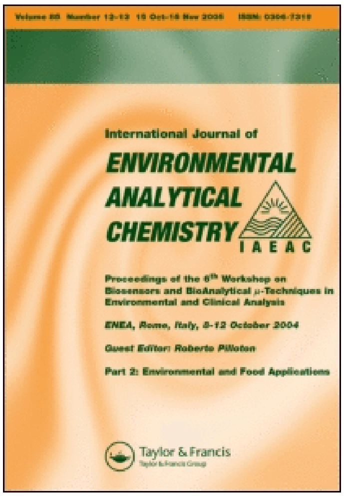

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Two Approaches for Sequential Extraction of Radionuclides in Soils: Batch and Column Methods

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TWO APPROACHES FOR SEQUENTIAL EXTRACTION OF RADIONUCLIDES IN SOILS: BATCH AND COLUMN METHODS

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A three-step sequential extraction protocol designed by Community Bureau of Reference (BCR) is applied to two types of soil (sandy and sandy-loam) which had been previously contaminated with a radionuclide aerosol containing ^{134}Cs, ^{85}Sr and ^{110m}Ag. This scheme is applied using both batch and column methods. The radionuclide distribution obtained with this scheme depends both on the method and on soil type. Compared with the batch method, column extraction is an inadvisable method. Kinetic aspects seem to be important, especially in the first and third fractions. The radionuclide distribution shows that radiostrontium has high mobility, radiocaesium is highly retained by clay minerals whereas Fe/Mn oxides and organic matter have an important role in radiosilver retention.

KEY WORDS: Soils, sequential extraction methods, column method, radionuclides, radiocaesium, radiostrontrium, radiosilver.

INTRODUCTION

The increase in radionuclide levels in the environment after the Chernobyl accident has renewed interest their study in the different environmental compartments. Knowledge of the interactions between radionuclides deposited and soil components is important for the prediction of radionuclide behaviour in soils, as well as the transfer of radionuclides from soil to plants (and from these to man through the food chain), upon the availability of radionuclides in the soil. To determine this, aqueous extraction followed by an extraction with ammonium acetate is the most generally used procedure to study the mobile fraction, as a sum of both aqueous and exchangeable fractions[1].

To date it has generally been accepted that the most appropriate way to evaluate the different phases in which radionuclides may occur is based on sequential extraction schemes. As for heavy metals, sequential extraction schemes of radionuclides are based mainly on that proposed by Tessier et al.[2] and subsequent modifications thereof[3-6]. However, only some sequential extraction procedures have been applied to radionuclides, mainly in order to examine radiocaesium behaviour[7-9].

In this paper, a sequential extraction scheme, designed to be used by the participants in an intercomparison study organized by the BCR for heavy metals in soils and sediments, is applied to radionuclides in soils[10]. This scheme has three steps, with HAcO, $NH_2OH.HCl$ and H_2O_2-NH_4AcO as extractant reagents. Operationally, the first reagent can be related to exchangeable and bound to carbonate metals, the second is an efficient reagent for the extraction of metal bound to reducible Fe/Mn oxide phases and the third reagent is related to metals bound to oxidizable organic material and sulphides. In this paper, this scheme is applied to two types of soil (sandy and sandy-loam) which were previously contaminated by a radionuclide aerosol which simulates a nuclear accident. The radionuclides studied are ^{134}Cs, ^{85}Sr and ^{110m}Ag.

Several studies have been carried out with radiocaesium and radiostrontium[8,11-12], but there are no reports of ^{110m}Ag behaviour, although it is one of the radionuclides that would appear in case of a nuclear accident. The chemical characteristics of silver justify the use, in this case, of the three-step scheme designed for heavy metals.

Usually, sequential extraction schemes are applied in batch, but several studies of migration and leaching have also been carried out in column[13-14], in order to provide a more realistic simulation, but no studies are available using both methods in sequential extraction schemes. Therefore, a comparison between the two methods, which allows to study the influence of kinetics in equilibria, would be useful, and this is one of the aims of this study.

EXPERIMENTAL

Contamination

A square meter of two types of soil was contaminated at the Centre d'Études Nucléaires of Cadarache (Aix-en-Provence, France), with a radioactive aerosol, in order to study the behaviour of radionuclides in agricultural systems. The radionuclide levels obtained in soil samples after contamination were similar to those found in zones with a high impact of the Chernobyl accident[15-16]. After contamination, real conditions were simulated in a greenhouse, to be able to obtain results that could be applied to real accident.

The radioactive aerosol used in sample contamination was a thermically generated, by means of a graphite tube from a tablet formed by compounds of 16 elements which are representative of those that may be emitted to atmosphere in a nuclear accident. The stable elements which form the tablet are: Fe, Zr, Cr, Ni, Ag, In, Sn, Cd, I, Cs, Te, Sr, Ba, Ru, Ce and U, the radioactive elements being ^{134}Cs, ^{85}Sr (as carbonates) and ^{110m}Ag (in metallic form). These elements were activated by means of neutron activation[17].

Samples

Two types of soil were selected with contrasting properties to compare radionuclide behaviour. Soil 1 (sandy-loam) came from the experimental fields at the University of Barcelona (Spain) and soil 2 (sandy) was from Cadarache (Aix-en-Provence, France).

A plot of 10 × 15 cm^2 was sampled to a depth of 2 cm the day after contamination, with a plastic spoon. Soils were air dried and stored in polyethylene bottles for analysis. Due to the impossibility of carrying out all the experimental work simultaneously, sequential extractions were done from four days to two months after the day of contamination.

Instrumentation

Activity measurements of ^{134}Cs, ^{85}Sr and ^{110m}Ag were measured in liquid, filter and soil fractions by high-resolution gamma spectrometry, using an intrinsic Ge detector (CANBERRA GR2020), with 25.1% relative efficiency and 1.9 keV of resolution (FWHM) at 1.33 MeV, connected to a multichannel analyzer (CANBERRA SERIES 35 PLUS) with 4096 channels. Calibration was carried out with an Amersham cocktail of isotopes for different geometries and densities (filter, liquid, sandy soil and sandy-loam soil). The time of measurement was between 40,000 and 80,000 seconds. Radionuclide activities were corrected taking into account the contamination day and expressed in $Bq.kg^{-1}$ of dry weight of initial soil.

Three photopeak standard deviations were considered as a quantification limit.

Reagents

All reagents were analytical grade. All standard and reagent solutions were stored in polyethylene bottles. All material was washed with HNO_3 10 % and distilled water before use.

Sequential extraction procedure

(A) Batch method Soil samples were weighed (about 12–13 g), their activity measured and sequentially extracted. The extracting procedure can be defined according to:

Fraction 1 40 ml/g of HAcO 0.11 mol/l was added to the soil. The suspension was shaken for 16 hours at room temperature in 250 ml polyethylpentene bottles, using an end-over-end shaker.

The supernatant was decanted off after centrifugation at 3,500 rpm for 40 minutes. The residue was washed with distilled water and centrifuged again and the resulting supernatant was added to the first and subsequently filtered through Whatman 542 filters. Filter and liquid activities were measured by high-resolution gamma spectrometry.

Fraction 2 40 ml/g of $NH_2OH.HCl$ 0.1 mol/l (pH 2 with HNO_3) was added to the residue, which was resuspended by vigorous manual shaking and the suspension was shaken for 16 hours at room temperature. Subsequent treatment was as explained above.

Fraction 3 (3a) 10 ml/g of H_2O_2 30 % (pH 2 with HNO_3) was added to the residue, the residue was resuspended and the suspension was allowed to digest for one hour at room temperature, a further hour at 85 °C and, subsequently allowed to evaporate to a few ml.

(3b) 10 ml/g of H_2O_2 30% (pH 2 with HNO_3) was added to the moist residue and the suspension was allowed to digest for an hour at 85°C and, subsequently reduced to few ml.

(3c) 50 ml/g of NH_4AcO 1 mol/l (pH 5 with HAcO) was added to the moist residue and the suspension was shaken for 16 hours at room temperature. Subsequently treatment was as described in FRACTION 1, but the centrifugation time was raised to 50 minutes. Activity in soil residue was also measured by high-resolution gamma spectrometry.

(B) Column method Soil samples were weighed (about 65 g) and their activity was measured and they were then placed in a borosilicate glass column, which contained a porous plate and a water jacket. A flow of extractant, falling by gravity from a liquid column of approximately 5 cm width × 30 cm long, passed through the soil, which filled a space of 5 cm width × 5 cm long. The residence time of the extractant was try to be the same as the shaking time in batch method, that is to say, about 160 ml/h in fractions 1 and 2, 325 ml/h in fraction 3a, 650 ml/h in fraction 3b and 200 ml/h in fraction 3c. In fractions 3a and 3b, water at 85°C was pumped through the water jacket. Between extractants, about 325 ml of distilled water was used to wash the soil residue and this solution was joined to previously extracted solution. No centrifugation was needed and the extract was filtered through Whatman 542 filters. Liquids, filters and soil residue were measured by high-resolution gamma spectrometry.

RESULTS AND DISCUSSION

Soil characterization

Main characteristics of both types of soil were determined as summarized in Table 1[18]. Sandy texture correlates with low organic matter and clay contents and both properties are responsible for low cation exchange capacity with an outstandingly low K^+ level. Sandy-loam soil has higher adsorption capacity and cation content, with higher content of organic matter as well as carbonates. However, this type of soil has a lower Fe and Mn content than sandy soil. Both types of soil have a high illite content in the clay fraction.

Batch results

The results of radionuclide distributions are the mean of sequential extractions carried out with soils coming from two contamination processes. The initial activities of soils studied can be seen in Table 2. The specific activities are expressed in $Bq.kg^{-1}$, with ± 2σ, and corrected to the contamination day. No influence of the contamination process has been taken account in radionuclide distribution.

Table 1 Characteristics of the soils.

	pH H_2O	*pH KCl*	*% OM*	*% $CaCO_3$*
Soil 1	7.5	7.1	2.40	5.86
Soil 2	6.7	6.0	0.22	0.00

Texture and clay mineral composition (%).

	Texture	*CS*	*FS*	*CSi*	*FSi*	*Illite*	*Kaolinite*	*Vermiculite*
Soil 1	Sandy-loam	36.8	16.4	15.6	13.6	13.9	2.1	1.6
Soil 2	Sandy	86.2	4.1	0.2	1.7	5.1	2.7	-

Exchangeable cations (cmolq.kg^{-1}) and total Fe/Mn content (µg.$^{-1}$).

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^{+}	*Fe*	*Mn*
Soil 1	9.15	1.85	0.35	1.54	1.65	7640	66
Soil 2	1.56	0.19	0.11	0.10	1.86	29017	479

(A) Study of ^{85}Sr distribution Figure 1a shows, by means of a bar chart, ^{85}Sr percentages in each fraction. Percentages are calculated from the sum of specific activities of all fractions, the percentage of residual fraction being the sum of soil residue percentage plus percentages of filter specific activities.

As may be expected[8,11,19], ^{85}Sr is highly soluble, being almost totally extracted in Fraction 1 and also detected in Fraction 2 (about 10 % of total extraction). For this radionuclide, a similar behaviour is seen in both sandy-loam and sandy soils.

(B) Study of ^{134}Cs distribution Figure 1b shows, by means of a bar chart, ^{134}Cs percentages in each fraction.

The distribution of ^{134}Cs depends on the type of soil. In sandy soil (soil 2) Fraction 1 is very low, Fraction 2 about 20% and with a slightly higher extraction in Fraction 3 (30%). The residual fraction is the largest, as expected for this radionuclide, which has a high interaction with clay minerals, especially with illite [1,7,20]. Distribution in sandy-loam soil (soil 1) is different from that in sandy soils. Fraction 1 being almost negligible and Fraction 2 being lower than in sandy soil (5%), probably due to the lower content in Fe and Mn oxides. Fractions 3 and residual are the highest, with similar percentages (slightly higher residual Fraction). The higher value of Fraction 3 in sandy-loam soil may be due to a higher content of organic matter than in sandy soil.

(C) Study of ^{110m}Ag distribution Figure 1c shows, by means of a bar chart, ^{110m}Ag percentages in each fraction, using batch method.

Table 2 Initial activities of samples in Bq.kg^{-1} (± 2σ).

	^{110m}Ag	^{134}Cs	^{85}Sr	*Contamination Day*
Soil 1	5790 ± 45	23450 ± 49	4460 ± 233	22 April, 1991
Soil 2	921 ± 16	2100 ± 14	412 ± 53	31 October, 1990
	3550 ± 35	14500 ± 32	4655 ± 353	22 April, 1991

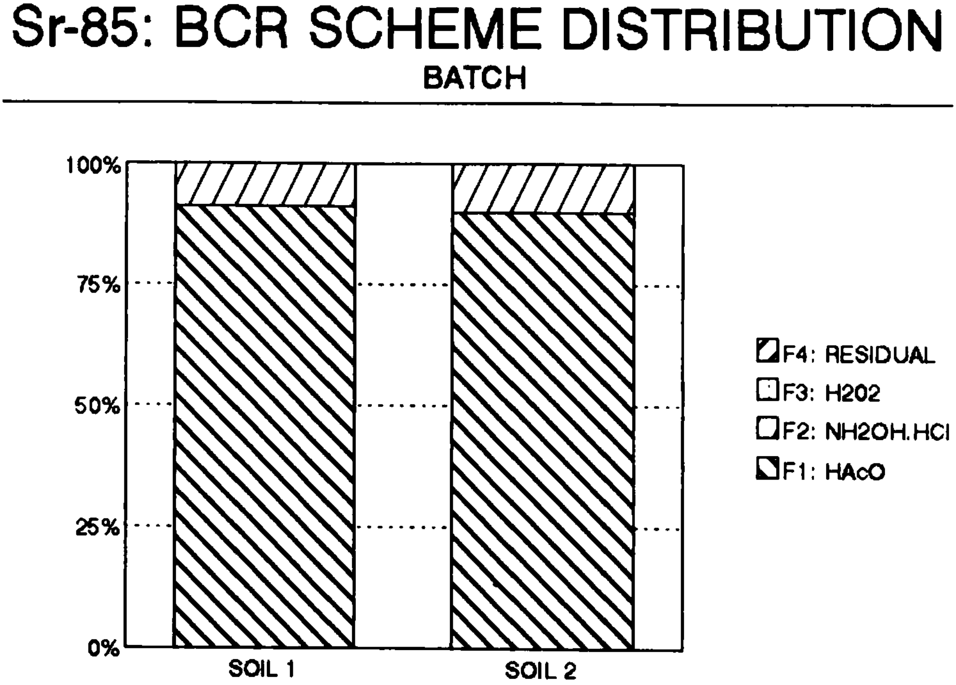

Figure 1a ^{85}Sr percentages in each fraction.

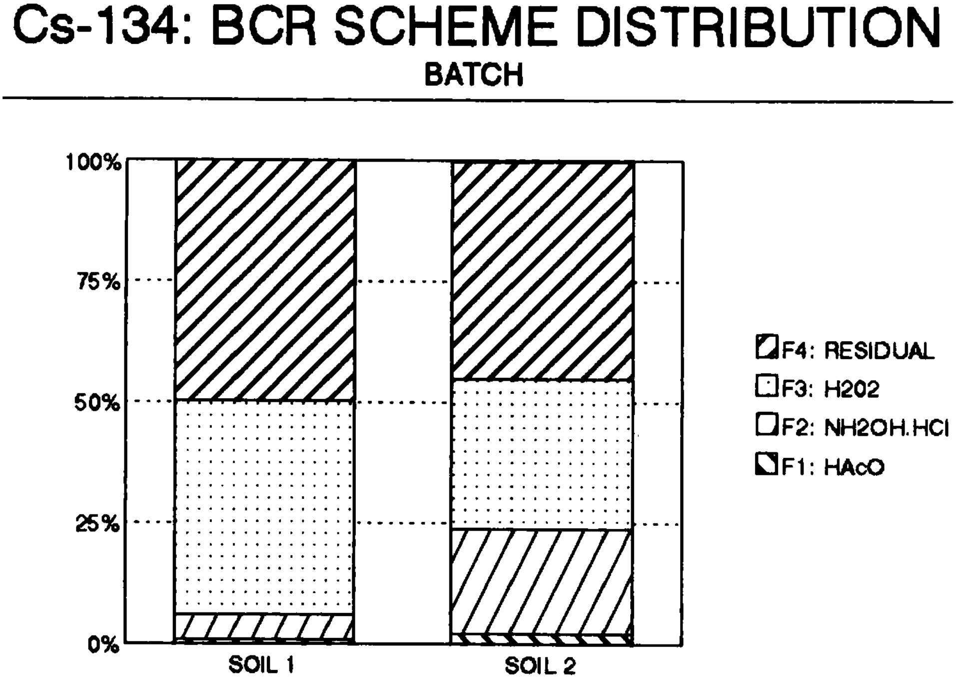

Figure 1b ^{134}Cs percentages in each fraction.

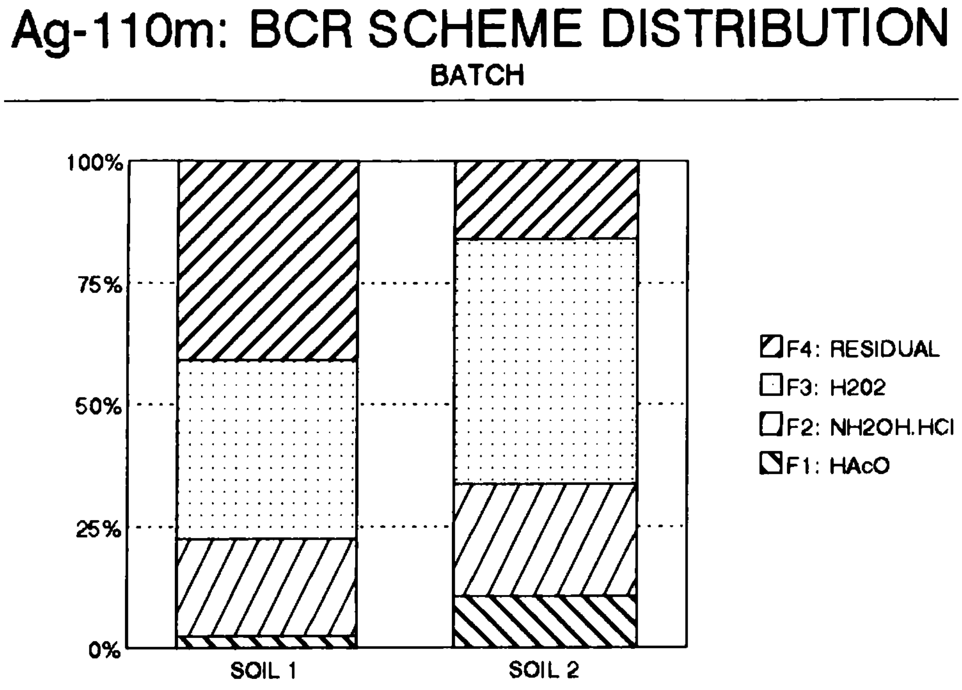

Figure 1c ^{110m}Ag percentages in each fraction.

For this radionuclide, different types of soil lead to significantly different values of distribution percentages. Fraction 1 has the lowest percentages in both sandy-loam and sandy soils, being lower in the former. Fraction 2 is very similar for both types of soil, with about 20% of extraction. Fraction 3 is the highest for this radionuclide: about 35 % in sandy-loam soil and about 50 % in sandy soil. Residual fraction is higher in sandy-loam soil (about 40 %) than in sandy soil (about 15 %). Therefore, organic matter and clay mineral seem to have an important role in ^{110m}Ag retention.

Column results

Sequential extractions were performed with the same soils studied in batch method and results are the mean of sequential extractions carried out. However, although in batch method reproducibility was good enough to mean calculations for all three radionuclides, in column method this was not possible for ^{110m}Ag. Mean values are thus no given for this radionuclide.

The lack of reproducibility could be explained in terms of experimental difficulties. The control of extractant flow, in order to give an extraction time similar to that used in the batch method, is very difficult at the end of the second fraction, and during the whole third fraction. Besides, the further we go along the scheme, the smaller the soil particles become, which leads to losses of soil particles and to a blockage of the porous plate, especially in sandy-loam soil experiments. These differences in flow rate and in extraction times seem to have a high

Table 3 ^{110m}Ag percentages in each fraction, using column method.

	1	*2*	*3*
F1: HAcO	-	-	2.4
F2: $NH_2OH.HCl$	40.2	29.2	89.3
F3: H_2O_2	44.2	21.3	5.4
F4: Residue	15.6	49.5	2.9

influence on radionuclide distributions, taking into account the kinetics of the different equilibria, especially in ^{110m}Ag distribution, as can be deduced for the disperse results obtained, as Table 3 shows.

(A)Study of ^{85}Sr distribution Figure 2a shows, by means of a bar chart, ^{85}Sr percentages in each fraction.

Using this method, a different behaviour is noticed in the two soil types. In sandy soil (soil 2), this radionuclide is almost totally extracted in Fraction 1 (90%), being also found in Fraction 2 (10%). In sandy-loam soil (soil 1), ^{85}Sr is found only in Fraction 1.

(B) Study of ^{134}Cs distribution Figure 2b shows, by means of a bar chart, ^{134}Cs percentages in each fraction.

There is a high soil influence, especially in Fractions 2 and residual. Fractions 1 are almost

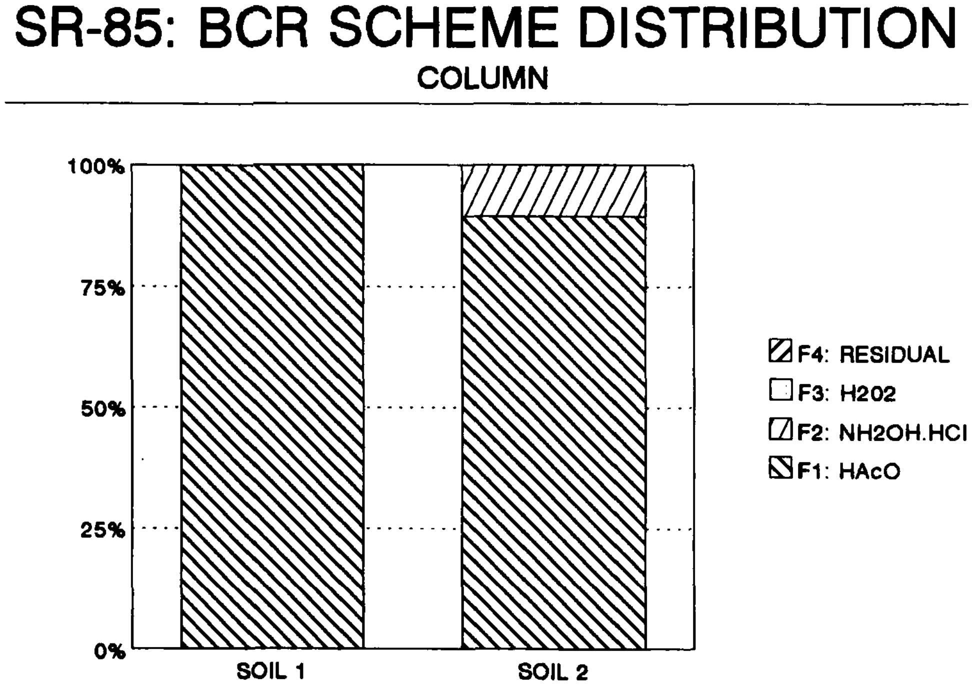

Figure 2a ^{85}Sr percentages in each fraction.

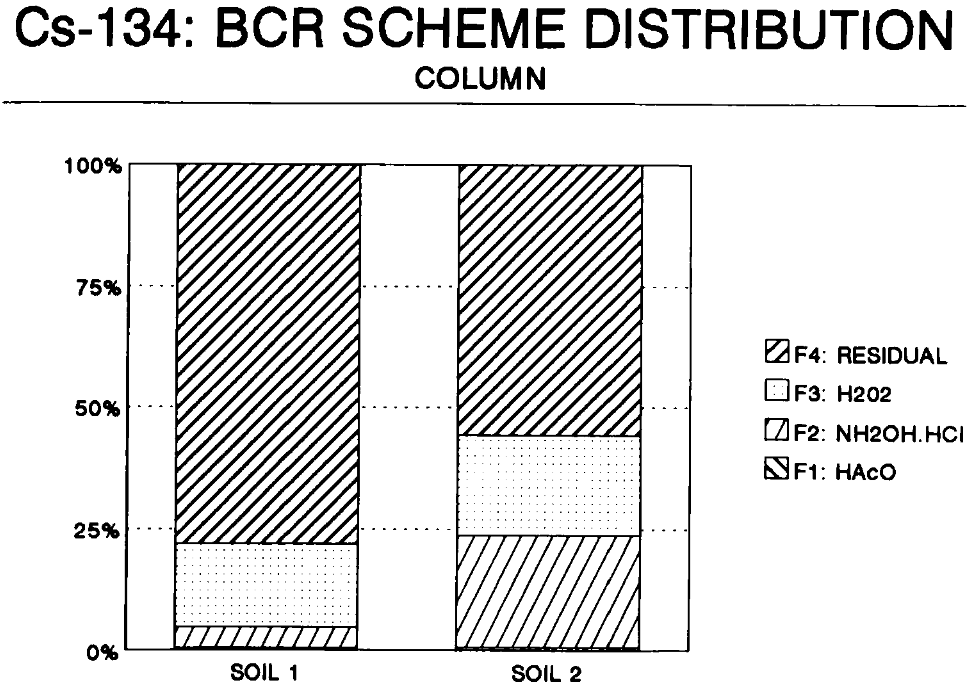

Figure 2b ^{134}Cs percentages in each fraction.

negligible for both types of soil and Fractions 3 are similar in both types of soil (about 20%). Fraction 2 is lower in sandy-loam soil (about 5%) than in sandy soil (about 25%). This behaviour can be attributed to the lower content in Fe and Mn oxides in soil 1. Residual fractions have high values, especially in sandy-loam soil, as can be expected from its higher content of clay minerals.

Batch-column comparison

From the results obtained, the partitioning of the radionuclides studied can be compared. In general, the column method is more cumbersome to perform than the batch method, due to experimental difficulties, as explained before. Some kinetic evidence suggests that the maximum extraction yield is not obtained in all fractions.

(A) ^{85}Sr distribution The only difference noticed between the two methods is the total extraction of ^{85}Sr in Fraction 1 of sandy-loam soil, using the column. In spite of the high solubility of ^{85}Sr, some influence of the method is observed, indicating the influence of the procedure: non equilibrium in column versus a more equilibrated situation in batch.

(B) ^{134}Cs distribution For this radionuclide both methods as well as type of soil significantly influence the final distribution of ^{134}Cs in the different fractions. In general, residual

fractions in column are higher than those obtained in batch, probably due to incomplete solubilization of the radionuclide in the previous fractions, especially in Fraction 3. On the other hand, there is method influence in Fraction 2, the type of soil being the most important feature.

(C) ^{110m}Ag distribution Both factors (method and type of soil) are important, but in this case the method is extremely important due to the lack of reproducibility obtained when applying extraction on column. Some kinetic influence may be supposed.

CONCLUSIONS

Column extraction, especially when it is applied to sandy-loam soils, is an inadvisable method, due to the important experimental drawbacks. Further work should be carried out in order to improve reproducibility.

Kinetic aspects seem to be important because different distributions are obtained when the column method is used, especially for radiocaesium (Fraction 3) and for silver, with respect to the batch distribution. These kinetic aspects lead to incomplete extractions.

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