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Fractionation of ^{137}Cs and ^{60}Co in soils by sequential extractions

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Comparison of six sequential extraction schemes either widely used or specifically developed for speciation of ^{137}Cs and ^{60}Co in two types of soil (Chromic Luvisol and Eutric Fluvisol) is presented. The results from the comparison show that extractable radiocesium in Chromic Luvisol (14%) is about three times lower than in Eutric Fluvisol (39%). For Chromic Luvisol the total extractable radiocobalt varies from 42 to 78% while the variation for Eutric Fluvisol is not so substantial (55–83%). The results show that BCR and NIST schemes developed for heavy metals are not efficient for radiocesium fractionation, but give very good results in the case of radiocobalt. The efficiency of a scheme is dependant not only on the type of radionuclide but on the type of soil as well. The best reagent for evaluation of bioavailable cesium is NH_4NO_3 or other NH^+_4-salt. Practically most of the radiocobalt is in extractable form in both soils (about 83%) and major part of radiocesium (more than 60% depending on the soil type) is strongly bound in the soils and not extractable.

Introduction

It is well established that the uptake of radionuclides (stable elements as well) from soil to plants depends to a great extent on their availability and bonding in the soil. The latter is determined by the physico-chemical properties of the radionuclide and the mechanical and chemical properties of the respective soil. The most widely used method for fractionation in soils is the application of sequential extraction schemes.[1–3] After THESSIER et al.[4] introduced this approach an enormous variety of schemes appeared the majority, however, distinguishing the following forms: free-bound or exchangeable; bound to carbonates; associated to Fe and Mn oxides; associated to organic matter and residual forms. Different reagents in various concentrations and experimental conditions (mainly pH and extraction times) are used for the same purpose. Thus, new variability factors in fractionation analysis (besides the natural ones) were introduced. It is already acknowledged that the type of reagent and experimental conditions play an extremely important role in the fractionation analysis.[3] To overcome this difficulty and attempting to standardize the approach the so called BCR (Community Bureau of Reference, at present Standards Measurements and Testing Programs to the Commission of European Community) three stage extraction scheme was introduced[5] for speciation (fractionation) of heavy metals. Obviously, however, this cannot be an universal solution for all elements and the National Institute for Standards and Technology, USA (NIST) developed a standard protocol for fractionation of heavy metals[6] in soils and sediments and also for speciation of actinides based on Thessier, procedure.[7] ^{137}Cs is among the most studied radionuclides and for its fractionation extractions schemes have been proposed[8] and used[9] in soils specific besides the different versions of THESSIER[4] and ZEIEN procedures.[10] There are relatively few comparisons of the applications of different schemes for speciation of one radionuclide (element) in the same soil. Usually literature data are compared and the conclusions are directed towards the applicability of the reagents[1–3] but not towards the efficiency of the schemes in respect to radionuclide and type of soil. Therefore, the aim of the present study is to compare six sequential extraction schemes either widely used or specifically developed for fractionation of ^{137}Cs and ^{60}Co in two types of soils. The soils are morphologically, chemically and typologically very well characterized and their transfer factors for ^{137}Cs and ^{60}Co to reference plants have been established previously. The results from the comparison will serve as a basis for more practical recommendations concerning the speciation of these radionuclides in soils.

Experimental

Characterization of soils and activity introduction

Two types of soils (Chromic Luvisol and Eutric Fluvisol) have been chosen for an experiment aiming to determine the transfer factors of radiocesium from soil to reference plants within the FAO\IAEA CRP "Classification of soil systems on the basis of transfer factors of radionuclides from soil to reference plants".[11] The experiment took place in the period of 2000–2003 and as a result the transfer factors for radiocesium and radiocobalt have been determined from both soils to wheat and cabbage.[12] The details about the soil characteristics and experimental conditions are given by DJINGOVA et al.[12] The fractionation investigations reported in the present paper were performed in 2006 about seven years after contamination of the soils, therefore, it might be reasonably assumed that equilibrium within the soil systems has been established. Table 1 gives some of the characteristics of both soils.

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Extraction procedures

Table 2 presents the sequential extraction schemes used in the study. Besides NIST (No. 5),[6] BCR (No. 4),[5] NIST protocol for actinides (No. 2)[7] and a version by Zeien (No. 1)[10] procedures two schemes especially developed for speciation of radiocesium (No. 3)[9] and radiocesium and radiocobalt (No. 6)[8] were used for comparison. The BCR procedure was slightly modified by dividing the third step into two (keeping the same conditions as in the original version) and introducing an intermediate measurement. In all schemes 5 *g* soil samples were used and after the respective extraction stage the residual soil was reserved for the next stage by centrifugation at 3000 rev/min for 15 minutes.

Measurement conditions

Measurements were performed using HPGe detector Canberra 7229 (energy resolution 1.8 and efficiency 16% at 1332.5 keV) coupled to a 4196-channel analyzer Canberra 35Plus.

Efficiency calibration has been done using national standard radioactive solutions and standard samples, produced and standardized at INRNE, Bulgarian Academy of Sciences. Accuracy and precision have been verified by participation in IAEA round robin tests.

Results and discussion

The schemes presented in Table 2 permit the following more general characteristics and comments.

Solutions of alkaline (Na^+, NH_4^+) or alkaline earth (Mg^{2+}) salts in the pH range 4.5–9.5 are usually used as extractants for exchangeable forms of the element. These salts easily extract the bioavailable fraction and their efficiency seems to be dependant on the type and concentration of the cation of the salt.

For extraction of the carbonate fraction usually slightly acidic (pH 4–5) solutions of acetate buffer or acetic acid or sodium acetate are used. The efficiency seems to depend on the concentration of both the acid and the salt, the latter having ion-exchange properties thanks to the Na cation.

Hydroxylamine hydrochloride in acid media is used to attack easily reducible oxides (mainly Mn). When used in alkaline media hydroxylamine hydrochloride acts as a reducing agent, however, in acidic media (as in the schemes in Table 2) it acts as an oxidizer and not as a reductant. During the process NH_4^+ is set free and acts as an ion-exchanger. The oxidizing efficiency depends on the concentration of the hydroxylamine hydrochloride and the acidity – on the quantity of the oxidized substances.

Hydrogen peroxide in acidic media is used to oxidize the organic matter being stronger oxidizer than hydroxylamin hydrochloride. The efficiency depends on the pH.

Table 1. General description of the investigated soils

Soil	pH (KCl/H_2O)	Ca, meq/kg	Mg, meq/kg	Na, meq/kg	K, meq/kg	Illite	Clay
CLS	4.7/5.6	197.0	93.0	0.4	78.0	29.3	35.7
EFS	6.1/6.6	142.0	38.8	2.6	6.0	22.9	29.1

CLS – Chromic Luvisol.
EFS – Eutric Fluvisol.

Table 2. Sequential extraction schemes

1[10]	2[7]	3[9]	4[3]	5[6]	6[8]
1M NH_4NO_3	H_2O	1M CH_3COONa	0.1M CH_3COOH	1M $MgCl_2$	2M CH_3COONa 2M CH_3COOH
1M CH_3COONa 1M CH_3COOOH	6% NaOCl	0.25M $NH_2OH{\cdot}HCl$ 0.25MHCl	0.01M $NH_2OH{\cdot}HCl$	1M CH_3COONa 1M CH_3COOH	0.01M $NH_2OH{\cdot}HCl$
0,04M $NH_2OH{\cdot}HCl$ 25% CH_3COOOH	1M CH_3COONa 25% CH_3COOH	1M $NH_2OH{\cdot}HCl$ 25%CH_3COOH	30% H_2O_2	0.04M $NH_2OH{\cdot}HCl$- 25% CH_3COOH	30% H_2O_2 1M CH_3COONH_4
30% H_20_2 0.01M HNO_3	0.04M $NH_2OH{\cdot}HCl$	30% H_2O_2 0.02M HNO_3	1M CH_3COONH_4	30% H_2O_2 3M CH_3COONH_4 20% NHO_3	0.1M NaOH
0.04M $NH_2OH{\cdot}HCl$ 25% CH_3COOOH					

Fractionation of ^{137}Cs

The results from the analyses of both soils (average from 3 replicates) are presented in Figs 1 and 2. On the abscissa the steps of the six extraction procedures are presented by numbers corresponding to those in Table 2. In brackets the total quantity (as % from the input concentration) of extracted Cs is given. On the ordinates the % extracted Cs and the pH of the solution during extraction are given. It is obvious that the results obtained by the different schemes are drastically different. For Chromic Luvisol the total extractable radiocesium varies between 0.79 to 13.7% and for Eutric Fluvisol – between 8.43 to 39.12%. There is also no similarity in the general trend. The following more detailed comments on the efficiency of the reagents can be done.

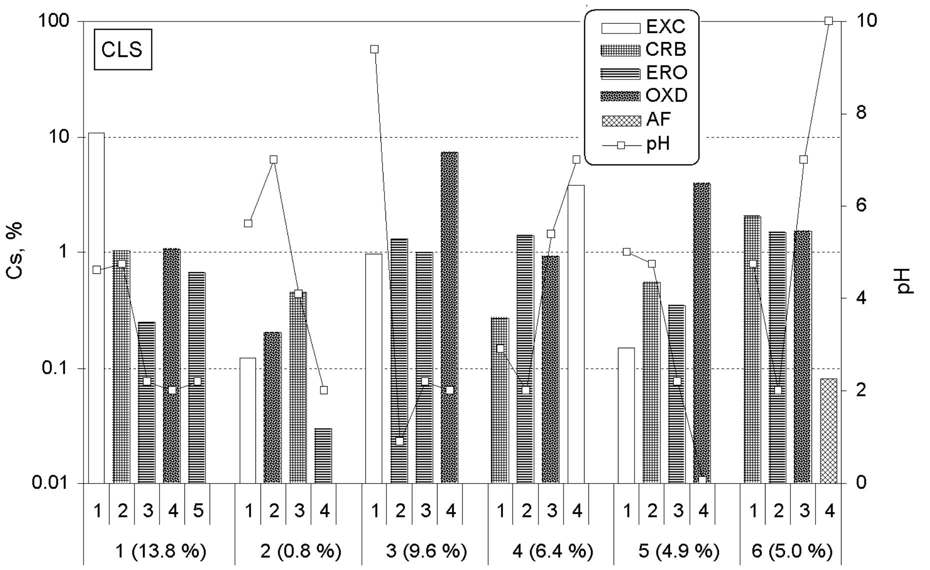

Fig. 1. Results for ^{137}Cs from six different extraction schemes in Chromic Luvisol soil. Abscissa: 1 to 6 numbers of extraction procedures; 1–5 sequence of extraction steps; ( ) total quantity as % from the input concentration of estimate radionuclides. Ordinates: percent extracted ^{137}Cs or ^{60}Co and the pH of the solution. Columns: MOB – mobile fraction; CRB – carbonate fraction; ERO – easy reducible fraction; OXD – oxidizable fraction; AF – acid free fraction; CLS – Chromic Luvisol; EFS – Eutric Fluvisol

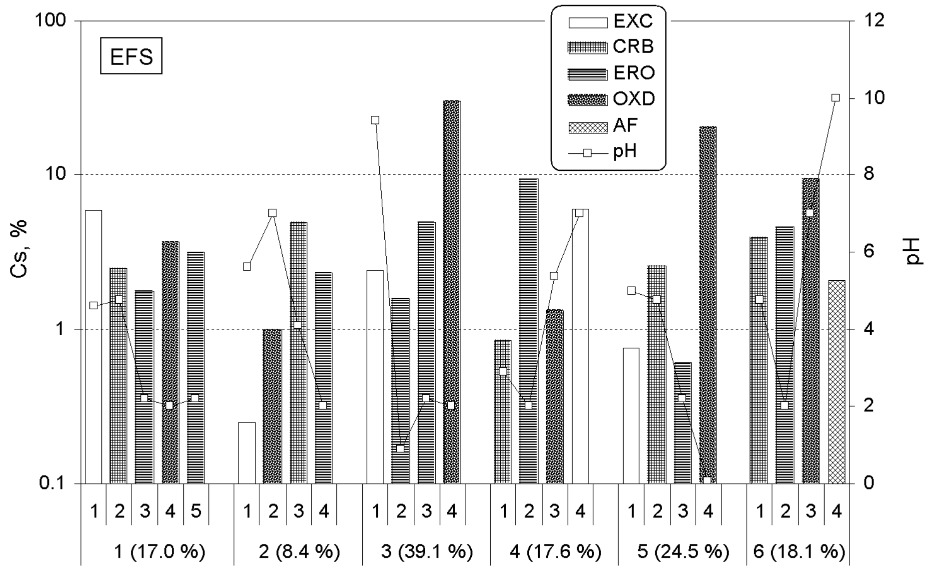

Fig. 2. Results for ^{137}Cs from six different extraction schemes in Eutric Fluvisol soil (see the notes in Fig. 1)

The results in Figs 1 and 2 indicate that bioavailable ^{137}Cs is about 11% in Chromic Luvisol and about 6% in Eutric Fluvisol. The most effective are reagents containing NH^+_4. This is expected having in mind that the ammonium cation (ionic radius 1.43 Å) is an analog to Cs (radius 1.65 Å) and K and replaces them easily. The replacement of Cs with Na (0.98 Å) is energetically unfavorable and with Mg (0.8 Å) sterically hindered.

The capacity for ion-exchange extraction of ^{137}Cs decreases in the following order of: $NH_4^+ > Na^+ > Mg^{2+} > H_2O$.

Usually the extraction of the exchangeable radiocesium is a first step in a procedure but even at a later stage (4–4) the NH^+_4 reagent is an effective ion-exchanger. According to SCHULTZ et al.[7] the preceding oxidation destructs the organic layer of soil particles and liberates the radionuclide. However, as the results show the available radiocesium cannot be extracted effectively because there is no ion-exchanger ([H] – $10^{-5.4}$ mol/L) and obviously it readsorbs and the extraction is further possible only with an ion-exchanging reagent.

Radiocesium bonded to carbonates is up to 2% in Chromic Luvisol and up to 4% in Eutric Fluvisol. The reason for the higher values in 2–3 might be the lack of preliminary treatment with a cation reagent. The acidity is not important (highest acidity 4–1) but the concentration of acetic acid and sodium acetate plays significant role. It might be presumed that in 6–1 exchangeable radiocesium is extracted besides carbonate bound thanks to the availability of Na^+ while in 4–1 no ion exchange component is present.

The easily reducible fraction is about 1.5% in Chromic Luvisol and up to 9.5% in Eutric Fluvisol. The extraction is highest using method 4, however, there is no preceding extraction of exchangeable radiocesium while in method 3 there is [3.1+(3.2+3.3) = 9%] and the sum is not different from the result in 4–2 (9.4%). The lower degree of leaching from Chromic Luvisol might be due to the presence of less reducible components (Mn oxides) in this soil.

About 7% of radiocesium in Chromic Luvisol and 30% in Eutric Fluvisol are bonded to organic matter. Generally, this is the most effective extraction of radiocesium. Hydrogen peroxide destructs the organics even more effectively then NaOCl but to extract the liberated radiocesium an ion-exchanger is necessary.[3] It might be either part of the oxidizer (5–4) or next step in the procedure (4–4). The oxidizer itself is effective if the media is acidic enough. This explains the relatively low extent of extraction at 4–3 (pH 5.4). The highest extraction is established in 3–4 and 5–4 where the solution has highest acidity and no effective ion-exchanger is used before that. Good extraction is achieved in 6–3 although the solution is neutral but the presence of ammonium ions confirms their importance in the extraction of radiocesium.

The results and above consideration lead to the following conclusions. The extractable radiocesium in Chromic Luvisol (14%) is about three times lower than in Eutric Fluvisol (39%). In Chromic Luvisol the extractable radiocesium is mostly in the mobile fraction (being almost twice higher than the exchangeable radiocesium in Eutric Fluvisol) while it is in the organic fraction in Eutric Fluvisol. This fact explains the higher TF from Chromic Luvisol to wheat and cabbage in comparison to Eutric Fluvisol established earlier[12] which was not expected having in mind the properties of both soils. This is also one more evidence that the mobile radiocesium is decisive for the transfer from soil to plant.[8,13] Therefore, in TF investigations it might be enough representative if only extraction with ammonium containing reagent is performed as TWINING et al.[13] have done. It is worth mentioning that for both soils the major fraction containing radiocesium is the organic fraction if an effective ion exchanger is not used (3–4; 4–5; 5–4; 6–3) but with varying percentage. This is an indication that the major part of radiocesium in the organic fraction is bound to easily soluble metal-organic complexes which are effectively leached by NH_4NO_3. The treatment with hydroxylamine hydrochloride does not influence the leaching of organic bound radiocesium the concentration of $[H^+]$ being not enough to displace radiocesium. On the other hand, the only relatively stable results are obtained for oxide bound radiocesium in all procedures. Procedures 1 and 3 use two stages for discerning between easily reducible and resistible oxide bound radiocesium. The sum is similar to the results in 4–2 and 6–2 especially for Chromic Luvisol. Although it might be expected[7] that the introduction of an oxidizing step (1–4) between the two hydroxylamine hydrochloride treatments will lead to a higher extraction this is not confirmed for radiocesium.

The efficiency of the extraction schemes for radiocesium based on total extracted percentage is the following: 1>3>4>6>5>2 for Chromic Luvisol and 3>5>6>4~1>2 for Eutric Fluvisol. Thus, generally for both soils method 3 gives satisfactory results. However, the best information about mobile bioavailable radiocesium is obtained after leaching only with ammonium salt (preferably a nitrate).

Fractionation of ^{60}Co

Figures 3 and 4 present the results obtained by the six schemes for ^{60}Co.

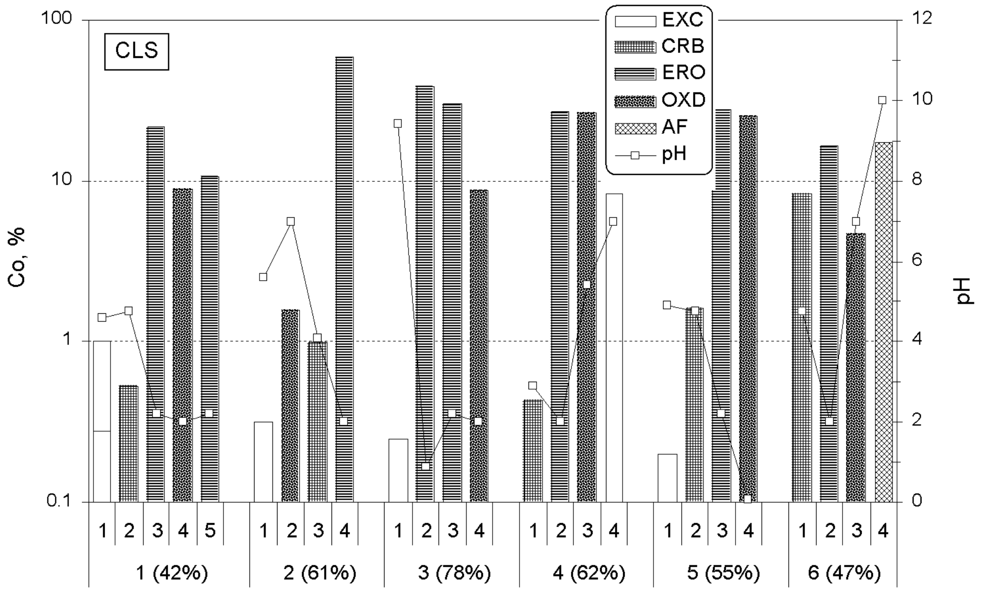

Fig. 3. Results for ^{60}Co from six different extraction schemes in Chromic Luvisol soil (see the notes in Fig. 1)

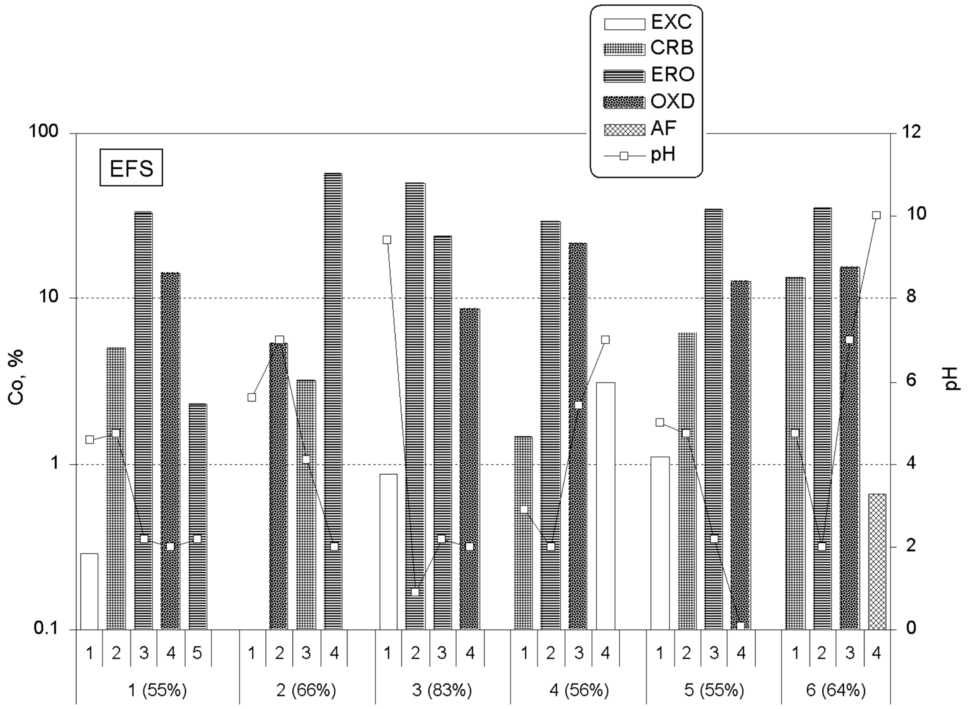

Fig. 4. Results for ^{60}Co from six different extraction schemes in Eutric Fluvisol soil (see the notes in Fig. 1)

For Chromic Luvisol the total extractable radiocobalt varies from 42 to 78% while the variation for Eutric Fluvisol is not substantial (55–83%). Besides, there is certain similarity in the results, radiocobalt is mostly included in the reducible followed by the organic fraction.

Exchangeable radiocobalt is below 1% in both soils. This is the least effective extraction step for radiocobalt and this refers also even to Mg^{2+} which ionic radius (0.78 Å) is very near to the radius of Co^{2+} (0.82 Å). Similarly to radiocesium relatively most radiocobalt is extracted with NH_4^+ reagent but as a last step in a procedure (4–4). The reason is that obviously radiocobalt is held in places not easily accessible mostly in easily reducible and organic components and only after their destruction becomes available for ion-exchange reagents.

The carbonate extraction leaches more radiocobalt from Eutric Fluvisol (up to 5%) than from Chromic Luvisol (below 1%). The most effective are 5–2 and 6–1. The acidity of the solution does not play any significant role (the most acidic 4–1 is not the most effective) if an ion-exchange reagent is lacking. The high extraction results in 6–1 might be due to the fact that this is the first step in the procedures.

The extraction of the reducible fractions leaches similar percentage radiocobalt from both soils. Highest results are obtained by method 3. It is the only scheme that includes steps for easily reducible Mn-oxide fraction (step 2) and for Fe-oxides and sesquioxides (step 3). Besides step 3–2 is with the lowest pH and step 3–3 with highest concentration of the reagent compared to the respective steps in the other procedures. Thus the total percentage of radiocobalt in the oxide fraction amounts to 69% in Chromic Luvisol and 74% in Eutric Fluvisol. Radiocobalt in the organic fraction for both soils in procedure 3 amounts to about 9%. This is in contrast to the results by the other schemes where about 30% of the radiocobalt in Chromic Luvisol and 20% in Eutric Fluvisol are extracted as organic bound fraction. Scheme 2 gives similar results for the radiocobalt in the reducible fraction and organic fractions to scheme 3 although only one step with $NH_2OH\cdot HCl$ is applied. The oxidation of the organics, however, precedes the determination of the reducible phase. Obviously, in the case of radiocobalt the conclusion of SCHULZ et al.[7] that the introduction of an oxidizing step before the hydroxylamine hydrochloride treatments will lead to a higher extraction is valid. In the rest of the schemes the determination of the reducible fraction is before the organic fraction which leads to lower results for radiocobalt in the reducible and higher results in the organic fractions.

All these considerations lead to the following more general conclusions. Practically most of the radiocobalt is in extractable form in both soils. The major part is in the reducible fraction followed by the organic fraction. This confirms the conclusions reached in fractionation studies of stable cobalt.[14–16] The least part of radiocobalt is in exchangeable form. It is below 2% if the extraction step is first in the procedure and up to 8% if the step is after oxidation. Most efficient are schemes Nos 3 and 1.

Conclusions

The comparison of the efficiency of six sequential extraction schemes for fractionation of radiocesium and radiocobalt resulted in the following conclusions.

BCR and NIST schemes developed for heavy metals are not efficient for radiocesium fractionation. Both schemes provide similar results for radiocobalt. NIST protocol for actinides is not efficient for radiocesium but gives very good results in the case of radiocobalt. This result is a strong evidence that the efficiency of the SEC schemes is highly dependant on the radionuclide (element) of interest. When both radionuclides are investigated together a reasonable compromise might be the application of the scheme of KNOX et al.[9]

Of the two schemes developed for fractionation of radiocesium[9] and for radiocesium and radiocobalt the scheme of WASSERMAN et al.[8] is not very efficient for the investigated soils. The reason most probably is that the Brazilian soils for which this scheme has been developed are very different from the two investigated soils. This is an indication that the efficiency of a scheme is dependant not only on the type of radionuclide (element) but on the type of soil as well. This assumption is supported also by the difference in the efficiency of the schemes for the investigated soils Chromic Luvisol being more problematic than Eutric Fluvisol.

The best reagent for evaluation of bioavailable cesium is NH_4NO_3 or other NH_4^+ salt.

In the investigated soils radiocesium is either in the exchangeable or in the organic fraction while radiocobalt is mostly in the reducible followed by the organic fraction. The major part of radiocesium (more than 60% depending on the soil type) is strongly bound in the soils and not extractable while radiocobalt is up to 83% in the extractable fractions.

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References

1. A. FIGURIAS, I. LAVILLA, C. BEUDICHO, J. Environ. Monit., 4 (2002) 823.
2. H. R. VON GUNTEN, P. BENES, PSI Bericht Nr. 94-03, Paul Scherer Institute, Villigen, Switzerland, 1994.
3. J. HLAVAY, T. PROHASKA, M. WEISZ, W. WENZEL, G. STINGEDER, Pure Appl. Chem., 76 (2004) 415.
4. A. TESSIER. P. G. C. CAMPBELL, M. BISSON, Anal. Chem., 51 (1979) 844.

5. U. P. QUEVAUVILLER, H. MUNTAU, B. GRIEPINK, BCR Information EUR 14763 EN, Community Bureau of Science, 1993.
6. C. MCMAHON I. KENNETH, J. LUCEY, L. VINTRO, P. MITCHELL, H. DAHLGAARD, http://www.nist.gov/sigmaxi/Posters00/Abst/mcmahon
7. M. SCHULTZ, W. BURNETT, K. INN, J. Environ. Radioact., 2 (1998) 155.
8. M. A. WASSERMAN, E. R. ROCHEDO, A. C. FERREIRA, C. C. CONTI, A. G. VIANA, F. BARTOLY, J. C. WASSERMAN, D. V. PEREZ, IAEA-TECDOC, 1497(6), 2006, p. 39.
9. A. KNOX, T. HINTON, D. KAPLAN, WSRC – TR- 2001, p. 455.
10. H. ZEIEN, Doctoral Thesis, Rheinische Friedrich-Wilhelms-Universität Bonn, 1995.
11. IAEA-TECDOC-1497, IAEA, Vienna, 2006R.
12. R. DJINGOVA, P. KOVACHEVA, B. TODOROV, B. ZLATEVA, I. KULEFF, J. Environ. Radioact., 82 (2005) 63.
13. J. M. TWINING, P. SHOTTON, K. TAGAMI, T. PAYNE, T. ITAKURA, R. RUSSEL, K. WILDE, G. MCORIST, H. WONG, IAEA-TECDOC-1497, 2006, p. 21.
14. R. G. MCLAREN, D. M. LAWSON, S. SWIFT, European J. Soil Sci., 37 (1986) 223.
15. D. GOMBERT, Nucl. Technol., 108 (2001) 90.
16. P. BHATTACHARYYA, K. CHAKRABARTI, A. CHAKRABORTY, S. TRIPATHY, K. KIM, M. A. POWELL, Ecotoxicol. Environ. Saf., 17537511 (2007).