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Bio-geochemical behavior of ^{90}Sr and ^{137}Cs in tropical soil

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Abstract. In this work TF values for ^{90}Sr and ^{137}Cs were measured for reference plants grown in lysimeters containing soils representative of large agricultural areas in Brazil: Ferralsol, Nitisol and Acrisol. These results were discussed in the light of pedological analyses and results from the follow sequential chemical extraction protocol: 1) slightly acidic phase containing readily bioavailable elements; 2) easily reducible phase containing elements bound to Mn oxides; 3) oxidizable phase containing elements bound to labile organic matter; 4) alkaline phase containing mainly elements bound to Fe compounds; 5) resistant phase not potentially available to crops. These results showed that the main soil factors influencing the ^{137}Cs transfer to these soils were: exchangeable K, organic matter and iron oxides content. These results showed that ^{90}Sr plant uptake was influenced by exchangeable Ca. All these finds are in accord with previous studies and seems confirm the vulnerability of Ferralsol and Acrisol to ^{137}Cs contamination.

1. INTRODUCTION

The study of radionuclides in agricultural areas is of general concern because, once in the soil, most of them can recycle within the biota, similarly to nutrients. Interactions between radionuclides and soil depend on the chemical form of element and some soil properties such as pH, mineralogical composition, organic matter content and nutrient status [1-3]. Plant uptake of radionuclides will be dependent on these interactions and will also depend on the metabolic and physiological characteristics of the species. Knowledge of the mobility of radionuclides in soils is needed to assess potential hazards from radionuclide inputs into the food chains. One manner to assess the potential mobility of radionuclides in soils is the use of sequential extraction procedures to describe the distribution of radionuclides in soil as a function of some physico-chemical conditions [4].

This work generated data on transfer factors of radionuclides (^{137}Cs and ^{90}Sr) from soil to reference plants in a range of soil systems (kaolinite and Fe-Al oxide rich soils, very acid soils with low nutrient contents) where transfer factors deviate substantially from the average established for temperate soils. The observed differences between soil-to-plant transfer factors obtained in some Brazilian soil systems are discussed in the light of pedology and geochemical partitioning procedures.

This work intends to provide parameters for environmental assessment models related with Brazilian soil conditions and to contribute to the identification of ecosystems that are more vulnerable to radioactive contamination, so that emergency response planning can be optimized.

2. MATERIAL AND METHODS

Maize (*Zea mays*, L.) and cabbage (*Brassica oleracea,* L. var. capitata) were grown in masonry lysimeters (1m^3 each) installed in a restricted area of the Institute for Radioprotection and Dosimetry (CNEN/Brazil). Five lysimeters were filled with an Al rich soil, artificially contaminated with ^{137}Cs in 1992 and with ^{90}Sr in 2000; one lysimeter was filled with an Fe rich soil (Nitisol), artificially contaminated for the experiment with ^{60}Co and ^{137}Cs in 1996; two lysimeters were filled with another type of iron rich soil (Ferralsol), artificially contaminated for the experiment with ^{90}Sr and ^{137}Cs in 2000; One lysimeter was filled with the Acrisol soil (Kaolinite rich), artificially contaminated for the experiment with ^{90}Sr and ^{137}Cs in 2000. The artificial contamination for Cs and Co was done spraying a contaminated solution in every 2 cm of soil, layer by layer, up to 40 cm; a layer of 40 cm of uncontaminated soil was placed beneath. The contamination with ^{90}Sr was done directly in the lysimeters, spraying the solution in the surface of soil. Another Ferralsol (Al rich) was collected in the city of Goiânia, from a site where a radiological accident with ^{137}Cs occurred in 1987 [6]. Three lysimeters were filled with this Goiânia soil, contaminated in 1987. Table 1 shows the main clay mineral type and ^{137}Cs and ^{90}Sr activities in the studied soils.

Table 1. Soil Type (FAO Classification), Clay Mineral Type (In Order Of Predominance), ^{137}Cs, time after ^{137}Cs contamination and ^{90}Sr Activity (Bq/Kg d.w.± Sd) of Studied Soils.

FAO classification	Ferralsol (n=5)	Ferralsol Goiânia (n=3)	Nitisol (n=1)	Ferralsol iron rich (n=2)	Acrisol (n=1)
Main clay Mineral type	gibbsite, kaolinite	gibbsite, kaolinite	hematite, goethite, vermiculite	hematite, goethite	Kaolinite
^{137}Cs in soil	7.01E+03± 9.71E+02	1.97E+03± 9.57E+02	6.77E+03	7.08E+03 ± 1.10E+03	3.34E+03
time after ^{137}Cs contamination	10 years	15 years	6 years	2 years	2 years
^{90}Sr in soil	6.22E+02± 2.32E+02		9.88E+02	4.23E+02 ± 4.75E+01	3.04E+02

Plants and soils were dried, ground and sieved through a 2 mm screen before direct measurement of the of ^{137}Cs activity by gamma ray spectrometry using a Ge detector. Efficiency was about 10% for the geometry used (pot of 250 g). Counting errors were lower than 5%. The amount of ^{90}Sr in soil and plants was determined by measuring the beta activity of Y-90 in a Berthold Low Background Proportional Counter (detector diameter 5 cm) [8].

The transfer factor (TF) for reference plants (corn and cabbage) was determined following the IUR (International Union of Radioecologists) protocols [5]: TF =A_p/A_s, where, A_p = Activity in the edible part of the plant (Bq.kg^{-1} dry weight) and A_s = Activity in the soil (Bq.kg^{-1} dry weight).

The Soils Office of the Brazilian Agricultural Research Corporation (EMBRAPA-Solos) performed soil analyses and clay mineralogy determinations according to their standards manual [7].

Sequential extractions were performed in soils samples as described in Table 2. Details of the analytical protocol can be found in [4]. All the extracts were analyzed by gamma ray spectrometry using a Ge detector, for the determination of ^{137}Cs.

Table 2. Protocol of Sequential Extraction Considering Geochemical Signification by Phase.

PHASE	*EXPERIMENTAL CONDITION*	*GEOCHEMICAL SIGNIFICATION*
Slightly acidic	$CH_3COOH + CH_3COONa$ 1:1; pH 4.7; At room temperature (RT).	easily bioavailable
Easily Reducible	$NH_2OH.HCl$ (0.1 M); pH 2; RT.	mainly bound to Mn oxides
Oxidizable	H_2O_2 (30%) + CH_3COONH_4 (1M); pH 2; RT.	bound to labile organic matter
Alkaline	NaOH (0.1 M); pH 12; RT.	bound to Fe compounds
Resistant	Aqua regia + HF. Heat to 50°C/ 30mim.	not mobilized in previous phases

3. RESULTS AND DISCUSSION

3.1 Chemical and physical properties of studied soils

The main chemical and physical properties of the studied soils are presented in table3. The Ferralsol presents a sandy clay loam texture, low cation exchange capacity (CEC) soil. The contents of exchangeable K and Ca and the pH value of this soil are higher than normally observed in the field and is probably due to the application of fertilizers and lime in previous experiments. The mineralogical analyses indicate the predominance of gibbsite and presence of kaolinite in the clay mineral fraction. The Goiânia soil is also a Ferralsol, but it is an urban soil with a higher nutrient content and CEC. Only urea has been applied in these lysimeters when necessary for a better development of the crops. The mineralogical analyses of the clay fraction indicate the presence of gibbsite and kaolinite.

The Nitisol is an acid silty clay loam soil, with high nutrient content and low CEC. The mineralogical analysis indicates the presence of hematite, goethite and traces of vermiculite.

The Ferralsol iron rich is an acid soil, rich in iron oxides, with clay texture, low nutrient content and low CEC. The mineralogical analysis indicates the predominance of hematite and goethite in the clay mineral fraction. The Acrisol is an acid sand soil with low nutrient content and low CEC. The mineralogical analysis indicates the predominance of Kaolinite.

The Ferralsol together with Acrisol, represents more than sixty percent of Brazilian agricultural soils. Their main restriction for some crops is the low nutrient contents and acidity. These properties are also expected to produce high soil to plant transfer of radionuclides such as Cs and Sr.

Table 3. Pedological Analyses Of Artificially Contaminated Soils And Goiânia Soil.

	Ferralsol	Ferralsol Goiânia	Nitisol	Ferralsol iron rich	Acrisol
Exch. K (cmol kg^{-1})	0.12	0.10	0.18	0.06	0.08
Exch. Ca (cmol kg^{-1})	3.9	11.5	4.0	0.8	1.0
CEC (cmol kg^{-1})	4.8	12.3	6.1	5.2	6.3
PH in KCl	6.3	8.2	4.2	4.5	5.4
OM (%)	2.1	2.0	2.1	1.6	0.5
Clay (%)	18	16	49	77	9
Sand (%)	71	68	10	19	82
Al_2O_3 (%)	11	11	10	30	4
Fe_2O_3 (%)	3	5	13	23	2

3.2 Behaviour of ^{137}Cs

Higher values of ^{137}Cs TF for maize and for cabbage growing in 2002 occurred mainly associated with soil recently contaminated (Ferralsol Iron rich and Acrisol in Figure 1). Lower TF values occurred mainly with the Nitisol and values where comparable with recommended TF values for maize and cabbage cultivated in temperate soils according with IUR [5].

Generally, there is a negative correlation between the Cs TF and the pH [6,7]. Our results show that the most acid soil (Nitisol) presented the lowest transfer, but the other acid soil types, presented higher TF values. In previous study with the Ferralsol, it was possible to observe that increases in pH by liming was able to reduce Cs plant uptake [10].

Besides the influence of pH, it is known that the clay mineral type can also influence the TF: in the presence of a 2:1 clay mineral type, the fixation of ^{137}Cs in the internal faces can occur a short time after contamination (less than 3 years), reducing transfer to plants [9]. The Nitisol soil is the only soil type that contains traces of vermiculite and it was contaminated with ^{137}Cs in 1996, which allows enough time for Cs fixation. This can partly explain why, despite of the similar ^{137}Cs concentrations in soil compared with the other soils and lower pH (see Tables 1 and 3), the TF was lower for maize and cabbage growing in the Nitisol compared with plants growing in the other soils (Figure 1). These can not be justified by ageing of contamination because we studied also soils contaminated 9 years or 4 before the Nitisol that presented higher TF values for Cs than it was observed for plants growing in Nitisol (Figure 1). This behavior was also observed for radish cultivated in the Nitisol when compared with Ferralsol [10].

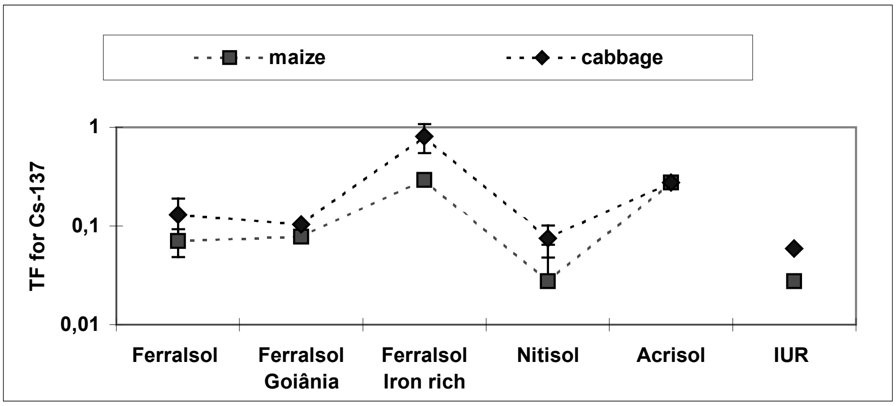

Figure 1. ^{137}Cs TF values for maize and for cabbage growing in 2002.

Due to chemical similarity between potassium and caesium plants cannot distinguish between them [3]. Considering that, it is expected that soils containing higher concentrations of exchangeable potassium should decrease caesium root uptake, due to competition for carriers involved in root uptake. Figure 2, shows that effectively, only soil with very low exchangeable K content showed a high TF. Frissel *et al.,* [11] suggest that cereals growing in soils with exchangeable K^+ concentrations smaller than 0.5 cmol kg^{-1} are expected to present very high Cs TFs, above that limit, other factors seem to determine the TF for Cs. Our results seems corroborate these suggestion.

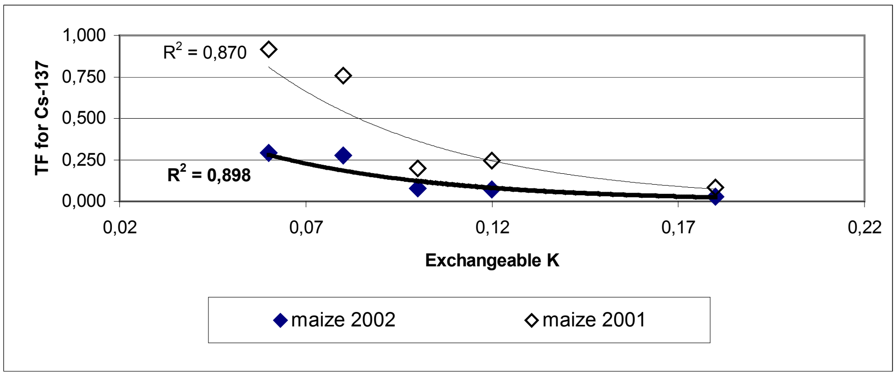

Figure 2. ^{137}Cs TF values for maize in two crops period versus exchangeable K (cmol kg^{-1}).

The ^{137}Cs distribution on Goiânia soil and on the Ferralsol (Al rich) shows that similarities in soil properties determine similarity in the geochemical partitioning (Figure 3) despite of differences in total concentration and time elapsed from the contamination (see Table 3). More than 10 years after contamination, about 70% of the total ^{137}Cs in these soils is distributed among the mobile geochemical phases, meaning that changes in the physical-chemical conditions in soil can liberate Cs to the soil solution, and from 3% to 57% of the total ^{137}Cs in these soils are still potentially readily to be available for root uptake. The ^{137}Cs in the *resistant phase* corresponds mainly to resistant compounds not destroyed in the previous phases and so is possibly not available for transfer to soil water. The soils with old contamination (Ferralsol, and Goiânia soil) contained the higher values of ^{137}Cs in this phase (see figure 3).

Iron oxides are important compounds in most Brazilian soils. More than 60% of the ^{137}Cs was mobilized in the *alkaline phase*, showing that these compounds are important sink for ^{137}Cs (see Figure 3). The Ferralsol Iron rich presented lower content of Cs associated; maybe with the ageing of the contamination it will be significantly incorporate in this compound, reducing transfer to plants as occurred for Nitisol.

The ^{137}Cs in the *oxidizable phase* (organic bound), for the Ferralsol, Goiânia soil and the Nitisol were similar. These results were attributed to the fact that organic C content are also similar in these soil types. Despite the low carbon content in the tropical soils, more than 10% of the ^{137}Cs was bound to organic compounds (see Figure 3).

The ^{137}Cs levels in the *slightly reducible phase* did not correlate with any soil property. This phase is associated with manganese oxides that are present as traces compounds in the majority of tropical soils. The ^{137}Cs associated with this phase was generally below 20%.

Figure 3 shows that the ^{137}Cs readily available for plants (*slightly acidic phase*) was highest in the Ferralsol (Fe rich) and the Acrisol. For the Ferralsol (Al rich) and Goiânia soil, the ^{137}Cs in the *slightly acidic phase* were similar as was the TF to maize and to cabbage. This fraction was lowest in the Nitisol (3%) and the TFs in this soil were generally lower than in the other soils, as discussed previously. This corroborates the hypothesis that Cs fixation occurs in this soil, which contains traces of vermiculite, thus reducing transfer to plants. It seems clear that Cs fixation is not a process that occurs systematically: Since 1996, about 10% of total ^{137}Cs concentration present in Goiânia soil remains readily available for root uptake. Studies with radish since the contamination in 1987 until 2000, showed that no significant difference in the TF in this soil [10]. It seems that in absence of competitive concentration of K or other similar ion to Cs in the bioavailable phase, plants will absorb Cs proportionally according mainly with physiological differences, as is possible to see in figure 4. The *slightly acidic phase* correlates linearly with TF, showing that it serves as a good indicator of plant availability when there is no mechanism able to avoid plant uptake: maize$_{2002}$ r=0.95 (n=12; p=0.999 r >0.80) and cabbage $_{2002}$ r=0.85 (n=12; p=0.999 r >0.80).

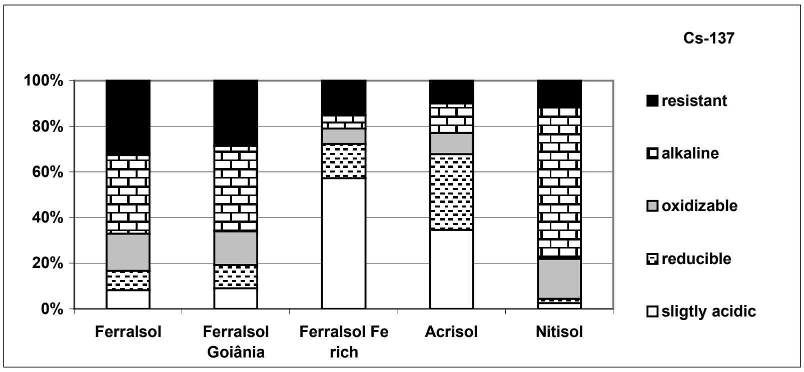

Figure 3. Geochemical partitioning of ^{137}Cs in tropical soils.

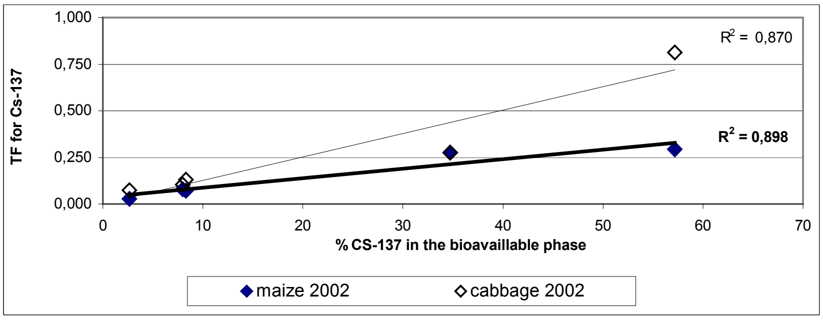

Figure 4. ^{137}Cs TF values for maize and for cabbage in relation to % of ^{137}Cs in the bioavailable phase.

The results of these experiments seems to show that soils with low fertility due to soil acidity, very limited fertilization and/or an extremely low exchangeable K content, are those more sensitive to ^{137}Cs contamination, because they give higher TFs than fertile soils [11]. These characteristics are predominant in the savanna's areas in Brazil, and in these areas countermeasure as K fertilization and liming should to be effective.

3.3 Behaviour of ^{90}Sr

According with figure 5, Nitisol present lower TF and the Ferralsol iron rich present the highest TF. The ^{90}Sr TF values observed for maize and cabbage in all soils were lower than recommended TF values for maize and cabbage cultivated in temperate soils [5] except for unfertile soils. This result could not be accounted for by the differences in the soil activity for ^{90}Sr (see Table 1) nor by time elapsed after contamination, since all soils were contaminated in 2000.

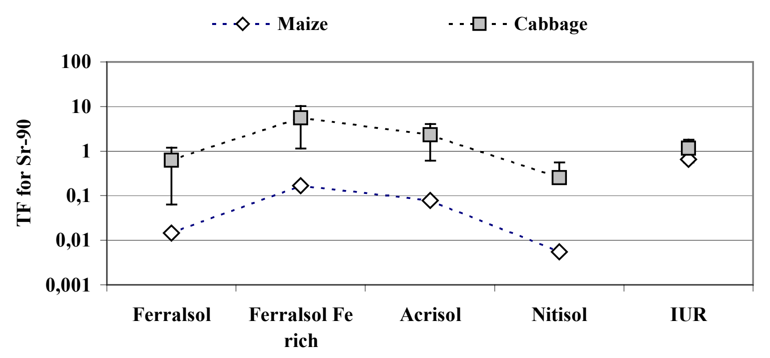

Figure 5. ^{90}Sr TF values for maize and for cabbage growing in 2002.

The ^{90}Sr distribution for the studied soils is shown in the figure 6. The differences observed in the ^{90}Sr distribution is not related with time elapsed after contamination, since all soil was contaminated at the same week. In this figure it is clear that an important fraction of ^{90}Sr is in the bioavailable phase (>49%). When we compare this result with the results found in the available fase it is possible to see that even an important fraction of Sr is available for the root uptake in Nitisol, the plant uptake was litle and it can be explained by the high exchangeable Ca content that this soil present, that can compete with ^{90}Sr for root uptake due to their chemical similarity. It can be confirmed by the strong correlation between ^{90}Sr TF and exchangeable Ca. The correlation with pH was not so good as it was for the Ca because Nitisol is an acid soil with high content of Ca.

The Sr was also associated with Mn and Fe oxides in the studied soils. Fresh contamination can trouble interpretation because there is a tendency to reversible adsorption until the radionuclide could be in equilibrium with all soil compounds. The older contamination of these studied soils occurred with Cs and very good correlation was found between Cs in the phases and the main compound related with this phase, as showed previously.

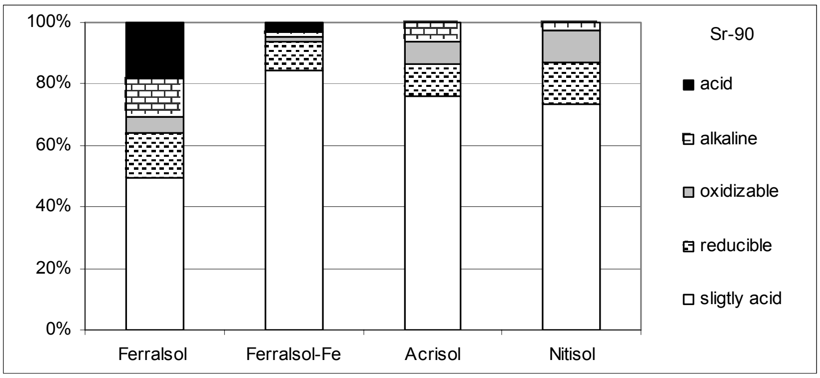

Figure 6. Geochemical partitioning of ^{90}Sr in tropical soils.

4. CONCLUSIONS

The integration of experimental methods results obtained in the laboratory with results obtained in field experiments seems to confirm that soils with low fertility originate from soil acidity, very limited fertilization and/or an extremely low exchangeable K content, are those are more sensible to ^{137}Cs contamination, because they present high plant uptake many years elapsed after contamination. These results showed that some Brazilian agricultural soils are very vulnerable to Cs contamination. Although it is clearly difficult to identify which soil property determines a given TF, the levels of ^{137}Cs obtained in the slightly acidic phase correlated well with the TF. These results were also coherent with some of the soil properties recognized in the literature as involved in the mechanisms of sorption of Cs (e.g. exchangeable K, organic matter and iron oxides content). The ^{137}Cs distribution in soil showed that Fe oxides are the main sink for this element in all type of soil and 15 years after contamination the ^{137}Cs was still available for plants. In the Nitisol, 5 years after contamination, very few ^{137}Cs was bioavailable (in the slightly acidic phase) and it presented low plant uptake. In the Nitisol, it is possible that the low ^{137}Cs transfer be also associated with fixation in the internal faces of 2:1 clay mineral type.

Soils with low exchangeable Ca are those are more sensible to ^{90}Sr contamination, because they present the highest soil to plant transfer, when compared with other soil types. The ^{90}Sr TF values observed for the studied tropical soils were lower than recommended TF values for temperate soils. These results showed that some countermeasures as K fertilization and liming can be effective for unfertile soils contaminated with Cs, while, Ca fertilization can produce effective results for soils contaminated with Sr.

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References

[1] Skarlou, V., *et al.*, *Geoderma* **72** (1996) 53-63.

[2] Wasserman, M.A.M. and Belém, L.J., Valores de Transferência do ^{137}Cs de Latossolos para Plantas Comestíveis, *VI Congresso Geral de Energia Nuclear*, Rio de Janeiro, Brasil. (1996) CD-ROM

[3] Papastefanou, C., *et al., J. Environ. Radioact.* **45** (1999) 59-65.

[4] Wasserman, M.A., *et al.*, Assessment of the Mobility and Bioavailability of ^{60}Co and ^{137}Cs in contaminated soils. *V Regional Congress on Radiation Protection and Safety*, Rio de Janeiro, Brasil, (2001), CD-ROM, 8 pages.

[5] International Union of Radioecologists. “Report of the Working Group Soil-to-Plant Transfer Factors”. (1989), pp. 87.

[6] Mendonça, A.H., Radiological Accident in Goiânia, Brazil: an Overview. *IV^{e} Symposium International de Radioecologie de Cadarache*, Cadarache, France (1988), A1-A8.

[7] EMBRAPA. *Manual de Métodos de Análise de Solo*. Embrapa-CNPS, Rio de Janeiro (1997)

[8] Petrow, H.G., Anal. Chem, **37** (1965).

[9] Riise, G., *et al.*, *J. Radioanal. Nucl. Chem.* **142** (1990), 531-538.

[10] Wasserman, M.A., *et al.*, *Radioprotection Colloques*, **37-C1**: 277-282. (2002).

[11] Frissel, M.J., *et al.*, *J. Environ. Radioact.*, **58** (2-3), 113-128**.** (2002).