^{226}Ra AND ^{210}Pb RELATIONSHIP IN SOLID WASTES AND PLANTS AT URANIUM MILL TAILINGS

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1. INTRODUCTION

After the uranium extraction from the ore, the waste residues (tailings) contain several radionuclides in elevated levels comparing to normal soils. Nearly all of the uranium progenies (^{230}Th, ^{226}Ra, ^{210}Pb and ^{210}Po) and the unextracted uranium fraction are present in tailings. These large quantities of tailings may provide a significant source of environmental and food chain contamination. The transfer of radioisotopes between different ecological compartments is frequently evaluated using ratios which relate the radionuclide content in one ecosystem compartment to that of another. For instance, the concentration ratio (CR), i.e., the ratio between radionuclide concentrations in tailings and plants can be evaluated. Radium-226, a long-lived alfa emitter, is a chemical analog of calcium. The ^{226}Ra uptake is similar to calcium in biological and ecological systems. The uptake of ^{210}Pb will follow the same pattern as natural lead. Plants do not require lead but in contrast they require the Ra/Ca group elements. The uptake of lead is mainly a function of the lead tolerance of the plant and the hydrogen ion concentration of the soil.

Kalin and Sharma (1982) reported that ^{226}Ra and ^{210}Pb uptake by indigenous species from inactive uranium mill tailings in Canada differ from the uptake of the elements by the same plants growing in soil. Ibrahim and Whicker (1992) reported that tailing acidity tends to enhance radionuclide availability for plant uptake. The transport of radionuclides to foliage and subsequent retention and absorption may play a role in plant contamination.

The main goal of this study is to evaluate the ^{226}Ra and ^{210}Pb relationship in tailings and plants growing at uranium mill tailings.

2. MATERIAL AND METHODS

2.1. The study area

The Urgeiriça uranium mine is located in the north of Portugal near Canas de Senhorim (Viseu). Radium extraction at the Urgeiriça mine started in 1913, moving exclusively to uranium production in 1944. The chemical treatment plant was constructed in 1951 and refurbished in 1967 (Bettencourt et al., 1990). Active mining has now ceased and it is intented to decommission the existing facilities in the near future. Tailings and fine residues from acid leaching (about 4×10^9 kg) have been deposited locally into heap covering an area of about 0.1 km^2. To minimise the dispersion of natural radionuclides into the environment, some tailings were revegetated with eucalyptus (*Eucalyptus globulus*) and pines (*Pinus pinea*). Additionally, native shrubs (*Cytisus* spp.) are growing at some of the tailings. Although tree planting and natural revegetation has covered much of the surface, several hectares are still effectively bare.

2.2. Sample preparation and analyses

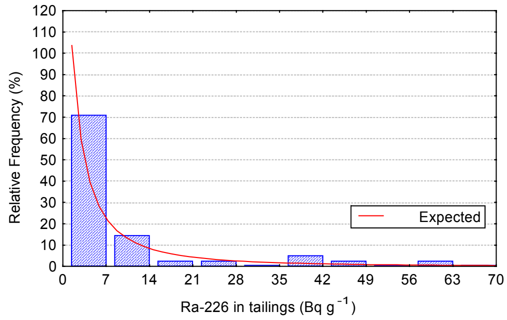
Six sampling campaigns were performed between May 1996 and February 1999. Plant and tailing (solid waste) samples from the root region of the plants were randomly collected at the tailings.

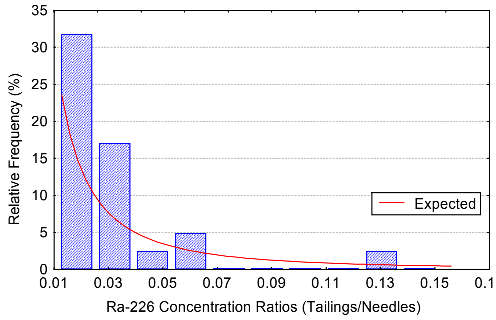
Tailing samples were dried at 40ºC, crushed, ground, homogeneized and sieved through a 1mm mesh sieve. Plants were washed to remove adhering soil particle and roots separated from the above-ground parts. The roots and the above-ground parts of the plants were air-dried and weighed. They were then dried at 110ºC, cooled and the dry weight was recorded. The dry samples were ashed at 550ºC for 8 hours in a furnace, cooled and weighed to obtain the ash weight of the samples. Aliquots of each sample (tailings ≈80 g; ashed plants:aerial parts ≈10 g and roots ≈1 g) were put into containers, hermetically sealed and left for about one month to assure the equilibrium between ^{226}Ra and its daugthers. The samples were then analysed for ^{226}Ra (through its progeny, namely ^{222}Rn and its gamma-emitting daughters) and ^{210}Pb by gamma spectrometry using, for the plant samples (aerial parts and roots), a well type detector (HpGe) with 140 cm^3 active volume and 25% relative efficiency and, for the tailings samples, two coaxial detectors (HpGe) with 160 cm3 active volume and 25% relative efficiency. The obtained spectra where analysed with the SAMPO 90 software. The systems were calibrated for several geometries using standard solutions of ^{210}Pb, ^{133}Ba and a mixed solution QCY44 from Amersham.

3. RESULTS AND DISCUSSION

3.1. Frequency distribution of ^{226}Ra and ^{210}Pb

The frequency distribution of ^{226}Ra concentrations in plant and tailing (Bq g^{-1}) and concentration ratios (CR) were examined using Kolmogorov-Smirnov test (Statistica for Windows 4.5 A Software, 1999). Data show that a normal as well as a log-normal distribution ($p > 0.05$) can not be rejected. However, the probability (p-value) that the data conform to a log-normal distribution is somewhat higher. As an illustration, the frequency distribution of ^{226}Ra in pines (roots, needles), tailings and the concentration ratios (tailing/roots and tailing/needles) are shown in Figure 1.





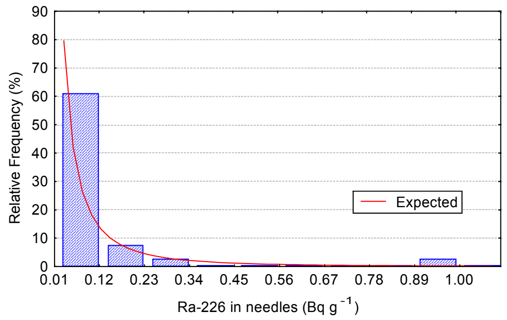
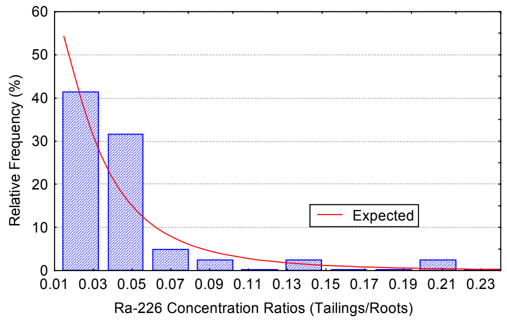


Figure 1- Frequency distribution of ^{226}Ra in pines (tailings, roots, needles and concentration ratios). The solid curve corresponds to a log-normal distribution of the values.



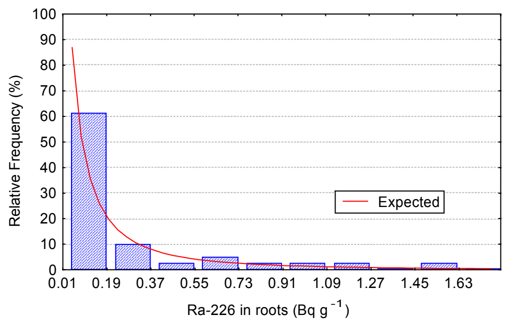
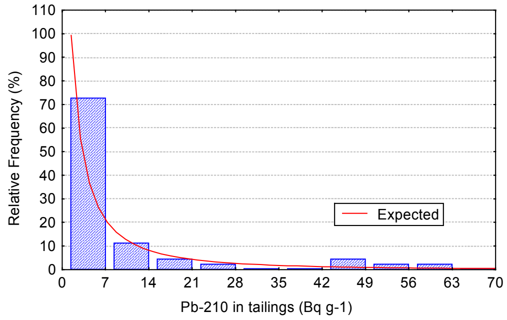
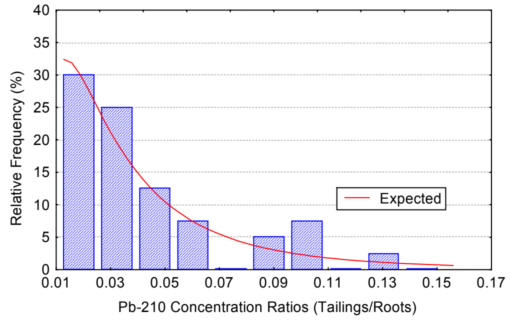


Table 1 presents the mean, median and range of concentration values for ^{226}Ra and ^{210}Pb and the corresponding concentration ratios (CR) in these samples. In general, the median and mean values are considerably different. A large range of values was observed which indicates a great variability of the data. For ^{226}Ra the great variability of the concentration ratios (CR) must be due to the lack of correlation between the tailing and plant concentrations. A comparison of the data shows that, the median ^{226}Ra activities (Bq g^{-1}) in roots (0.22) and aerial parts (0.12) for shrubs are higher than for pines (roots=0.10; needles=0.04) and eucalyptus (leaves=0.11). Consequently, the concentration ratios for shrubs are also higher by a factor of about 5. For the concentration ratios of ^{226}Ra in pines and eucalyptus the difference is only a factor of 2.

The frequency distribution of ^{210}Pb concentrations in pine and tailing (Bq g^{-1}) and concentration ratios (CR) are shown in Figure 2. Application of Kolmogorov-Smirnov test to these values shows that data follow a normal as well as a log-normal distribution ($p > 0.05$). Like observed to ^{226}Ra, the median values of ^{210}Pb in tailings, plants and concentration ratios are smaller than the corresponding mean values, which indicates a higher conformity of the data with a log-normal distribution.

A comparison of results shows that the median ^{210}Pb plant concentration values are of the same order of magnitude. The concentration ratio differences between the different plants are negligible.





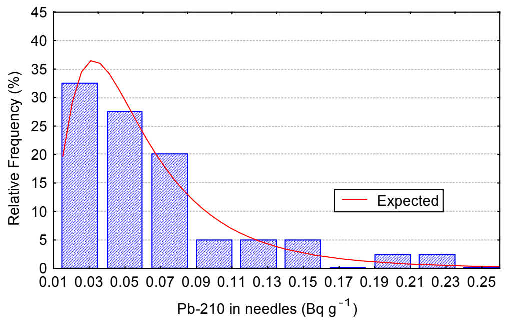
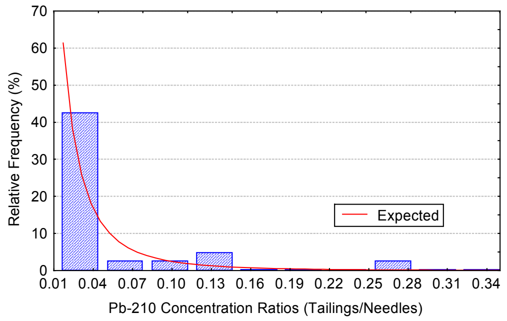


Figure 2- Frequency distribution of ^{210}Pb in pines (tailings, roots, needles and concentration ratios). The solid curve corresponds to a log-normal distribution of the values.



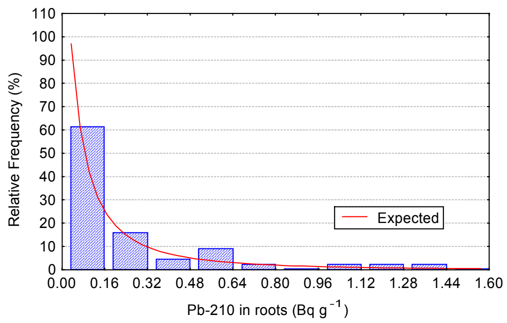


Table 1- Mean, median, range of ^{226}Ra and ^{210}Pb concentrations ($Bq\ g^{-1}$) and concentration ratios (CR) values for tailings and plants.

Species	Nº of Samples	Mean	95% Conf. Limits for Mean	Median	Range
		^{226}Ra			
Pines					
tailings	41	8.8	4.6-13.1	3.2	0.10-61.5
roots	41	0.23	0.12-0.34	0.10	0.002-1.6
needles	41	0.07	0.02-0.12	0.04	0.0002-0.99
CR (tailings/roots)	41	0.038	0.026-0.049	0.029	0.001-0.20
CR (tailings/needles)	41	0.018	0.011-0.026	0.013	0.00004-0.13
Eucalyptus					
tailings	26	14.2	6.9-21.5	3.7	0.11-57.1
leaves	26	0.26	0.11-0.42	0.11	0.004-1.7
CR (tailings/leaves)	26	0.053	0.027-0.080	0.032	0.0005-0.29
Shrubs					
tailings	22	2.3	1.0-3.6	1.6	0.11-12.6
roots	22	0.33	0.15-0.52	0.22	0.004-1.5
aerial parts	22	0.29	0.08-0.49	0.12	0.004-1.8
CR (tailings/roots)	22	0.16	0.075-0.25	0.120	0.017-1.0
CR (tailings/aerial parts)	22	0.09	0.066-0.12	0.077	0.016-0.20
		^{210}Pb			
Pines					
tailings	40	10.0	5.4-14.6	4.9	0.09-58.2
roots	40	0.26	0.15-0.36	0.12	0.005-1.4
needles	40	0.06	0.049-0.079	0.05	0.02-0.23
CR (tailings/roots)	40	0.039	0.030-0.049	0.030	0.001-0.13
CR (tailings/needles)	40	0.027	0.011-0.044	0.010	0.0005-0.28
Eucalyptus					
tailings	26	13.8	6.9-20.6	4.8	0.13-61.4
leaves	26	0.062	0.039-0.085	0.05	0.01-0.25
CR (tailings/leaves)	26	0.025	0.006-0.044	0.0087	0.0008-0.20
Shrubs					
tailings	19	3.2	1.6-4.9	3.0	0.08-15.8
roots	18	0.16	0.10-0.22	0.11	0.006-0.46
aerial parts	18	0.07	0.03-0.11	0.06	0.01-0.37
CR (tailings/roots)	18	0.063	0.041-0.084	0.051	0.015-0.15
CR (tailings/aerial parts)	18	0.046	0.016-0.077	0.025	0.004-0.25

3.2. Relationship between ^{210}Pb and ^{226}Ra

It is of interest to discuss the relationship between the two radionuclides analysed. In Figure 3 concentrations of ^{210}Pb in tailings (Bq g^{-1}) versus the ^{226}Ra concentrations in tailings (Bq g^{-1}) have been plotted. Table 2 shows the linear regression parameters. As expected the concentrations of both radionuclides are linearly related, with a regression coefficient (R) of 0.966. The y-axis intercept value is nearly zero (0.818 ± 0.467) and the slope of the line has a value of 0.960 ± 0.028. The slope value < 1 represents the ^{210}Pb/^{226}Ra activity ratio in the area and reflects a slight deficit of the progeny isotope. However, these two radionuclides seem to be close to secular equilibrium in the tailings.

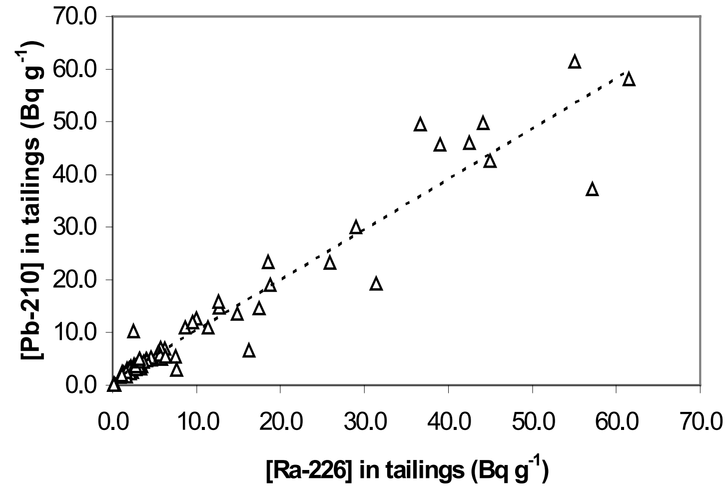
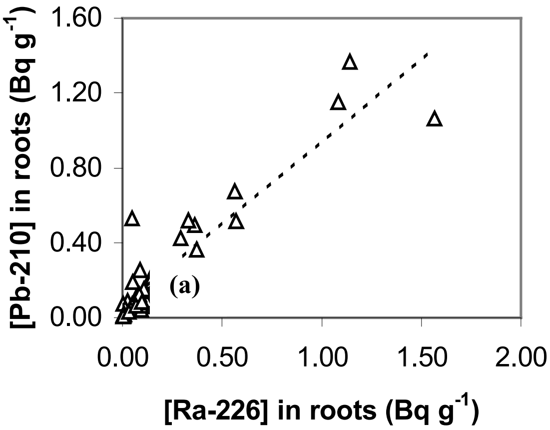


Figure 3- Relationship between ^{226}Ra and ^{210}Pb concentrations (Bq g^{-1}) in tailing samples.

The ^{210}Pb and ^{226}Ra relationship in pines, eucalyptus and shrubs were also analysed. The ^{210}Pb versus the ^{226}Ra concentrations in roots and needles (Bq g^{-1}) for pines are presented in Figures 4a and 4b respectively. An increase of ^{210}Pb concentration with the increase of ^{226}Ra concentration was observed. Both radionuclides are quite well linearly related (R = 0.923 for roots; R = 0.912 for needles). However, as before, an excess of ^{226}Ra was found with slope values of 0.881 ± 0.059 and 0.724 ± 0.056 for roots and needles respectively (Table 2). As shown in Table 2 a good correlation (R = 0.835) between both radionuclides in leaves for eucalyptus was also found. A slight correlation was observed between ^{210}Pb and ^{226}Ra in roots (R = 0.777) and aerial parts (R = 0.670) for the shrubs (Figure 5a and 5b). In this case, the ^{210}Pb/^{226}Ra activity ratios are 0.231 ± 0.043 and 0.108 ± 0.028 for roots and aerial parts respectively.

It can be seen that ^{210}Pb/^{226}Ra activity ratios decrease from pines to shrubs and eucalyptus. This indicates a clear deficit of ^{210}Pb in the plants, opposite to what was found in tailings. This deficit might be due to the lower mobility and transfer of ^{210}Pb from the tailings to the plants when compared to radium. The values found to aerial parts and roots (Table 2) show that, as expected, the mobility and transfer from tailings to aerial parts is lower than from tailings to roots. Additionally, the decreasing of the activity ratios from pines to shrubs and eucalyptus indicates a different transfer pattern between both radionuclides in these plants. This might be due to the metabolic differences between these plants. In addition, it might be considered that different plant species would exhibit somewhat different rooting depths. In general, for plants the secular equilibrium was not reached. This fact should be due to the differences on the incorporation of ^{226}Ra over ^{210}Pb in the studied plants.



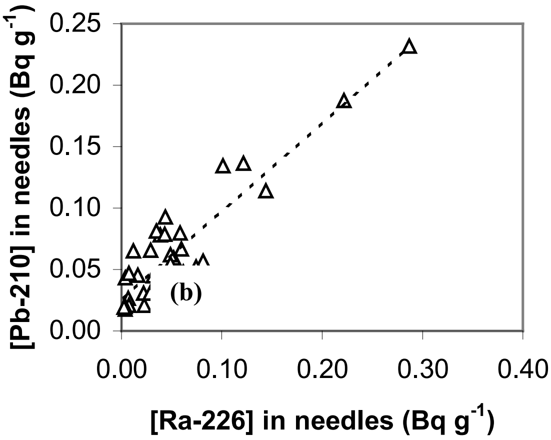


Figure 4- Relationship between ^{210}Pb and ^{226}Ra concentrations (Bq g^{-1}) in roots (a) and needles (b) to pines.

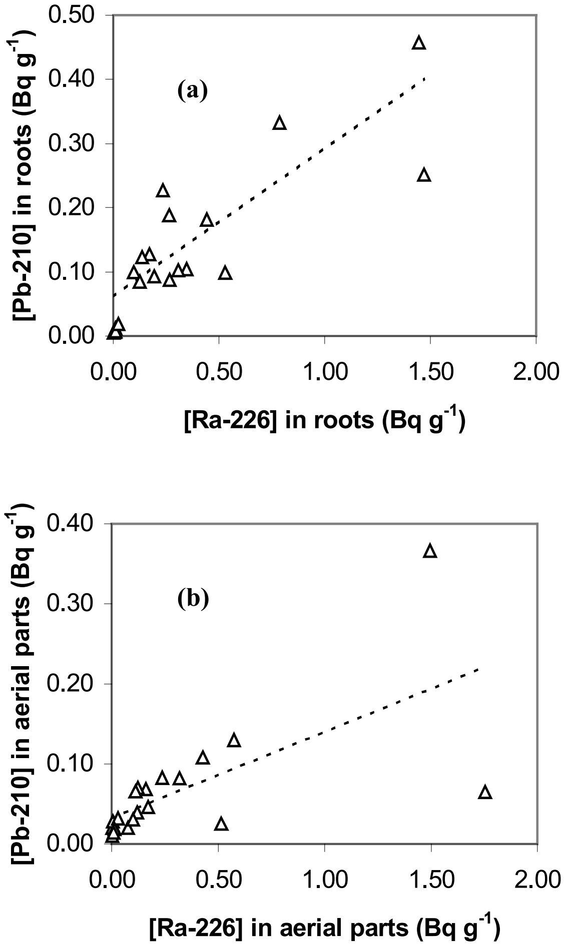


Figure 5- Relationship between ^{210}Pb and ^{226}Ra concentrations (Bq g^{-1}) in roots (a) and aerial parts (b) to shrubs.

The relationship between $^{210}Pb/^{226}Ra$ activity ratios and ^{226}Ra concentrations was also analysed. A constant relationship was observed between $^{210}Pb/^{226}Ra$ activity ratios and ^{226}Ra concentrations in tailings. However, for plants a different behaviour was found. The $^{210}Pb/^{226}Ra$ activity ratios versus ^{226}Ra concentrations in roots and needles to pines are plotted in Figure 6 (a) and (b) respectively. The curves indicate the variation of the activity ratios and can be expressed mathematically as a power function: $^{210}Pb/^{226}Ra = a\ [^{226}Ra]^{b}$. The following functions are obtained: $^{210}Pb/^{226}Ra = 0.667\ [^{226}Ra]^{-0.295}$ (R= 0.56) for roots; $^{210}Pb/^{226}Ra = 0.216\ [^{226}Ra]^{-0.595}$ (R= 0.82) for needles. Figure 7 (a) and (b) presents the $^{210}Pb/^{226}Ra$ activity ratios versus ^{226}Ra concentrations in roots and aerial parts to shrubs. As before, the curves reflect the variation of the activity ratios and can be expressed by the following functions: $^{210}Pb/^{226}Ra = 0.343\ [^{226}Ra]^{-0.256}$ (R= 0.73) for roots; $^{210}Pb/^{226}Ra = 0.105\ [^{226}Ra]^{-0.641}$ (R= 0.92) for aerial parts. The function $^{210}Pb/^{226}Ra = 0.09\ [^{226}Ra]^{-0.688}$ (R= 0.89) was obtained in leaves for eucalyptus.

These relationships show that activity ratios decrease for lower ^{226}Ra concentrations approaching to constant values for ^{226}Ra concentrations higher than about 0.1 Bq g^{-1}.

Table 2- Linear regression parameters (slope, y-interception and regression coefficients) for the ^{210}Pb and ^{226}Ra relationship in tailings and plants.

Species	Nº of Samples	Slope	Y-Intercept	Regression Coefficient (R)
Tailings	87	0.960 ± 0.028	0.818 ± 0.467	0.966
Pines				
roots	41	0.881 ± 0.059	0.063 ± 0.024	0.923
needles	36	0.724 ± 0.056	0.025 ± 0.004	0.912
Eucalyptus				
leaves	26	0.088 ± 0.012	0.031 ±0.006	0.835
Shrubs				
roots	22	0.231 ± 0.043	0.061 ± 0.023	0.777
aerial parts	22	0.108 ± 0.028	0.032 ± 0.015	0.670

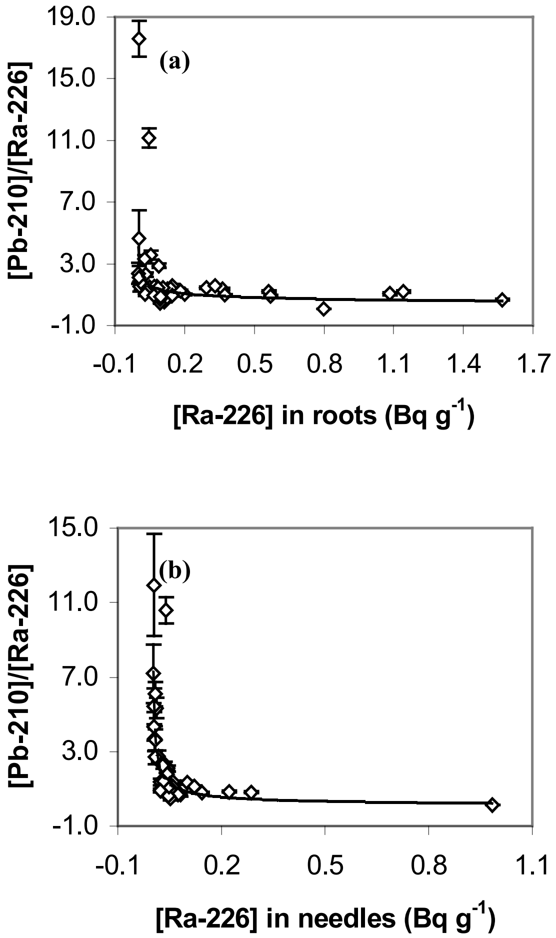


Figure 6- $^{210}Pb/^{226}Ra$ activity ratios versus ^{226}Ra concentrations in roots (a) and needles (b) for pines.

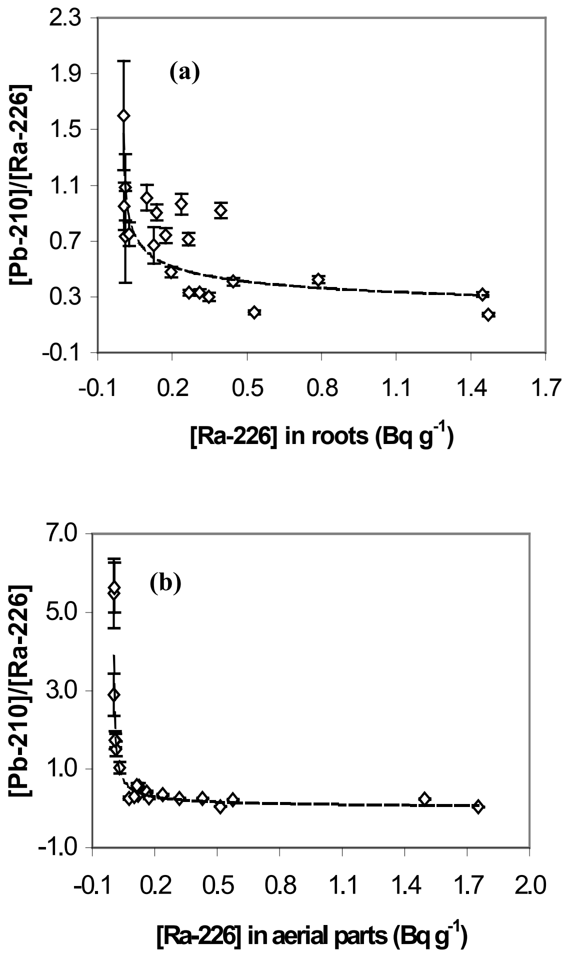


Figure 7- $^{210}Pb/^{226}Ra$ activity ratios versus ^{226}Ra concentrations in roots (a) and aerial parts (b) for shrubs.

4. CONCLUSIONS

It can be concluded that the frequency distribution of ^{226}Ra and ^{210}Pb concentrations in plants and tailings as well as the concentration ratios (CR) follow a log-normal distribution. The median ^{226}Ra concentration ratios for shrubs are higher than those obtained for pines and eucalyptus. On the other hand, the median ^{210}Pb concentration ratios are of the same order of magnitude. The ^{210}Pb and ^{226}Ra relationship in pines, eucalyptus and shrubs show a lower mobility and transfer of ^{210}Pb from the tailings to the plants when compared to the radium. The $^{210}Pb/^{226}Ra$ activity ratios decrease at lower radium concentrations in the tailings approaching to constant values for higher radium concentrations.

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