Biogeochemical behavior of ^{137}Cs and ^{60}Co in tropical soils

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Abstract. *Results of a sequential chemical extraction procedure for ^{137}Cs in an acidic Oxisol showed that 3 years after the contamination, 40% of total concentration was considered readily bio-available, 20% bound to organic matter and 40% bound to Fe and Mn oxides. Four years after, the ^{137}Cs distribution in this soil have been changed as a consequence of changes in soil properties: 8% bio-available, 16% bound to organic matter, 43% bound to Fe and Mn oxides and 33% strongly bound to soil compounds. Changes in the ^{137}Cs distribution in this soil were followed by reductions in soil to plant transfer factor (TF): $TF_{Oxisol1996} = 2,21 \pm 1,30$ (n=3) and $TF_{Oxisol2000} = 1,63 \pm 0,38$ (n=6). During the same period, the soil properties of a basic Oxisol remained almost the same, consequently the geochemical distribution and soil to plant transfer factor for ^{137}Cs did not change in this soil. The geochemical distribution in an acidic Alfisol showed that Mn oxides are the main sink for this element and no ^{60}Co was detected in the readily bio-available phase. In this soil, four years after contamination with ^{60}Co, it was not detected in plants.*

INTRODUCTION

The mobility of radionuclides in the soil-water system can favor the contamination of the food chain. Radionuclides associated to soils are adsorbed species (surface), precipitates or incorporated in mineral amorphous or crystalline structures. The determination of only the total concentration of radionuclides in soils is therefore not a satisfactory criterion to evaluate the risk of remobilization, and thus the potential dispersion and bio-availability, of these pollutants. For environmental risk assessment, it is necessary to determine how permanent is the trapping in the soil. One way to assess mobility of radioactive elements in soils is the use of sequential extraction procedures that intend to provide the partitioning of radionuclides in soil compounds, mainly affected by changes in physical-chemical conditions [1, 2]. For the investigation of pollutants in soils, numerous chemical extraction methods have been described (*e.g.* [3], [4], [5]), all these procedures intends to provide the a first approach of geochemical fractionation of elements affected by changes on physical-chemical conditions of soil.

Interactions between radionuclides and soil depends on the chemical form of element and some soil properties as pH, mineralogical composition, organic matter content and nutrient status [6, 7, 8, 9, 10]. The plant uptake of radionuclides will be dependent on interactions occurring in soils as well metabolic and physiological characteristics of the species [6].

The observed differences between ^{137}Cs soil-to-plant transfer factors obtained in an basic Oxisol soil accidentally contaminated in Goiânia, and in an acidic Oxisol and Alfisol artificially contaminated are going to be discussed in the light of pedology and geochemical partitioning procedures.

1.   MATERIALS AND METHODS

Lysimeters measuring 1 m^2 of area and with a depth of 1 m were installed in a restricted area of the Institute for Radioprotection and Dosimetry (CNEN/Brazil). The lysimeters were filled, from bottom to top, with: 15 cm of coarse material (sand and gravel), 30 cm of uncontaminated soil and 40 cm of

contaminated soil. Two types of soil were used in the experiments: an Oxisol soil and an Alfisol soil. Six lysimeters were filled with the Oxisol soil [11], contaminated with ^{137}Cs in 1992. One lysimeter was filled with the Alfisol soil [11], contaminated with ^{60}Co and ^{137}Cs in 1996. Each lysimeter received a liter of solution containing approximately 60 $\mu Ci\ L^{-1}$ of ^{137}Cs or ^{60}Cs. The solution was sprayed in every 2 cm of soil, layer by layer, up to 40 cm. Another Oxisol soil was collected in the city of Goiânia, in a site where the radiological accident occurred in 1987 [12]. Three lysimeters were filled with this soil (Goiânia soil).

Samples of soil were collected at the lysimeter filled with Oxisol and Goiânia soil in 1996 and at the same lysimeter in 2000, to perform sequential extraction analyses. Sequential extractions were performed following Tessier *et al.* protocol [5] for samples collected in 1996 (method 1) and following a modified version from Cannizzaro *et al.* (Method 2, [3]), for samples collected in 2000 (Table 1).

All the extracts were analyzed by gamma ray spectrometry using a Ge detector, for the determination of ^{137}Cs and ^{60}Co. The Soils Office of the Brazilian Agricultural Research Corporation (EMBRAPA-Soils) performed soil analyses and clay mineralogy determinations in order to characterize samples according to their standard manual [13].

The transfer factor was determined for radish ((*Raphanus sativus*, L.) following the IUR protocols to determine transfer factors [14]. Plants were collected and immediately separated in their different parts (roots and leaves), then washed. Plants and soils were dried, ground and sieved through a 2 mm screen before direct measurements of the of ^{137}Cs and ^{60}Co activity by gamma ray spectrometry using a Ge detector. Efficiency was known as to have an accuracy of about 10% for the used geometry (pot of 250 g). Counting errors were less than 3%.

Table 1. *Geochemical phases* and geochemical meanings of the tested methods

Geochemical phases	Geochemical meanings
Slightly Acid	Method 1: bound to carbonates + exchangeable
	Method 2: easily bio-available
Reducible	Method 1: bound to Fe and Mn oxides
	Method 2: bound to Mn oxides
Oxidizable	Method 1: bound to organic matter
	Method 2: bound to organic matter
Alkaline	Bound to resistant organic matter or iron compounds
Residual	Method 1: incorporated to crystal structure
	Method 2: Resistant compounds

2. RESULTS AND DISCUSSIONS

The main chemical and physical properties of studied soils are presented in table 2. The Oxisol soil was originally an acid soil with sandy clay loam texture, low cation exchange capacity (CEC) and low content of nutrient elements. The mineralogical analyses indicate the presence of gibbsite and kaolinite as main constituents of the clay mineral fraction. After 1996, phosphogypsum was applied in lysimeters filled with Oxisol soil for another experimental assay. In table 2, we can observe that the main changes occurred in the Oxisol between 1996 and 2000 concerns, pH, Ca^{++}, N, CEC, Al^{+++} and H^- probably due to agricultural practices and the experimental assay.

The Goiânia soil is also an Oxisol, but it is an urban soil with a higher nutrient content, probably due to the contributions from urban residues, like lime and cement (from building construction). No fertilization procedure was applied and the properties of the soils remained the same between 1996 and

2000. The mineralogical analyses of the clay fraction indicate the presence of gibbsite and kaolinite (table 2).

The Alfisol is an acid silty clay loam soil, with low nutrient content and low CEC. The mineralogical analyses indicate the presence of hematite, goethite and traces of vermiculite.

Table 2. Pedological analyses of artificially contaminated soils and Goiânia soil.

Parameters	Oxisol 1996 N=1	Oxisol 2000 N=6	Goiânia N=3	Alfisol N=1
pH (water)	4.3	6.3 ±0.6	7.8±0.1	4.9
pH (KCl 1M)	4.8	6.7 ±0.5	8.0±0.2	4.2
Sand (%)	70	73±3	68±2	10
Clay (%)	24	19±2	16±2	49
CEC (cmol$_c$ kg^{-1})	5.0	3.5±0.2	5.2±0.4	8.4
C (dag kg^{-1})	1.15	1.16±0.09	1.25±0.19	1.24
N (dag kg^{-1})	0.07	0.11±0.01	0.12±0.1	0.13
P (mg kg^{-1})	1	3±2	53±19	8
K$^+$ (cmol$_c$ kg^{-1})	0.09	0.09±0.04	0.23±0.02±	0.75
SiO$_2$ (dag kg^{-1})	3.7	3.4±0.3	5.4 ±0.7	15.7
Al$_2$O$_3$ (dag kg^{-1})	10.9	10.1±0.8	11.1±0.3	10.2
Fe$_2$O$_3$ (dag kg^{-1})	3.9	3.5±0.2	5.2±0.4	13.3
Ca^{++} (cmol$_c$ kg^{-1})	nd	1.6±0.4	4.4±0.4	nd
Mg^{++} (cmol$_c$ kg^{-1})	0.5	0.8±0.3	0.4±0.1	2
Al^{+++} (cmol$_c$ kg^{-1})	0.5	0.0	0.0	0.05
H$^+$ (cmol$_c$ kg^{-1})	3.8	0.5±0.1	0.5±0.1	5.5
^{60}Co (Bq/Kg d. w.) ± 1σ	-	-	-	3,1E3± 2.5 E1
^{137}Cs (Bq/Kg d.w.) ± 1σ	6.1E3 ± 7.9E1	5.9E3 ± 4.7E1	2.4E3 ± 3.7E1	6.2 E3 ±3.2 E1
Main clay mineral type (in order of predominance)	gibbsite, kaolinite	gibbsite, kaolinite	gibbsite, kaolinite	hematite, goethite, vermiculite

2.1 Geochemical partitioning of ^{137}Cs and ^{60}Co

In the figure 1 it is possible to note that in 1996, the Goiânia soil and the Oxisol presented differences on ^{137}Cs distribution, while in 2000 these differences disappeared. As consequence of fertilization, the Oxisol properties became very close to Goiânia soil properties (table 2). It can be observed that in 1996, ^{137}Cs present in Oxisol, was much more mobilized in slightly acidic phase than in 2000, while to Goiânia soil these values in 1996 remained similar to values in 2000 (figure 1). As the properties of Goiânia soil remained almost the same between 1996 and 2000, no significant differences in the results for slightly acidic phases using both methods were observed in this soil..

The results obtained for ^{137}Cs in the reducible phase, for Oxisol and Goiânia soil were higher in 1996 than in 2000. This result was mainly associated to used procedures. In the method 2, the reducible phase can be considered as slightly reducing, mobilizing mainly elements associated with Mn oxides, that is easily reducible. Part of ^{137}Cs, associated with iron oxides and some organic compounds, *observed in 1996*, will be mobilized in the basic phase and in the residual phase. In any case, it can be observed that iron oxides have an important role as a sink for ^{137}Cs (reducible and basic phases). Such behavior corroborates the findings of [15]. These authors obtained in four Canadian soil samples, using the sequential extraction method of Tessier, more than 40% of the total Cs associated with Fe and Mn oxides.
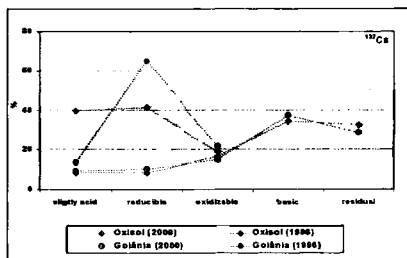
Figure 1. Geochemical partitioning of ^{137}Cs in Oxisol and Goiânia soil 1996 and 2000.

The results obtained for ^{137}Cs in the oxidizable phase (organic bound), for Oxisol and Goiânia soil were similar and didn't change with time, since results for 1996 and 2000 were also similar (figure 1). In this case, it was expected that as carbon content in both soils did not change, so the ^{137}Cs association with this compound remains the same after 4 years.

In the method 1, elements present in the residual phase are those that are present in the structure of primary minerals, or to a lesser extension, those trapped in the structure of secondary minerals. Release of elements bound to the lattice of minerals is not observable on a human time scale [4] and refers to the background levels for the region. *When using the method 1 in 1996, no significant radiocesium was observed in the residual phase of the Oxisol (1996) and the Goiânia soil (1996), where kaolinite and gibbsite are predominant in the clay fraction.* As the method 2 is lesser aggressive than method 1, elements that were not mobilized in previous phases will be in this residual phase. This phase correspond mainly to resistant compounds not destroyed before and possibly not available for transfer processes in the water cycle.

In figure 2, it is possible to compare the ^{137}Cs distribution with the ^{60}Co distribution for the Alfisol. In this figure it is clear that ^{60}Co is mainly associated with Mn oxides. This soil is rich in iron, and again the importance of this phase as a sink for ^{137}Cs is established. One important thing to note with this result is that no ^{60}Co was observed in the bioavailable phase and very little ^{137}Cs was present in this phase too. This result was very consistent with plant results, since *no ^{60}Co was detected in the plants (root or leaves)* and also very little ^{137}Cs was detected in the plants as can be seen in the figure 3.
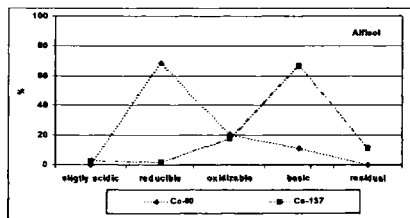

Figure 2. ^{60}Co and ^{137}Cs distribution in the Alfisol.

2.2 Transfer factor related to soil properties

Soil to plant transfer factor values for ^{137}Cs obtained in the present study compared with some values from IUR [14] are shown in figure 3. In this figure, it can be observed that ^{137}Cs transfer factor values for radish were slightly higher than the values obtained by IUR group at temperate climate TF=0.05 ± 0.05; (n=9) [14]. The tendency of tropical soils to present TF values higher than values obtained in temperate climate was observed before for roots, cereals and beans groups [10, 16, 17, 18].

The modifications on Oxisol properties, promoted changes on ^{137}Cs partition as well as in bio-availability, as can be seen by ^{137}Cs transfer factor values for radish in the this figure 3: $TF_{Oxisol2000} = 1,63 \pm 0,38$ (n=6) and $TF_{Oxisol1996} = 2,21 \pm 1,30$; (n=3). In the results obtained in 2000, the ^{137}Cs distribution on Goiânia soil was very similar to results obtained in 1996: $TF_{Goiânia2000} = 0,57 \pm 0.09$; (n=3) and $TF_{Goiânia1996} = 0,56 \pm 0,13$ (n=2).

Compared to Goiânia soil and Oxisol, Alfisol has significant differences in their properties, as pH, clay mineralogy, clay content and exchangeable K, which have influences on the ^{137}Cs transfer factor. Generally, there is a negative correlation between the Cs plant transfer factor and the pH [2, 9, 19]. Besides the pH influence, it is known that the clay mineral type can also influence the transfer factor: in the presence of 2:1 clay mineral type, the fixation of ^{137}Cs in the internal faces of these clays can occur few time after contamination (less than 3 years), reducing transfer to plants [2]. The Alfisol soil was contaminated with ^{137}Cs and ^{60}Co in 1996, while radish was sowed in 2000, that represents time enough for Cs fixation. This can partly explain why, despite of the similar ^{137}Cs concentrations in soil with Oxisol 1996 and lower pH (see table2), the concentration is lower for radish growing in Alfisol compared with radish growing in Oxisol 1996 $TF_{Alfisol2000} = 0,32$ (single data) and $TF_{Oxisol1996} = 2,21 \pm 1,30$; (n=3). This behavior was observed before for maize cultivated in the same lysimeter [18]. Even it seems clear that it is difficult to identify the main parameters that determines a given transfer factor data, the results obtained in slightly acidic phase of sequential extraction was very consistent with the transfer factor results: only 3% of total concentration of ^{137}Cs was considered readily available for root uptake.
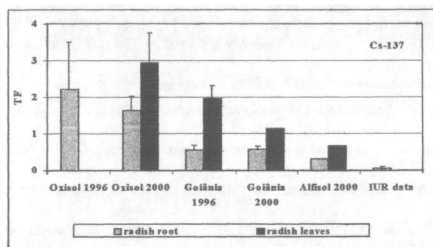

Figure 3. [137]Cs transfer factor values (TF) for radish, including IUR data values [14].

3. CONCLUSIONS

Changes in bio-availability of ^{137}Cs in Oxisol were mainly due to changes in soil properties. The results for both sequential extraction methods used in this study shows that ^{137}Cs is mainly associated with iron oxides in Al rich soil or Fe rich soil. [137]Cs can be strongly retained in the soil particles of the 3 soils independent of the presence of 2:1 clay mineral. In the Alfisol, it is possible that reduction in ^{137}Cs transfer be associated

to fixation in the internal faces of 2:1 clay mineral type, while in the Oxisol reduction in transfer was mainly attributed to better nutrition conditions.

The ^{60}Co distribution showed that Mn oxides are the main sinks for this element. Four years after the contamination no ^{60}Co was detected as bio-available in soil and in the same way it was not detectable in plants. A slightly reducible condition seems able to mobilize important fraction of ^{60}Co in Alfisol.

The conditions for extraction used in the slightly acidic phase was very consistent with the transfer factor results, showing that it can be considered as the bio-available fraction in soil.

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