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Hyperfine and radiological characterization of soils of the province of Buenos Aires, Argentina

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Abstract. The depth profile concentration of both natural and anthropogenic gamma-ray-emitter nuclides were determined in soil samples collected in an area located at 34° 54.452' S, 58° 8.365' W, down to 50 cm in depth, using an hyper-pure Ge spectrometer. The soil samples were also characterized by means of Mössbauer spectrometry and X-ray diffraction. The activities of ^{238}U and ^{232}Th natural chains remain constant in depth at 41 Bq/kg and 46 Bq/kg, respectively, while the ^{40}K activity increases from 531 Bq/kg to 618 Bq/kg between 2.5 cm y 25.5 cm of depth. The only anthropogenic detected nuclide is ^{137}Cs , whose activity changes from 1.4 Bq/kg to values lower than the detection limit (L_D) for depths below 25 cm, exhibiting a maximum at 10 cm beneath the surface. The Mössbauer spectra show two magnetic sextets associated with $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , as well as two Fe^{+3} and Fe^{+2} doublets, probably originated in octahedral and tetrahedral sites of paramagnetic phases. The Fe^{3+} paramagnetic signal relative fraction increases up to 82% at the expense of the $\alpha\text{-Fe}_2\text{O}_3$ one when de depth increases. No correlation between Fe_3O_4 and the ^{137}Cs was identified.

1. Introduction

The concentration of metals and radionuclides in uncontaminated soil is primarily related to its origin and to pedogenetic processes. However, human activities can strongly modify the natural concentrations due to the presence of residues or accumulation of elements caused by the release of effluents to the environment. On a long-term scale, soil is the major source of nuclides entering the food chain or contaminating the ground water [1]. Consequently, the knowledge of the distribution of radionuclides in soils becomes extremely important. Once the distribution and profiles of nuclides are determined, to predict the nuclide dispersion in the soil, it is necessary either to modify existing models [2, 3] or to develop new ones to include the local conditions and to account for the very complex system that soil is. Indeed, nuclide transport in soil is strongly affected by the soil composition, pH, concentration of inorganic ions, redox potential, concentration of organic mater, physical and chemical properties, etc. [2, 3]. In addition, it has been suggested [1] that magnetite plays an important role for the radionuclide migration in soils.

Within this frame, we have started to study of soils belonging to a densely populated area of the Province of Buenos Aires, Argentina. The northeastern plain of Buenos Aires province exhibits an undulating topography which results from the erosion by tributary streams of the Paraná and La Plata rivers. This is an important agricultural and industrial area where nuclear power plants and research nuclear reactors are located, adding to the natural inventory small amounts of activities of anthropogenic nuclides. Despite the long term nuclear activity in the region, no systematic study has

been carried out until now to establish the natural conditions of the soils. Hence, it is essential to determine the radioactive baseline for undisturbed soils and their chemical and physical properties to be able later to understand the degree of pollution that the anthropic activities may have produced and to establish reliable models that predict the possible dissemination of radionuclides. To this end, the natural radioactive element contents of gamma-emitters in soil profiles at different depths have analyzed and, at the same time, the soil properties have been characterized by x-ray diffraction and Mössbauer spectrometry. In this contribution, the first findings in an area close to the La Plata district located at about 50 km from the Argentine Federal Capital are reported.

2. Experimental

The samples for radiological analysis were collected with a special spade of 3 cm high and 30 cm wide, while the corresponding ones for Mössbauer spectroscopy were taken with small plastic tubes. After collection, the samples were dried at 363 K, crushed and sieved through a 2 mm mesh without previous separation. The sampling was performed at depths down to 50 cm from the surface.

For gamma spectroscopy (GS), the soil was properly accommodated in a Marinelli-type box, sealed and kept for nearly three weeks before analysis to achieve the secular equilibrium. The spectra were taken inside an EG&G Ortec low background chamber, using a high-resolution hyper-pure Ge gamma EG&G Ortec spectrometer in the range of 30 keV to 1.8 MeV with a standard electronic chain and 8192 channels multichannel. Energy calibration was performed with ^{60}Co , ^{133}Ba , ^{137}Cs and ^{152}Eu sources. The efficiency calibration was carried out using an admixture of known amounts of naturally occurring ^{176}Lu and ^{138}La long-lived isotopes, dispersed in a soil substrate [4]. The absolute efficiency and the energy resolution of the 1332 keV ^{60}Co line were 0.5 % and 1.9 keV, respectively. The room background was determined and peak corrections were done to the soil spectrum. The spectra were recorded during four days and analyzed with a commercial program.

Mössbauer spectra (MS) were recorded between 30 K and room temperature in a 512 channels conventional constant acceleration spectrometer with a $^{57}\text{CoRh}$ source of approximately 10 mCi of nominal activity. Velocity calibration was performed with a 12 μm thick $\alpha\text{-Fe}$ foil at room temperature. Isomer shifts are referred to this standard. The spectra were numerically analyzed using hyperfine field and quadrupole distributions [5].

The structural analyses were done by X-ray diffraction (XRD) with a Philips PW1710 diffractometer ($\text{CuK}\alpha$ radiation) in the Bragg-Brentano geometry, with a step mode collection of 0.02° , 1 s by step, with 2θ ranging from 10° to 100° . The patterns were analyzed using the PowderCell program [6] and the structural data were obtained from ref. 7.

3. Results and discussion

The XRD patterns showed a broad background and many peaks among which illite, feldspar and quartz could be identified, in good agreement with previous studies carried on in a close area [8]. The fractions of the different detected phases – being illite the most abundant– remain nearly constant within the monitored depth. Because of the statistical uncertainty of the X-ray data, the existence of other phyllosilicates different from illite cannot be ruled out.

Figure 1 shows some selected Mössbauer spectra from the collected samples recorded at different temperatures. Two main contributions to the spectral area are observed; a magnetically split signal and a central set of doublets. The fitting procedure was carried out using hyperfine distributions with Voigt-shaped line profiles. Table 1 displays the resulting fitting parameters, which have been assigned as described below, and whose values remain almost constant for all depths.

While the parameters of the sextets belong unequivocally to $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , the assignment of the Mössbauer parameters of the doublets is more uncertain because different Fe species have similar parameters that overlap in the same region of the spectra [9-12] –e.g. hydroxides, finely divided Fe oxides in superparamagnetic relaxation regimes, or Fe ions partially substituted for other ions, like Al or Mn. The magnetically split signal of Fe_3O_4 is noticeable only down to 25.5 cm. The Fe^{3+} doublets may arise from paramagnetic clay minerals and other silicates or super-paramagnetic Fe oxides and

related minerals. Because of the small particle size, the low crystallinity degree and the low iron concentration in paleosols and soils of Buenos Aires Province [13], the detection of iron oxides or oxyhydroxides by means of XRD is very difficult [14]. For example, the X-ray data did not reveal the presence of hematite or magnetite even after searching for their most intense peaks. The lack of noticeable changes at low temperatures (see Figure 1) inhibits the unambiguous assignment of the contribution of the doublets to the existence of superparamagnetic phases. Therefore, the determined interactions can only be related to the Fe^{3+} and the Fe^{2+} octahedral and tetrahedral sites in paramagnetic species [9-12]. It is worth mentioning that illite is the species that can take the higher contents of Fe, and hence, it is likely that the main Fe^{3+} doublet area be related to this phase. The Fe^{2+} signal cannot be originated in Fe oxides found in the soil and therefore can only be associated to the clay minerals existent in the samples.

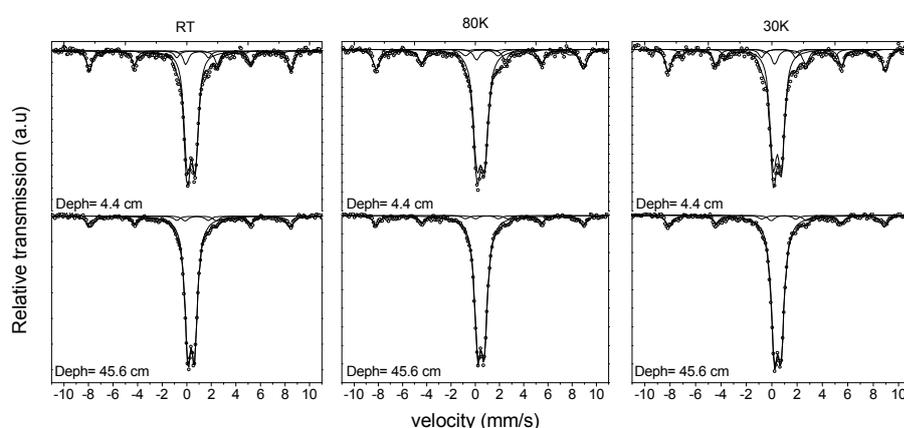


Figure 1: Mössbauer spectra of two different analyzed depth at RT (left), 80K (center) and 30 K (right). The thick solid line is the result of the fitting as described in the text. The thinner lines are the components of parameters shown in Table I.

The evolution of the RT relative fractions of the different Fe environments with depth is shown in Figure 2a. It is observed that the main component to the MS corresponds to the Fe^{3+} doublets, followed in importance by the $\alpha\text{-Fe}_2\text{O}_3$ sextet. It is worth mentioning that the Fe^{3+} fraction increases up to 82% at the expense of the $\alpha\text{-Fe}_2\text{O}_3$ one.

The determined gamma activities for the natural nuclides of the ^{238}U and ^{232}Th resulted 41 Bq/kg and 46 Bq/kg, respectively, remaining constant in depth. Regarding the activity of the ^{235}U chain was always lower than the L_D (0.02 Bq/kg). The ^{40}K activity varies from 531 Bq/kg to 618 Bq/kg between 2.5 cm and 25.5 cm of depth, as shown in Figure 2b. The only anthropogenic nuclide detected was ^{137}Cs , with a decreasing activity from 1.4 Bq/kg (2.5 cm depth) up to values lower than the corresponding L_D (0.2 Bq/kg) at a depth of 25.5 cm (see Figure 2b). The surface activity is compatible with the fallout of the nuclear weapons tests in the South Pacific [15]. Regarding the ^{137}Cs depth profile and its correlation with Fe_3O_4 , controversial results on their sorption by Fe_3O_4 have been reported [1, 16, 17]. By comparing the present results displayed in Figures 2 it can be seen that there is not an apparent correlation between the ^{137}Cs activity and the MS relative fraction of Fe_3O_4 . Further experiments and theoretical developments are in progress to fully describe the local soil characteristics entering in the existing models to really account for the diffusion coefficient and convection velocity of ^{137}Cs in the plain of Buenos Aires province. The soil characterization by structural, hyperfine and magnetic techniques will allow developing a model to understand the diffusion of the elements produced by the nuclear and industrial activities produced in the area.

Table 1: Hyperfine parameters obtained after fitting the Mössbauer spectra at room temperature using an extended Voigt-based fitting method. For doublets: average values of isomer shift $\langle\delta\rangle$ (mm/s) with respect to α -Fe, quadrupole splitting $\langle\Delta\rangle$ (mm/s), and relative fractions rf (%). For sextets: average magnetic field, $\langle H\rangle$ (T), quadrupole shift ε (mm/s) and relative fractions rf (%). The numbers between parentheses denote the Gaussian widths, σ (mm/s).

Depth (cm)		2.3	4.4	9.4	18.3	25.5	29.8	37.3	45.6	48.9
Fe ³⁺	$\langle\delta\rangle$	0.37(0.15)	0.37(0.16)	0.38(0.14)	0.37(0.14)	0.38(0.14)	0.37(0.15)	0.36(0.14)	0.36(0.14)	0.36(0.15)
	$\langle\Delta\rangle$	0.60(0.12)	0.60(0.09)	0.59(0.16)	0.59(0.14)	0.58(0.13)	0.53(0.12)	0.53(0.14)	0.53(0.13)	0.53(0.10)
	rf(%)	58 ± 3	63 ± 3	61 ± 5	59 ± 2	61 ± 1	73 ± 2	73 ± 2	73 ± 2	73 ± 2
Fe ²⁺ (Site I)	$\langle\delta\rangle$	0.54(0.22)	0.55(0.10)	0.60(0.16)	0.55(0.17)	0.56(0.14)	0.53(0.25)	0.51(0.20*)	0.51(0.22)	0.52(0.00)
	$\langle\Delta\rangle$	1.49(0.20)	1.63(0.15)	1.57(0.16)	1.49(0.15)	1.55(0.19)	1.47(0.10*)	1.48(0.20)	1.50(0.20)	1.51(0.47)
	rf(%)	11 ± 2	9 ± 2	12 ± 3	12 ± 1	12 ± 1	12 ± 2	11 ± 1	11 ± 1	11 ± 2
Fe ²⁺ (Site II)	$\langle\delta\rangle$	0.93(0.20)	0.88(0.00*)	0.82(0.20)	0.88(0.25)	0.88(0.15*)*	0.91(0.10*)	0.90(0.10*)	0.90(0.10*)	0.84(0.25)
	$\langle\Delta\rangle$	2.8(0.0*)	3.1(0.0*)	3.1(0.0)	3.1(0.2)	3.0(0.2)	3.0*(0.3*)	3.0*(3*)	3.0*(0.1*)	3.0(0.3*)
	rf(%)	6 ± 1	6 ± 1	7 ± 2	7 ± 1	7 ± 1	5 ± 1	5 ± 1	4 ± 1	5 ± 1
α Fe ₂ O ₃	$\langle\delta\rangle$	0.38(0.00)	0.38(0.04)	0.38(0.07)	0.38(0.02)	0.38(0.00*)	0.38(0.00*)	0.36(0.00*)	0.38(0.00*)	0.38(0.01)
	$\langle\varepsilon\rangle$	-0.10(0.00)	-0.11(0.00)	-0.12(0.01)	-0.11(0.01)	-0.10(0.00)	-0.10(0.01)	-0.10(0.00*)	-0.11(0.03)	-0.11(0.02)
	$\langle H\rangle$ (T)	51(1)	51(1)	50(0)	51(1)	51(1)	50(1)	51(1)	51(1)	51(1)
	rf(%)	17 ± 2	17 ± 2	18 ± 4	17 ± 1	21 ± 1	11 ± 1	12 ± 1	12 ± 1	11 ± 1
Fe ₃ O ₄ (Site A)	$\langle\delta\rangle$	0.3(0.0)	0.3(0.0)	0.3(0.0)	0.3(0.0)					
	$\langle\varepsilon\rangle$	0.00	0.00	0.00	0.00					
	$\langle H\rangle$ (T)	48(1)	48(0)	49(1)	49(1)					
	rf(%)	6 ± 2	3 ± 3	1 ± 3	2 ± 1					
Fe ₃ O ₄ (Site B)	$\langle\delta\rangle$	0.7(0.3)	0.6(0.0)	0.6(0.0)	0.7(0.0)					
	$\langle\varepsilon\rangle$	0	0	0	0					
	$\langle H\rangle$ (T)	44.0(0.2)	46.0(0.1)	45.8(0.2)	44.0(0.2)					
	rf(%)	2 ± 1	2 ± 2	3 ± 2	3 ± 1					

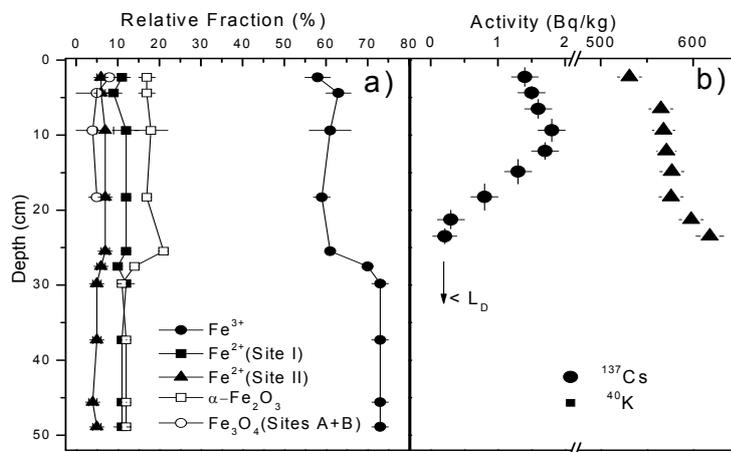


Figure 2: a) Evolution of the Mössbauer relative fractions. b) ^{137}Cs and ^{40}K profiles. (LD is the detection limit and the horizontal and vertical bars represent the activity errors and analyzed soil depth, respectively).

4. Conclusions

The results reported in this contribution –for samples taken from the surface down to a depth of 50 cm– are the first ones to establish the baseline activity for the naturally occurring gamma emitter radionuclides in an area around Buenos Aires. The ^{238}U and ^{232}Th chains were detected in the soil samples. The ^{40}K activities are in agreement with previous reported data. The only anthropogenic detected nuclide was ^{137}Cs arising from the fallout of the South Pacific weapon test. No correlation has been found yet between the magnetite fraction and the ^{137}Cs activity. More studies are in progress.

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