

Study of the behaviour of natural radionuclides in a Mediterranean actual system

A. Agüero and P. Pinedo

CIEMAT/DIAE, Avda. Complutense 22, 28040 Madrid, Spain

Abstract. There is a lack of information for Mediterranean climate conditions and ecosystems from the point of view of characterization of real data, to obtain parameter values to be applied in the modeling of the behavior of natural and artificial radionuclides following hypothetical releases from a radioactive waste repository. So there was designed a project dealing with the study and determination of physical, chemical and radiological parameters from local and regional data obtained in an area of the southwest of Spain where and old uranium mine was being restored.

The project, running during two years, has been financed by the National Company for Radioactive Waste Management in Spain (ENRESA) and has been coordinated by the CIEMAT Research Center with the collaboration of the Department of Physics of the Extremadura University.

Results of the project have been the characterization of the biosphere system considering meteorological, geological, and hydrological data. Chemical and physical characterization of local soils and crops associated, surface waters and sediments samples, have been considered. Radiological measurements of U, Th and Ra contents in soils, vegetables, sediments and waters have been taken.

Range of several parameter values obtained have shown good agreement with literature data published, this will permit the application of these values to the modeling issues of biosphere in the performance assessment of radioactive waste repositories under Mediterranean climate conditions, as well as for a forecasting of similar conditions that will occur in the future in other temperate areas.

1. OBJECTIVES

Main objectives of the investigation have been to characterize the area, considering climatic and meteorological conditions, geological features, hydrogeology, soils development, ecological conditions and anthropological features. These are considered under Biosphere System Description. Determination of parameter values for the transfer of uranium isotopes in the biospheric area has been performed. The methodology followed to select isotopes, sample types and sample points and materials and methods used to obtain the data for determining parameter values is described afterwards. The last part of the paper reports on examples of experimental and empirical values obtained for solid-liquid distribution coefficients in soils and sediments of the biospheric area under study.

2. BIOSPHERE SYSTEM DESCRIPTION

The area has been characterised regionally, considering an area of 10 Km of radius; and locally, considering an extension of 50 Km².

Regional climate is Temperate Mediterranean (naming type Cs) [1]. Mean precipitation in this case is in the range between 300 and 900 mm per year. There is a pronounced precipitation maximum during cooler months, summer being nearly if not absolutely dry. This feature of dry summers and wet winters classify the regional climate of the area as Mediterranean sub humid. Mean temperatures are in the range between 14 and 17 Celsius degrees. Real evapotranspiration obtained from local data is in the range between 470 and 490 mm per year.

Local geology is characterised by granites and shales. Altitudes are in the range between 400 and 500 m height. Groundwater flow, regionally, follows topographical features, mountains are the recharge zones and rivers and streams are the discharge zones. Local flows are over regional flows and constitute the hydrogeological systems of the soils developed over granites and altered surface granitic rocks.

Soils developed from granitic rocks, are classified as two types of Entisols following USDA, 1975 [2] classification, Typic Xerorthent with low depth of A horizon and B horizon absent. And Aeric Haplaquent, with an important contrast between its two horizons and high organic matter content in the surface soil. These are saturated part of the year.

Soils developed over shale materials are slightly acids and form the typical agricultural soils in the local area, parameters characterizing these soils are presented in Table 1.

Agricultural crops present in the area are mainly wheat and barley. Legume crops are not very common. Potatoes crops only represent roots, bulbs and tubers.

3. RADIONUCLIDES SELECTION

In order to perform the study under actual conditions, the isotopes selected were ^{238}U , ^{234}U , ^{230}Th and ^{226}Ra , belonging to the uranium series, and ^{232}Th and ^{228}Th from the thorium series. They have been chosen due to their presence in the mineralization of the old mine and due to their long half lives. Radionuclides movement can be observed as tracers in the soils, plants, water and sediments present in the system.

Artificial radionuclides selected, has been ^{36}Cl , ^{99}Tc and ^{233}U and stable Iodine. These were selected because they have high importance in the contribution to the dose from the analysis of international exercises of assessment of HLW disposal [3].

4. SAMPLING POINTS AND TYPE OF SAMPLES

Two sets of samples have been selected. Local samples and samples from a reduced area of aprox. 3 km² surrounding the mine.

Local samples taken are shown in Figure 1 (aprox scale 1:50000). A first field campaign was performed on June 1998. Four soil local samples were chosen (SU-1, SU-2, SU-3 and SU-4 in Figure 1), due to the different rock substrate types. Three lithologies are present in the area. Two sediment samples (SE-1 and SE-2 in Figure 1) and five water samples (A1, A2, A4, A5, A6 in Figure 1) were chosen. In the case of sediments, from the geographical point of view, and in the case of the water, to cover the main seasonal stream running in the area.

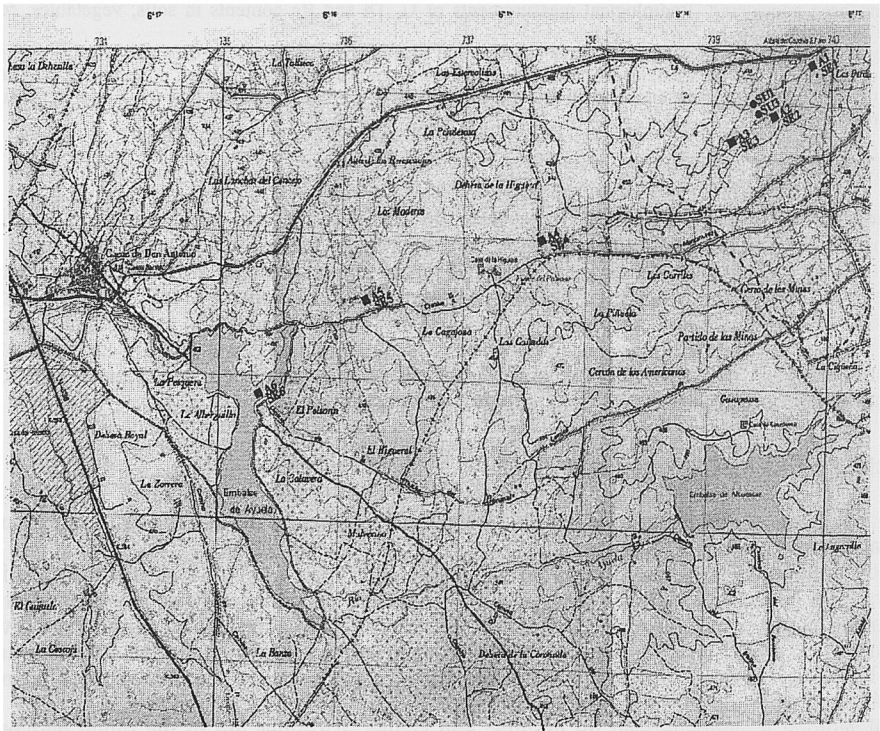
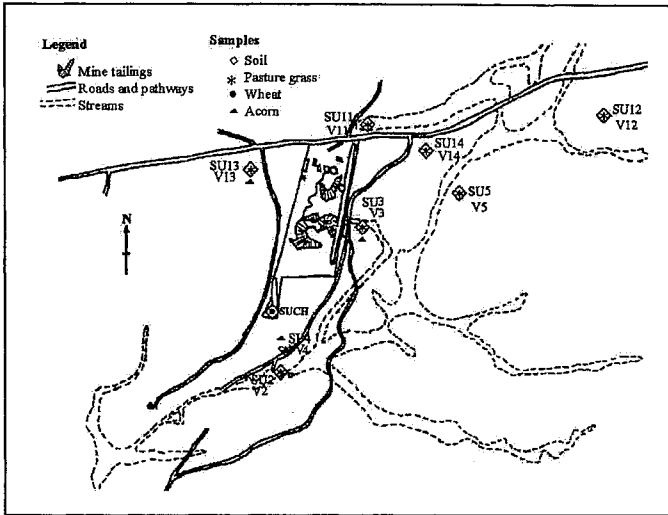


Figure 1. Local sampling points

Legend of Figure 1:

- SE-1 and SE-2 Bed load sediments before and after the mine.
- SU-1. Soil developed over porfirc granites
- SU-2. Soil developed over shales
- SU-3. Soil developed over alluvial sediments of the stream
- SU-4. Soil developed over moscovite granites
- A1, A2, A4, A5, A6: Water and suspension load mass associated

Experimental parameters measured for each local sample includes chemical composition, pH, texture, bulk density and solid-liquid distribution coefficients for the artificial radionuclides. In the case of water and sediment samples, activity concentration of each isotope and load suspension mass in water has been determined, too.



Legend:
 SU11+SU12+SU13+SU14= Composed sample soil SU1 over granites substrate.
 SU2: Soil developed over terrace sediments of the main stream.
 SU3 and SU4: Soils developed over granites substrate
 SUCH: Soil developed over granites for wheat cultures
 V11+V12+V13+V14= Composed sample of pastures V1.
 VCH: Winter wheat sample.
 V13 and V4: Acorn samples.

Figure 2. Sampling points (approx. scale 1:8000) in the area surrounding the mine.

Samples taken in the reduced area surrounding the mine have been (see Figure 2)¹ soils (5 samples), associated pasture grasses (5 samples) and acorns (2 samples) from the *Quercus rotundifolia* trees growth on the soils selected. Four sampling campaigns were performed, during a one year period, considering the four seasons of the year. Soil and pasture samples were taken in June (representing medium precipitation and moderate-low temperatures), September (dry conditions with high temperatures), December (medium precipitation and medium-high temperatures) and April (high precipitation and low temperatures). Acorn samples were taken in September and December field campaigns.

One extra sampling point of soil (SCH, presented in Figure 2) was chosen to seed Winter Wheat, in the field and in a growth chamber in the laboratory, in order to obtain soil to plant transfer factors for the natural isotopes selected.

Experimental data obtained includes texture of soil, chemical composition of soils and vegetation samples, and activity concentrations of isotopes in soils and vegetation.

5. MATERIALS AND METHODS

For each soil location in the field, is disposed a square iron frame with an area of 0.25 m². The cover vegetation, including roots, is taken, to obtain pasture samples. Soil is digged 10 cm depth and material is screening at a pore size of 2 mm. using a steel sieve, collecting approximately 5 kg. of samples. In the laboratory the soil material is screening to obtain particle size distribution of each sample, and radiochemical analysis is performed.

Vegetation samples (pasture grass and acorns) are washed in the laboratory, to remove particle soils adhered to the surface. They are dried and triturated to make the radiochemical analysis.

¹Notation to distinguish samples is SU-X for local and SUX for the reduced area.

Water samples were filtered (around 60 L. of water per sample point) *in situ* and acidulated (to avoid precipitation of radionuclides in the recipient and development of organic material) with 3 mL concentration of H_2SO_4 per litre of sample. Sediment samples have been treated similarly to soil samples described above.

The radiochemical method for soil, sediment, water and vegetation samples, followed up to the preparation of the high-resolution alpha sources was based on the chemical separation of uranium and thorium by an anionic exchange resin [4] and the subsequent electrodeposition of the source [5].

Winter wheat (*Triticum aestivum*, Yecora variety) was seeded *in situ* (SUCH sample point in Figure 2). The seed was done on April and the harvest was done in September.

A total number of 8 pots filled with soil from SUCH point in Figure 2, (40 cm. depth and 20 cm diameter) were placed in a growth chamber in the laboratory. Daily cycles were programmed, temperature, moisture and sunlight. After five months (simulating meteorological conditions corresponding to December to April in a Mediterranean climate) the growth of the wheat plants was complete. The plants were irrigated during the three first months in order to simulate rainfall at the site.

For the wheat crop samples, the Environmental Radioactivity Laboratory of CIEMAT performed the radiochemical analyses for uranium, thorium and radium; following published analytical procedures [9, 10].

Experimental values of K_d for the artificial isotopes has been obtained with the batch method, in the Laboratory of "Caracterización Hidrogeoquímica de Emplazamientos" of CIEMAT [13]. The determination have been done with a low solid/liquid relation (1/10) to obtain measurements under realistic environmental conditions. Three determinations have been obtained for each sample.

6. PARAMETER VALUES OBTAINED FOR SOLID-LIQUID DISTRIBUTION COEFFICIENTS FROM EXPERIMENTAL AND EMPIRICAL METHODS

6.1 Experimental method

The physical characterization of soils and sediments to analyse its sorption properties, is presented in Table 1 for the local samples. Bulk density has been determined from two measurements of each sampling point. Texture have been obtained from the mean of tree determinations.

Table 1. Physical characterization of the local soil and sediment samples

Substrate type	Sampling Point	SOILS				SEDIMENTS	
		Porfiric Granite	Shales	Alluvial	Moscovite Granite	SE 1	SE2
Bulk dens.	(Kg m ⁻³)	2680	2740	2650	2690	2710	2720
Texture		Loamy	Loamy	Sandy	Sandy	Sandy	Sandy

K_d values given in the following tables, for the local samples, corresponds with the average of three experimental determinations. Here are shown results for technetium and uranium.

K_d values for ^{99}Tc (TcO_4^-) are shown in Table 2. These are low (order of $10^{-3} m^3 kg^{-1}$) except for sampling point SE-2, that is one order higher, but inside the literature ranges [9].

Table 2 K_d experimental values for technetium ($7.35 \cdot 10^{-7} M = 0.073 mg/L$)

Sampling point	Initial pH	Final pH (14 d)	K_d (m ³ /kg)	σ	(IAEA, 1994) Range
SU-1	6,9	6,99	$6,4 \times 10^{-4}$	$0,5 \times 10^{-5}$	1.1E-5 - 9.E-2
SU-2	6,71	6,98	$8,9 \times 10^{-4}$	$1,0 \times 10^{-4}$	1.1E-5 - 9.E-2
SU-3	7,36	7,11	$5,2 \times 10^{-4}$	$0,5 \times 10^{-5}$	3.7E-6 - 5.E-3
SU-4	7,54	7,3	$6,0 \times 10^{-4}$	$0,7 \times 10^{-5}$	3.7E-6 - 5.E-3
SE-1	7,65	7,27	$4,9 \times 10^{-4}$	$0,3 \times 10^{-5}$	0.0 - 1.E-1
SE-2	7,75	7,29	$5,45 \times 10^{-3}$	$2,0 \times 10^{-4}$	0.0 - 1.E-1

Table 3 shows K_d values obtained for uranium (UO_2^{2+}). Two different concentrations of ^{233}U (2.11×10^{-6} and $4.45 \times 10^{-7} M$) have been used due to results obtained for the first and higher concentration,

that shows a big dispersion between samples. To avoid complexes formation or solute precipitation a lower concentration was then used.

Table 3. Experimental K_d values obtained for two initial activity concentrations of ^{233}U .

Sampling point	U-233 ($2.11 \cdot 10^{-6}$ M = 0.492 mg/L)				U-233 ($4.45 \cdot 10^{-7}$ M = 0.104 mg/L)				(IAEA, 1994) Range
	Initial pH	Final pH (14 d)	K_d (m^3/kg)	σ	Initial pH	Final pH (14 d)	K_d (m^3/kg)	σ	
SU-1	6,64	6,81	2,069	0,119	6,8	7,68	1,183	0,116	5.5E-5 – 20.
SU-2	6,47	7,11	2,505	0,094	6,77	7,85	1,432	0,154	5.5E-5 – 20.
SU-3	6,98	7,47	0,634	0,020	7,34	8,38	0,438	0,043	1.7E-5 – 9.0
SU-4	7,07	7,62	0,386	0,007	7,46	7,98	0,338	0,020	1.7E-5 – 9.0
SE-1	7,18	7,38	$7,3 \times 10^{-2}$	4×10^{-4}	7,66	7,94	$7,7 \times 10^{-2}$	$7,6 \times 10^{-3}$	2.E-2 – 1.0
SE-2	7,38	7,63	$3,6 \times 10^{-2}$	4×10^{-4}	7,6	8,02	$3,7 \times 10^{-2}$	$2,5 \times 10^{-3}$	2.E-2 – 1.0

^{233}U has been added as uranile nitrate, but the evolution of pH is in both cases towards more basic values. Experimental results shown high sorption in general, but there is a clear difference among type of samples (soils and sediments). Loamy soils (SU-1 and SU-2) show a higher sorption as it is referred in the literature [9]. Sandy soils (SU-3 and SU-4) show a lower sorption as could be expected. For sediments, values obtained fit to the typical range [9].

To explain these variations, the chemical composition of the soils and sediments have been correlated with the experimental K_d values obtained. For example, it is observed in Figure 3 a strong dependency of K_d value with the iron content (Fe_2O_3) up to around 1.8 % and, a slight dependency for higher iron content.

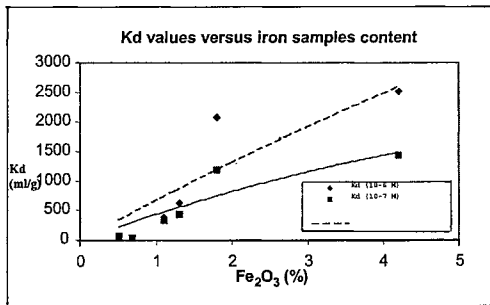


Figure 3. Relation K_d vs. Iron content of the soils and sediments regional samples.

It is observed the same tendency in both cases of uranium initial activity concentrations, although values are lower for the lower concentration indicating that increasing the tracer concentration all the possible sites for sorption are occupied.

6.2 Empirical method

From experimental basis, [10] have proposed an empirical approach to calculate K_d for radionuclides from the soil to plant transfer factors (TF) measured, on the basis of the strong correlation between TF and K_d , following the equation: $\ln K_d = a + b(\ln TF)$,

Where a is a constant and depends on the soil texture and b is equal to -0.5 .

Texture of soils of the biospheric area surrounding the mine, have been obtained. Soil to plant transfer factors mean values have been obtained from the measured concentrations in pasture and soils, of uranium, thorium and radium, from the four field sampling made. Distribution coefficients estimated from the above equation and experimental soil to plant transfer factors used, are shown in Table 4.

Table 4. Uranium, thorium and radium K_d values estimated from the empirical method.

Sampling point	Texture	Experimental I Uranium TF	K_d (m^3/kg) Uranium	Experimental Thorium TF	K_d (m^3/kg) Thorium	Experimental Radium TF	K_d (m^3/kg) Radium
SU1	Sandy	8,472E-02	2,834E-02	1,623E-01	2,048E-02	1,333E-01	2,259E-02
SU2	Loamy	1,038E-01	8,934E-02	1,473E-01	7,502E-02	1,414E-01	7,657E-02
SU3	Loamy	1,179E-01	8,383E-02	4,636E-02	1,337E-01	2,780E-01	5,461E-02
SU4	Sandy	9,371E-02	2,694E-02	2,934E-01	1,523E-02	1,300E-01	2,288E-02
SU5	Loamy	7,372E-02	1,060E-01	7,483E-02	1,052E-01	2,602E-01	5,644E-02

Value ranges obtained from the literature [9] for sandy soils for uranium ($1.7E-05 - 9.0$), thorium ($4.5E-02 - 2.0E+02$) and radium ($8.2E-4 - 3.0E+02$). For loamy soils and uranium ($5.5E-05 - 2.0E+01$), thorium (3.3) and radium ($7.4E-02 - 1.8E+04$).

7. CONCLUSIONS

K_d values obtained from the batch method, for technetium in soils and sediments local samples shown low sorption behaviour, this is according to literature data. On the other hand K_d values obtained for uranium-233, shown high sorption values, with clear dependency of type of sampled soil and iron content of the sample.

Empirical values estimated for solid-liquid distribution coefficients are not comparable directly with experimental values obtained, because the measurements have been made on different soil samples. In any case estimated K_d values are one or two orders of magnitude lower than experimental ones and are more close to the central distribution values of literature range.

K_d parameter values and other characteristic parameters (texture, density, moisture content, mass suspension load, organic matter content, soil to plant transfer factors), obtained from the study will be considered for the uncertainty analysis in Performance Assessment exercises to be performed in the future.

Acknowledgments

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References

1. Trewartha. An Introduction to Climate. 4th Edition, McGraw Hill (1968).
2. United States Soil Survey Staff (USDA), Soil Taxonomy. A Basic System of Soil Classification for Making and Interpreting Soil Survey. Agriculture Handbook. (1975)
3. Pinedo, P. and Agüero, A. Contribuyentes principales a la dosis potencial debida a almacenamientos geológicos profundos. *Radioprotección. SEPR*, (2000). N° Extraordinario Septiembre. pp. 56-58.
4. Vera Tomé, F., Jurado Vargas, M. & Martín Sánchez, A. Yields and losses at each step in preparing uranium and thorium samples for alpha spectrometry. *Applied Radiation and Isotopes*, **45**, (1994) pp. 449-452.
5. Vera Tomé, F., Jurado Vargas, M. & Martín Sánchez, A. SIMPLEX method for optimization of experiments. Application to electrodeposition in alpha spectrometry. *Nuclear Instruments and Methods in Physics Research*, **A348**, (1994) pp.183-187.
6. CIEMAT PR-X2-01. Procedimiento para la determinación de ^{230}Th en suelos. (1994).
7. CIEMAT-PR-X2-09, Procedimiento para la separación radioquímica y determinación, mediante espectrometría alfa, de uranio en aguas, suelos, sedimentos y muestras biológicas. (1996).
8. Hernández Benítez, A. I. Resultados de las determinaciones de parámetros de sorción realizadas en muestras del proyecto BIOREFS. Octubre 1999. CIEMAT internal report.
9. IAEA. Handbook of parameter values for the prediction of radionuclide transfer in temperate environment. Technical Report Series n1 364. (1994). Vienna
10. Sheppard, M. I & Thibault, D. H. Default soil solid/liquid partition coefficients, K_d s, for four major soil types: A compendium. *Health Physics*, **59**, (1990) pp. 471-482.