cited historic fallout, releases into the environment from operations of the Almaraz Nuclear Power Plant (CSN, 2001).

MATERIALS AND METHODS

The region of Extremadura, which has an area about 46100 km^2, is located in Western Spain bordering Portugal. The four dairy farms used for the samples were in the townships of Azuaga (AZ1), Granja de Torrehermosa (GT1), Almaraz (AL2) and Romangordo (RO2). The townships of AZ1 and GT1 are separated by approximately 160 km from the towships of AL2 and RO2. The samples from the first three sites (AZ1,GT1, and AL2) were of cow milk, and those from RO2 were goat milk. The climate in both zones is of a Mediterranean type with continental features and a certain oceanic influence from the Atlantic. The dairy farms identified as AL2 and RO2 are in the vicinity of the Almaraz Nuclear Power Plant

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(ANPP). This consists of two pressurized light-water reactors (PWR) units, which came on line in 1981 and 1983, with a nominal capacity of 930 MWe.

Each month, 5 liter samples of whole milk were collected at each of the four sites. They were evaporated to dryness at 90°C, and the residues were triturated and calcined at 400°C. This procedure considerably reduces the samples' volume and eliminates much of the organic matter present, whereas the loss of ^{137}Cs by volatilization is negligible. Finally, the samples were put into 190 cm^3 cylindrical capsules for gamma spectrometric analysis using HPGe detectors. After this analysis, the samples were again calcined, this time at 600°C for 24 hours, in order to eliminate all the organic matter prior to the selective extraction of radiostrontium. The method used (HASL, 1976) consisted of retaining the strontium in the form of chloride in an anion resin, avoiding interference from calcium with an EDTA solution. The radiostrontiums were then eluted with NaCl aq., and finally precipitated as $SrCO_3$ onto a 5 cm diameter striated steel planchet. The beta emissions of the precipitate were then measured in a gas-flow proportional counter. The radionuclides ^{40}K and ^{137}Cs were assayed using a high resolution, low background gamma spectrometer consisting of a coaxial n-type intrinsic germanium detector with a relative efficiency of 25.6%, and a resolution of 1.85 keV and a peak-Compton ratio of 57:1 for the 1332.5 keV ^{60}Co emissions. The photopeaks that were systematically analyzed were that of ^{40}K at 1460.7 keV with an absolute intensity of 10.7%, and that of ^{137}Cs at 661.7 keV with an absolute intensity of 85.1%. For the measurement of the ^{90}Sr activity, a gas-flow proportional counter was used previously calibrated as a function of source thickness with a set of ^{90}Sr + ^{90}Y standards, obtaining a beta efficiency at zero thickness of 32%.

RESULTS AND DISCUSSION

Table 1 lists the mean values and standard deviations (S.D.), and the maximum and minimum values of the ^{40}K, ^{137}Cs, and ^{90}Sr activity levels in the milk samples collected at the four locations.The table also gives the percentages of samples whose artificial activities were above the detection limit (the percentages for ^{40}K are not given because net activities were determined in 100% of the cases). The mean activity levels detected for ^{40}K are similar to those reported by other workers in different parts of the world: 47690 ± 1740 $Bq\cdot m^{-3}$ (Lloyd et al., 1973); 44110 ± 16020 $Bq\cdot m^{-3}$ (Shukla et al.,1994). In the same sense, applying the correspondence between milk's natural potassium concentration and its ^{40}K activity to the obtained activity values, the estimated natural potassium concentration in all the samples of milk analyzed is within the range 1.18 - 2.78 $g\cdot L^{-1}$. This is again coherent with the ranges reported in the literature: 1.74 ± 0.06 $g\cdot L^{-1}$ (Voors and Van Weer, 1991); 1.54 ± 0.14 $g\cdot L^{-1}$ (Lloyd et al.1973). The measured values of ^{40}K activity, and the corresponding estimates of the natural potassium concentration in the milk, are practically equal for the four dairy herds, independently of the species involved.

Table 1. Statistics of the ^{40}K, ^{137}Cs, and ^{90}Sr activity levels determined in the milk samples from the 4 locations studied.

Sampling site	(AZ1)	(GT1)	(AL2)	(RO2)
Kind of milk	Cow	Cow	Cow	Goat
$^{40}K \pm$ SD ($Bq \cdot m^{-3}$)	48314 ± 6101	48030 ± 5021	46840 ± 6186	48729 ± 7614
Range ($kBq \cdot m^{-3}$)	32.4 – 62.3	39.7 – 62.3	33.6 – 64.0	35.0 – 68.9
$^{137}Cs \pm$ SD ($Bq \cdot m^{-3}$)	16 ± 5	18 ± 7	17 ± 9	67 ± 33
Percentage A>LID (%)	36	26	45	98
Range ($Bq \cdot m^{-3}$)	9 - 29	6 - 32	8 - 50	67 – 160
$^{90}Sr \pm$ SD ($Bq \cdot m^{-3}$)	25 ± 13	24 ± 8	46 ± 26	270 ± 106
Percentage A>LID (%)	100	98	99	100
Range ($Bq \cdot m^{-3}$)	10 - 78	7 - 49	9 - 132	100 – 560

The measured ^{137}Cs and ^{90}Sr activity levels are similar to the values reported by other workers in different parts of the northern hemisphere: (Imanaka and Koide, 1990), (Pommé et al, 1998), (JRC, 1997). As one observes in Table 1, there were substantial differences between the activities of both ^{90}Sr and ^{137}Cs depending on whether the samples were cow milk or goat milk. In particular, the goat milk activity levels were systematically higher than the cow milk levels. In the case of ^{137}Cs, this behaviour was apparent both in the percentage of samples that possessed activities above the detection limit -- the AZ1, GT1, and AL2 (cow milk) percentages were very similar to each other but notably less than the RO2 (goat milk) percentage -- and in the mean values of those activities -- lower by approximately a factor of 4 in AZ1, GT1, and AL2 than in RO2. Similarly, the mean levels of ^{90}Sr activity for AZ1, GT1, and AL2 were 6 to 11 times lower than the mean activity for the samples collected at RO2. These results clearly reflect the difference in the efficiency with which the metabolisms of the two species of dairy animals incorporate these two artificial radionuclides. This is described by the IAEA (IAEA,1994) in its summary of transfer factors fm($d \cdot L^{-1}$), which are systematically less in cow milk than in goat milk. The said transfer factors in that report are similar in range for these two radionuclides, although they are slightly less for ^{90}Sr than for ^{137}Cs (IAEA, 1994). As these transfer factors are calculated as the quotient between the activity concentration of the corresponding radionuclide in the milk ($Bq \cdot L^{-1}$) and that in the amount of feed ingested daily by the animal ($Bq \cdot d^{-1}$), can be deduced the fact that the analysed milk samples had systematically greater activities of ^{90}Sr than of ^{137}Cs is a consequence of radiostrontium also being present to a greater proportion than radiocaesium in the diet of the animals of the study. Indeed, this is what it has been found in measurements of samples of grass (Baeza et al, 2001) and shrubs (Baeza et al, 1999) collected in the proximity of the Almaraz Nuclear Power Plant

Figure (1) shows the temporal evolution of the ^{40}K, ^{137}Cs, and ^{90}Sr activity levels measured in the different milk samples over the period 1990-1999. To quantify this evolution, a linear regression of the logarithms of the activity levels of the three radionuclides for each sampling site as a function of time was performed, starting from the beginning of the sampling campaign T_0 with the aim

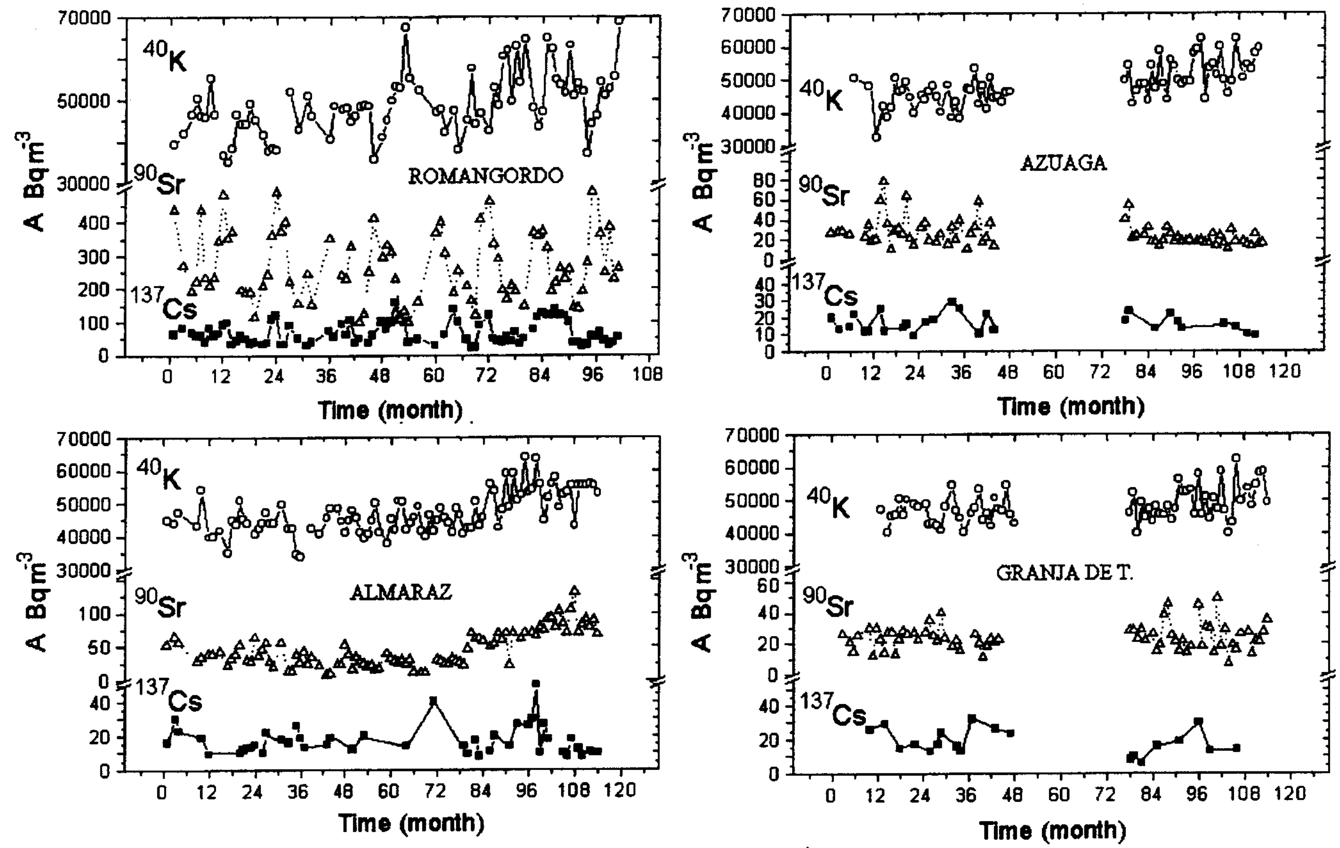

Figure 1. Monthly activity levels of ^{40}K, ^{137}Cs, and ^{90}Sr measured in the milk samples collected in the four locations studied

Table 2. Standard test of the null hypothesis H_0: b = 0 vs the alternative H_1: b ≠ 0. The test regions are the negative and positive 5% (total 10%) tails of Student's t distribution with N-2 degrees of freedom (DF).

Nuclide	Site	Temporal interval	DF	Statistic |t|	critical |t| at 0.1 level	Parameter b (month^{-1})
	GT1	1990 - 1999	65	3.1	1.68	$(1.1 \pm 0.3)\cdot 10^{-3}$
^{40}K	AZ1	1990 - 1999	68	6.8	1.68	$(2.5 \pm 0.3)\cdot 10^{-3}$
	AL2	1990 - 1999	94	6.8	1.68	$(2.3 \pm 0.3)\cdot 10^{-3}$
	RO2	1991 - 1999	78	5.0	1.68	$(2.5 \pm 0.5)\cdot 10^{-3}$
	GT1	1990 - 1999	18	1.7	1.75	$-(5.2 \pm 3.0)\cdot 10^{-3}$
^{137}Cs	AZ1	1990 - 1999	26	0.8	1.71	$-(1.3 \pm 1.6)\cdot 10^{-3}$
	AL2	1990 - 1999	43	0.7	1.68	$-(1.2 \pm 1.8)\cdot 10^{-3}$
	RO2	1991 - 1999	78	0.1	1.68	$(2.8 \pm 17.8)\cdot 10^{-4}$
	GT1	1990 - 1999	65	0.1	1.68	$(1.0 \pm 1.1)\cdot 10^{-3}$
	AZ1	1990 - 1999	67	3.4	1.68	$-(4.3 \pm 1.3)\cdot 10^{-3}$
^{90}Sr	AL2	1990 - 1999	91	5.2	1.68	$(8.9 \pm 1.7)\cdot 10^{-3}$
	RO2	1991 - 1999	77	0.04	1.68	$-(9.8 \pm 15.2)\cdot 10^{-4}$
	AL2	1990 - 1995	51	4.5	1.68	$-(1.4 \pm 0.3)\cdot 10^{-2}$
	AL2	1995 - 1999	46	10.3	1.68	$(3.3 \pm 0.3)\cdot 10^{-2}$
	RO2	1991 - 1995	41	1.9	1.68	$-(7.1 \pm 3.8)\cdot 10^{-3}$
	RO2	1995 - 1999	42	1.7	1.68	$(6.9 \pm 4.0)\cdot 10^{-3}$

of estimating the corresponding slopes.

$$Ln(A_i) = Ln(a) + b\cdot(t_i - T_0) \qquad (1)$$

Nevertheless, before assigning any significance to these values, a null hypothesis test to the data for N-2 degrees of freedom was applied, where N is the number of activity levels above the detection limit for each radionuclide and each source of the milk samples. The null hypothesis H_0 is b = 0 versus the alternative H_1, b≠0. Hence, if the null hypothesis (H_0) is rejected, i.e., the value of Student's t statistic is greater than the critical t for the confidence level considered, one can accept the statistical validity of the positive or negative value obtained for the slope. Table 2 gives the results of the application of the cited test, and the values of the slope corresponding to each radionuclide, sampling site, and time interval considered. With respect to the temporal evolution of ^{40}K, one sees from Table 2 that the hypothesis test confirms that the alternative hypothesis (H_1) is accepted at a 90% confidence level for all four sampling sites. The positive trends observed in the ^{40}K activity levels are therefore statistically significant, i.e., there is an increase in the potassium concentration in all the milk samples analyzed, independently of the dairy species. This is readily seen in Figure (2) in which we present box-and-whisker diagrams for the mean annual ^{40}K activity levels detected at the four sampling sites. The reason for this type of result could be a steady improvement in the diet of the animals, with a concomitant increase in the concentration of potassium in the milk.

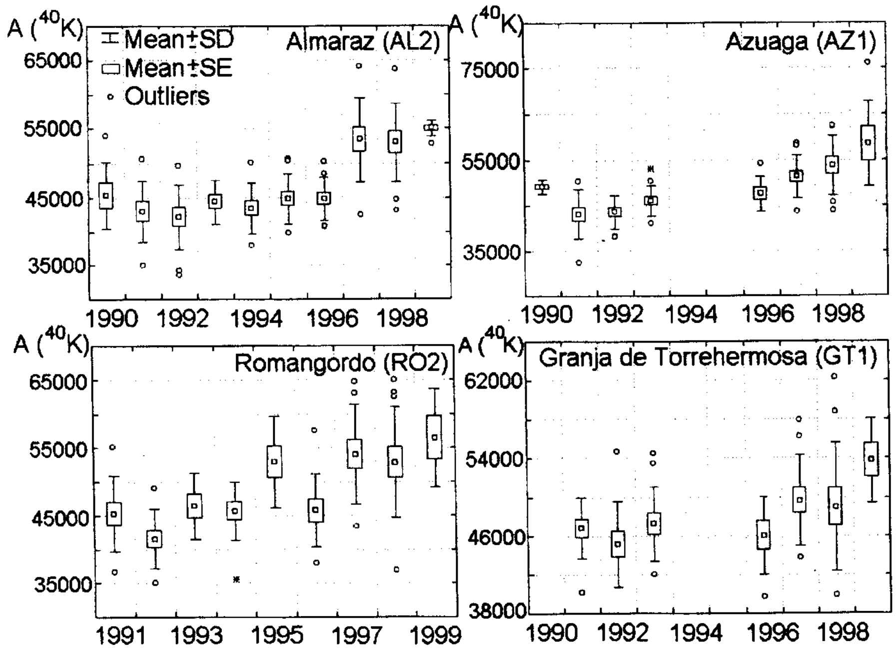

Figure 2. Box-and-whisker diagrams of the annual ^{40}K activity levels in Bq· m^{-3} measured in the milk samples of each location.

Table 2 also gives the results of the linear regression for the logarithms of the ^{137}Cs activity levels versus time. One sees that the slopes are negative for the three sampling sites producing cow milk, AZ1, GT1, and AL2, i.e., these activity levels decline over time in this type of milk, while the slope is positive for the goat milk samples from RO2, implying an increase of ^{137}Cs activity levels over time. Nevertheless, these results can not be assigned any statistically significance because the hypothesis test did not allow the null hypothesis to be rejected at a 90% confidence level. There are two reasons for this result. One is the smallness of the values of the detected activities, these being below the detection limit in a great percentage of the cow milk samples. The other is the relative importance of the variability of the measured activities superposed onto any possible trend. This variability is at least partially due to the climatological characteristics of Mediterranean ecosystems which encourage the feeding régime of the dairy herds of the present study to be changed over the course of the year from intensive to semi-extensive. For the case of ^{90}Sr, the slopes of the linear regressions of the logarithms of the activity levels versus time (see Table 2) are statistically significant and negative for the AZ1 samples, and statistically significant and positive for the AL2 samples. No trend was observable, however, for the other two sites, GT1 and RO2, for which the null hypothesis could not be rejected. Using the value of the negative slope, b, found in the AZ1 milk samples, it is possible to calculate the effective half-life, T_{ef}, from the expression $T_{ef} = - \ln 2/ b$.

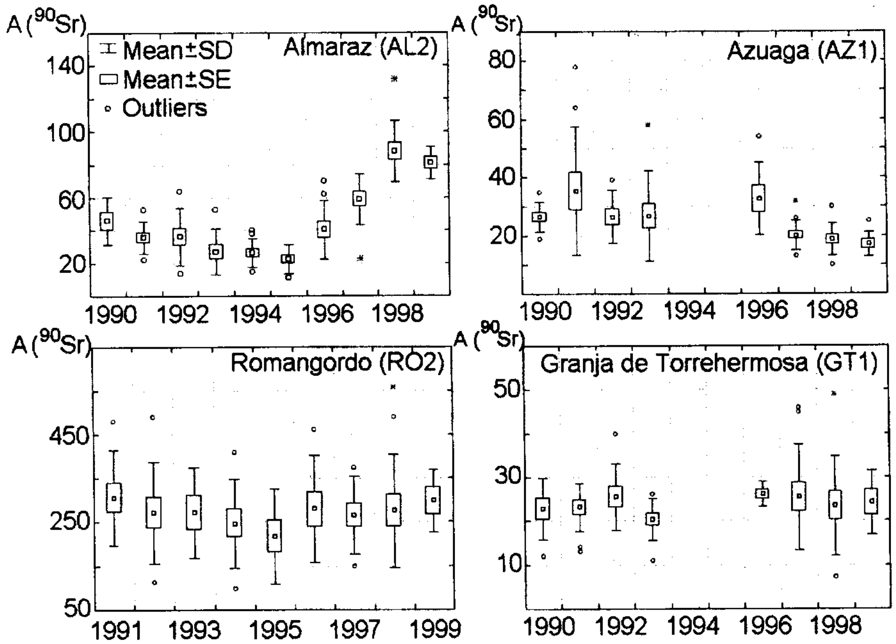

Figure 3. Box-and-whisker diagrams of the annual ^{90}Sr activity levels in $Bq \cdot m^{-3}$ measured in the milk samples of each location.

The result for ^{90}Sr is 13.4 ± 4.1 yr which coincides with that found in other studies, 10.1 - 14.8 yr (Friedli et al, 1991), in which the presence of this radionuclide is also primarily due to fallout from atmospheric nuclear weapons tests. Figure (3) shows the temporal evolution of the mean annual radioactive levels of ^{90}Sr for the four sampling sites, confirming visually the validity of the results of the hypothesis test, i.e., the steady de-activation of the AZ1 samples, and the increase in activity of the AL2 samples beginning in 1995. To a lesser degree, beginning with that same year there is also an increase in the activity present in the goat milk from the sampling site RO2 which, together with AL2, could in principle be affected by the radioactive impact on its environment of the operation of the Almaraz Nuclear Power Plant. Therefore, the trend followed by the milk samples collected in those two sites, AL2 and RO2, was analyzed considering separately the measurements before 1995 and those after 1995. The corresponding results are also listed in Table 2. At a 90% confidence level, there is a steady re-activation of ^{90}Sr in the milk samples from these two sites.

As it has been mentioned above, the two sampling zones have a Mediterranean climate characterized by the alternation of wet and dry seasons. Since this affects the availability of pasture, it also conditions the diet of the dairy herds considered in the present study, and may be reflected in a seasonality of the detected activity levels. One would expect any effect to be especially notable for the goat milk,

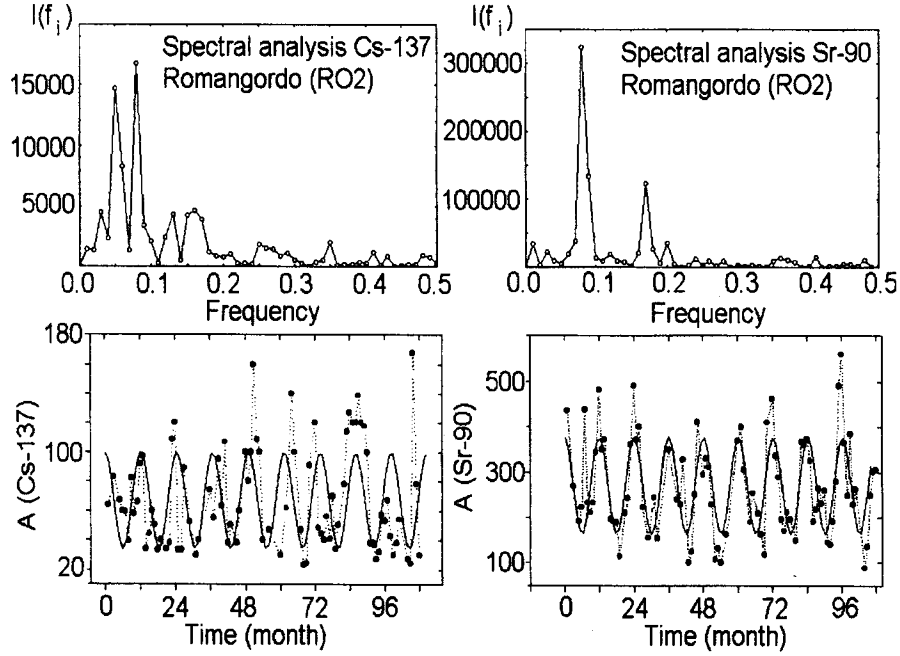

Figure 4. Top. Periodograms of the activity levels of ^{137}Cs and ^{90}Sr measured in the goat milk samples from RO2. Bottom. Plot of the simple sinusoidal model superposed on the measured monthly activity levels in Bq· m^{-3} of ^{137}Cs and ^{90}Sr.

since the management of the goat herds is fundamentally extensive. Therefore, it was verified whether such an effect existed in the activity levels of ^{90}Sr and ^{137}Cs measured in the goat milk samples from RO2. The two time series corresponding to these radionuclides were put under a Fourier analysis, which considers the series to be a superposition of sinusoidal components of different frequencies. It was thus obtained a periodogram for each series. This is a plot of the intensity $I(f_i)$ versus f_i, where $f_i = i/N$ corresponds to the i-th harmonic of the fundamental frequency N^{-1}, above the Nyquist frequency of 0.5 cycles per sampling interval (Hewitt, 1992). Figure (4) top show the periodograms for the activity levels of ^{137}Cs and ^{90}Sr measured in the RO2 goat milk samples. As can be seen, the periodograms reflect the existence of a clear seasonality with dominant frequencies of $f_{Cs\text{-}137} = 0.083$ and $f_{Sr\text{-}90} = 0.081$, corresponding to periods of 12.0 and 12.3 months, respectively. Hence, one of the causes of the observed variability in the activity levels is the alternation of wet and dry seasons typical of Mediterranean climates which not only conditions whether or not there is any pasture but also the capacity of transfer of radionuclides to the pasture from the soil (Baeza et al, 2001). Figure (4) bottom show the temporal evolution of the ^{137}Cs and ^{90}Sr activity levels, and, superposed, the simple periodic sinusoidal evolution resulting from using for each of these series the period obtained from the Fourier analysis, adjusting the mean value and the amplitude of each sinusoidal curve to the mean activity levels and standard deviations given in Table 2 for ^{137}Cs and ^{90}Sr, respectively.

The mean values of the effective dose equivalent due to ^{137}Cs and ^{90}Sr incorporated by ingestion of the milk from the dairy herds studied were calculated. It was considered two characteristic populations, identified in the following as children and adults. The results are summarized in Table 3.

Table 3. Effective dose equivalent of ^{90}Sr+^{137}Cs ($mSv \cdot y^{-1}$) from ingestion of milk.

	Equivalent effective dose ^{90}Sr+^{137}Cs ($mSv \cdot y^{-1}$) ± ε	
Sampling site	**Childs**	**Adults**
Granja de T. (GT1)	$(2.9 \pm 0.8) \cdot 10^{-4}$	$(8.1 \pm 2.4) \cdot 10^{-5}$
Azuaga (AZ1)	$(3.1 \pm 1.4) \cdot 10^{-4}$	$(8.4 \pm 3.8) \cdot 10^{-5}$
Almaraz (AL2)	$(5.2 \pm 2.6) \cdot 10^{-4}$	$(1.4 \pm 0.8) \cdot 10^{-4}$
Romangordo (RO2)	$(2.9 \pm 1.2) \cdot 10^{-3}$	$(8.2 \pm 3.0) \cdot 10^{-4}$

As can be seen, the dose incorporated by consuming goat milk from RO2 is greater in both populations (children and adults) than by consuming cow milk from any of the other three sites, AZ1, GT1, or AL2. This was an expected result since the ^{90}Sr and ^{137}Cs activity levels were substantially greater in the goat milk than in the cow milk samples. Also the effective incorporated dose is greater for the children than for the adults consuming the same types of milk because of the different activity-to-dose conversion factors for these two populations (IAEA, 1996). Finally it has to be noted that, in all the cases studied, the effective doses incorporated by the two populations are far below the limit established in current Spanish legislation of 1 $mSv \cdot y^{-1}$ (BOE, 2001), which is derived from a transposition of the European guidelines (DOCE, 1996). In the most unfavourable case, the dose from incorporation of ^{90}Sr and ^{137}Cs is 400 times less than legislated limit.

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