

Competition of Organic and Mineral Phases in Radiocesium Partitioning in Organic Soils of Scotland and the Area near Chernobyl

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Radiocesium (RCs) partitioning has been studied in four organic soils, with an organic matter (OM) content from 46 to 99%. For each soil, two fractions were derived after removing fats/waxes and humic/fulvic acids (humin + mineral) and after further removal of the mineral matter by an HF/HCl treatment (humin). Characterization by ICP–OES, FTIR, and XRD showed that the removal of mineral matter by the HF treatment was complete. Illitic material was observed in all the soils, with the exception of that with 99% OM. Two patterns of adsorption and desorption were observed. For the 99% OM soil and all the humin fractions, the increase of NH_4 in the solution did not affect the RCs distribution coefficient (K_D), and no differences were observed between the desorption yields obtained with $\text{CH}_3\text{COONH}_4$ and CaCl_2 (around 80% for each extractant). For the other three soils and their humin + mineral fractions, an increase of NH_4 led to a decrease in K_D , and desorption yields were lower with CaCl_2 than with $\text{CH}_3\text{COONH}_4$. This indicated that, in the latter soils, RCs was associated with specific sites in the illitic material. Finally, the increase in K_D in the humin + mineral fraction as compared with the initial soil suggested that humic/fulvic acids influence RCs interaction with the mineral phase.

Introduction

More than a decade after the Chernobyl accident, radiocesium (RCs) is still of concern in areas contaminated by the radioactive plume because of its high plant availability in organic soils and thus the high transfer into the food chain (1). The adverse economic impact in the New Independent States (NIS) of the former Soviet Union and in some areas of western Europe that results when the level of RCs in crops and/or milk exceeds the permitted dose means that there is a need for research dealing with its interaction with the soil phase in order to be able to design treatments capable of decreasing cesium availability in organic soils.

RCs is known to interact mainly with specific sites in illitic clay minerals, called frayed edge sites (FES) (2). The interaction with the regular exchange complex (REC) (organic

acids and planar sites in clays) is usually weak (3). There is evidence from adsorption–desorption experiments that, as in mineral soils, cesium in organic soils becomes progressively more strongly held, especially when illitic minerals are present although the time scale of this process is longer for organic than for mineral soils (4–6). However, RCs partitioning in organic soils is not yet completely understood. The high availability of RCs in these soils has been explained by some authors in terms of an interaction with the organic matter phase that blocks the access to mineral sites, so preventing fixation by the mineral phase (7) while maintaining RCs in an easily exchangeable form. Other studies indicate that it is the mineral phase (illitic minerals) that controls RCs interaction even in soils with a high organic matter content (6, 8, 9) and that RCs may also occur in an exchangeable form in the specific sites in the illite fraction because of a low rate of collapse in this type of soil (10).

The partitioning of RCs between mineral and organic phases in highly organic soils must be known to be able to understand the mechanisms related to the RCs–soil interactions and to design countermeasures based on soil properties (11). Recently, a methodology based on the changes of the RCs solid–liquid distribution coefficient according to the concentrations of competitive species in the solution in equilibrium with the soil phase has been shown to be capable of showing whether the adsorption was controlled by the specific sites in the mineral phase (12). In addition to the adsorption approach, the desorption approach, which may define an exchange-available RCs fraction in given experimental conditions, can also be applied to investigate partitioning since there is a clear dependence of the RCs desorption yield on whether a divalent or a monovalent cation is used in the extraction (13, 14).

To clarify the role of each phase in soil–RCs interaction better, in this paper the behavior of RCs has been compared in four different soils, with organic matter content ranging from around 40 to almost 100%. Three well-defined moieties for each organic soil: initial soil, humin + mineral fraction, and humin fraction have also been isolated. The information stemming from the use of both adsorption and desorption approaches allowed identification of the phase that most influenced RCs behavior, by comparing the results obtained with the whole soils and each of their fractions.

Materials and Methods

Soil Samples. Four organic soils were used:

(1) Bragin, from the Bragin region of Gomel in Belarus, about 150 km northeast of Chernobyl. A Terric Histosol peat soil with pH_{KCl} 5.9, cation exchange capacity (CEC) 103 $\text{cmol}_c \text{ kg}^{-1}$, and organic matter (OM) content of 69%.

(2) Komsomoletz, from the Komsomoletz region of Obninsk in Russia, about 200 km northeast of Chernobyl. A Terric Histosol peat soil with pH_{KCl} 6.2, CEC 114 $\text{cmol}_c \text{ kg}^{-1}$, and OM 84%.

(3) Hatton, from the Moss of Fishrie, Scotland, National Grid Reference NJ 823592. A peat of the Hatton Association developed over Middle Old Red Sandstone with pH_{KCl} 2.4, CEC 237 $\text{cmol}_c \text{ kg}^{-1}$, and OM 99%.

(4) Birnie, from Birnie Hill, Glensauigh Research Station, Scotland, National Grid Reference NO 663 795. A peaty podzol of the Strichen Association, Gaerlie series with pH_{KCl} 3.2, CEC 62.2 $\text{cmol}_c \text{ kg}^{-1}$, and OM 46%.

The Bragin and Komsomoletz soils were taken from plowed plots. The Hatton soil was from undisturbed moorland, and the Birnie soil was from a moorland site where heather had been burned 10–12 years previously and the

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TABLE 1. Weight Percentage of the Fractions Obtained from Soil Samples

soil	organic matter (%)	sum of organic fractions (%)	fats and waxes (%)	fulvic and humic acids (%)	humin (%)	mineral matter (%)
Birnie	45.9	43.8	3.3	29.1	11.4	56.2
Bragin	67.0	65.2	2.2	52.9	10.1	34.8
Komsomoletz	83.9	79.4	3.1	54.5	21.8	20.7
Hatton	98.6	95.8	7.0	36.9	51.9	4.2

TABLE 2. Mineral Composition of the Soils Determined by XRD Analysis^a Using Co and CuK α

radiations	Birnie		Bragin		Komsomoletz		Hatton	
	Co	Cu	Co	Cu	Co	Cu	Co	Cu
albite	24	20	9	5	6	1	7	ND ^b
anhydrite	ND	ND	ND	ND	2	3	39	44
calcite	ND	ND	5	7	33	24	ND	ND
hematite	ND	1	1	1	7	4	ND	ND
hornblende	ND	ND	6	2	ND	ND	ND	ND
illite	13	14	4	7	7	6	ND	ND
magnetite + maghemite	ND	ND	2	4	14	23	ND	ND
periclase	ND	ND	ND	ND	ND	ND	38	45
orthoclase	11	7	8	6	7	2	4	ND
quartz	52	58	66	68	24	37	11	11
ash % ^c	54		33		16		2	

^a Values are expressed as a percentage of the ash. ^b ND, not detected. ^c Expressed with respect the initial soil.

area subsequently managed by sheep grazing. Samples were air-dried and freed of fresh plant material. They were screened through 1-mm sieves and homogenized before analysis.

From each soil, two fractions (humin + mineral and humin) were isolated after sequentially removing fats and waxes, humic and fulvic acids, and the mineral matter according to the methodology subsequently described.

Humin + Mineral. The air-dried soil was refluxed for 16 h with an ethanol/toluene mixture (1:1 v/v) to remove fats and waxes. After drying the soil residue at room temperature, humic and fulvic acids were extracted by end-over-end shaking for 16 h, with 40 mL g⁻¹ of 0.2 mol L⁻¹ NaOH. This extraction was carried out three times; the soil residue being separated and collected after each extraction by centrifugation at 2000g for 20 min. The final residue was neutralized with 6 mol L⁻¹ HCl, washed three times with 0.1 mol L⁻¹ HCl, washed three times with distilled water (10 mL g⁻¹), and finally freeze-dried. It was designated as the humin + mineral fraction.

Humin. A portion of the humin + mineral fraction was used to obtain mineral-free humin. The method used was based on a three-step digestion. In the first step, the sample was suspended in 0.1 mol L⁻¹ HF:0.1 mol L⁻¹ HCl (20 mL g⁻¹) and digested for 64 h. Subsequently, the sample was digested three times for 1 h in 5.5 mol L⁻¹ HF:1.1 mol L⁻¹ HCl (20 mL g⁻¹). Finally, the residual sample was suspended in 5.5 mol L⁻¹ HF (20 mL g⁻¹) and digested four times for 16 h. Digestions were carried out at room temperature. The presence of HCl in the first and second steps and the short extraction times in the second step, in which concentrated HF was used for the first time, were used to decrease the risk of formation of insoluble fluorides that cannot be removed by subsequent extractions (15). After digestions, the solid was recovered by centrifugation at 2000g for 20 min. To wash the sample material and to obtain a better removal of the mineral matter, the residue was suspended in a washing solution, and the supernatant containing low-density organic material (humin) was decanted off, leaving some sand-size particles that were thought to be insoluble fluorides. The

decanted supernatant was then centrifuged. This washing procedure was performed three times with 0.1 mol L⁻¹ HCl and three times with water. Finally, the organic-rich residue was freeze-dried.

Analytical Methods for Sample Characterization. *Organic Matter Content.* Soil samples were oven-dried overnight at 110 °C and then ashed at 450 °C for 16 h. The OM content was determined by the loss of weight on ignition.

X-ray Diffraction. The mineral composition of the soil samples was determined semiquantitatively by X-ray diffraction (XRD) using CoK α and CuK α radiations. Soil samples were ashed at 450 °C for 16 h and analyzed directly. Interpretation was by Rietveld full pattern fitting (16) using SIROQUANT (CoK α) and FULLPROF (CuK α) software programs.

Determination of Major Elements. Major elements such as Fe, Al, and Si were determined in humin + mineral and humin fractions by fusion with LiBO₂ and subsequent quantification by inductively coupled plasma optical emission spectroscopy (ICP-OES). In short, a sample (10–20 mg) was oven-dried overnight in a platinum crucible at 110 °C and then ashed in a muffle furnace at 550 °C for 16 h. The ash produced was thoroughly mixed with an amount of LiBO₂ equivalent to three times the weight of the sample and fused at 1000 °C for 30 min (17). After cooling to room temperature, the pellet obtained was dissolved in 0.9 mol L⁻¹ HNO₃, and the solution was subsequently diluted to 0.3 mol L⁻¹ HNO₃. The concentration of Fe, Al, and Si in the resulting solution was determined by ICP-OES.

Fourier Transform Infrared Spectroscopy. Infrared spectra of initial soil, humin + mineral, and humin fractions (1 mg in 13 mm diameter KBr pressed disks) were recorded on a Magna-IR Spectrometer 550 over the range of 4000–350 cm⁻¹. Spectra were recorded before and after oven drying the disks at 150 °C overnight.

K_D(Cs) Determination. The radiocesium (RCs) solid-liquid distribution coefficient (K_D(Cs)) was obtained in six scenarios, with the same concentration of Ca and K (0.1 and 0.01 mol L⁻¹, respectively) and increasing NH₄ concentrations (0, 0.5, 1.0, 2.5, 4.0, and 5.0 mmol L⁻¹). Samples (0.25 g) were

preequilibrated three times with 25 mL of these solutions; the supernatant being decanted off after each preequilibration following centrifugation at 13000g. Finally, the samples were shaken for 22 h with the same volume of each solution labeled with an almost carrier-free ^{134}Cs solution (Damri, CS134-ELSB45). $K_D(\text{Cs})$ values were calculated from ^{134}Cs levels in the supernatant before and after equilibration. The activity level added was 10^6 Bq kg^{-1} for samples with a significant content of mineral matter (initial and humin + mineral samples from Birnie, Bragin, and Komsomoletz) to ensure a good precision for the counting of the final solution and to make the Chernobyl contribution negligible if present. For samples with an almost negligible content of mineral matter (Hatton and all humin fractions), an activity level of 10^5 Bq kg^{-1} was enough to get a suitable final activity in the supernatant because of their low adsorption capacity. Considering these levels of contamination, the stable Cs loading was $10^{-4} \text{ mmol of Cs/kg of soil}$ for the first samples and $10^{-5} \text{ mmol of Cs/kg}$ for the second samples, these loadings being lower than the stable Cs content in the original soil (Birnie, 2.4×10^{-2} ; Bragin, 4.9×10^{-3} ; Komsomoletz, 2.2×10^{-3} ; and Hatton, $9.8 \times 10^{-5} \text{ mmol kg}^{-1}$).

Determination of Radiocesium Available Fraction. The available fraction of RCs was measured in the samples previously contaminated with ^{134}Cs by equilibration in the Ca-K scenario. After the adsorption experiment, the supernatant was removed, and the moist sample was immediately suspended with $1 \text{ mol L}^{-1} \text{ CH}_3\text{COONH}_4$ or $1 \text{ mol L}^{-1} \text{ CaCl}_2$ separately (40 mL g^{-1}), end-over-end shaken for 16 h, and centrifuged at 13000g. The ^{134}Cs was determined in the supernatant, and the desorption yield was related to the available fraction.

γ -Spectrometry. The counting rates of samples was determined by γ -spectrometry, using a solid scintillation detector with a 3-in. NaI (Th activated) crystal in a Packard Minaxi 5000 Series spectrometer. The measurements were carried out in 20-mL capacity polythene vials at constant efficiency and using a 544–664 keV window. The measurement time was set to obtain $\text{RSD} < 0.5\%$.

Results and Discussion

Sample Characterization. *Weight Distribution of Soil Fractions.* A compilation was made on the basis of the fractions defined by the treatments described in the Experimental Section. The percentage that each fraction represented was calculated from the loss of weight of the initial soil sample after each treatment. The fractions defined were fats and waxes from ethanol/toluene extraction; humic and fulvic acids from NaOH extractions; mineral matter from HF digestions; and humin as the residue remaining.

Table 1 shows the percentage of each fraction in the four soils. The organic matter (OM) content, quantified by the loss of weight on ignition, may be compared to the sum of the percentages of all the organic fractions derived from the treatments. Both the values showed good agreement for the four soils and indicated that there was no significant loss of sample ($<5\%$) after all treatments. The OM was not affected quantitatively by the different treatments, and the removal of mineral matter was effective. Conclusions from the percentage of each fraction present depending on the type of soil and the total OM content are not easily drawn. However, it was evident that the humin content was more closely related to the total OM content than were the fulvic and humic acids content.

Characterization of Mineral Matter by X-ray Diffraction. The results of the analysis are presented in Table 2. All soils except Hatton had a significant content of illite. Taking into account the weight of ash, the illite content was much greater for Birnie soil (7.0%) than for the Bragin and Komsomoletz soils (1.3 and 1.1%, respectively). The presence of illite was

TABLE 3. Fe, Al, and Si Content in Humin + Mineral (h+m) and Humin (h) Fractions and Percentage of Decrease between Them

soil	weight of sample		Fe			Al			Si		
	h+m (g)	h (g)	h+m ^a (mg)	h ^a (mg)	decrease (%)	h+m ^a (mg)	h ^a (mg)	decrease (%)	h+m ^a (mg)	h ^a (mg)	decrease (%)
Birnie	12.0	3.4	105 ± 2	4.1 ± 0.3	96.1	634 ± 16	5.7 ± 0.4	99.1	3211 ± 78	4.6 ± 0.2	99.9
Bragin	5.0	1.1	170 ± 2	3.4 ± 0.7	98.0	97.2 ± 0.6	1.7 ± 0.1	98.2	748 ± 18	0.60 ± 0.02	99.9
Komsomoletz	5.0	2.6	320 ± 1	2.1 ± 0.1	99.3	27.6 ± 1.2	3.7 ± 0.1	86.6	190 ± 8	0.83 ± 0.30	99.6
Hatton	10.0	9.2	42.6 ± 8.8	5.8 ± 0.6	86.4	4.8 ± 1.6	4.5 ± 0.2	6.8	12.9 ± 2.4	0.47 ± 0.01	96.4

^a Results are expressed as milligram of element present in the humin + mineral and humin samples (mean value ± standard deviation, n = 2).

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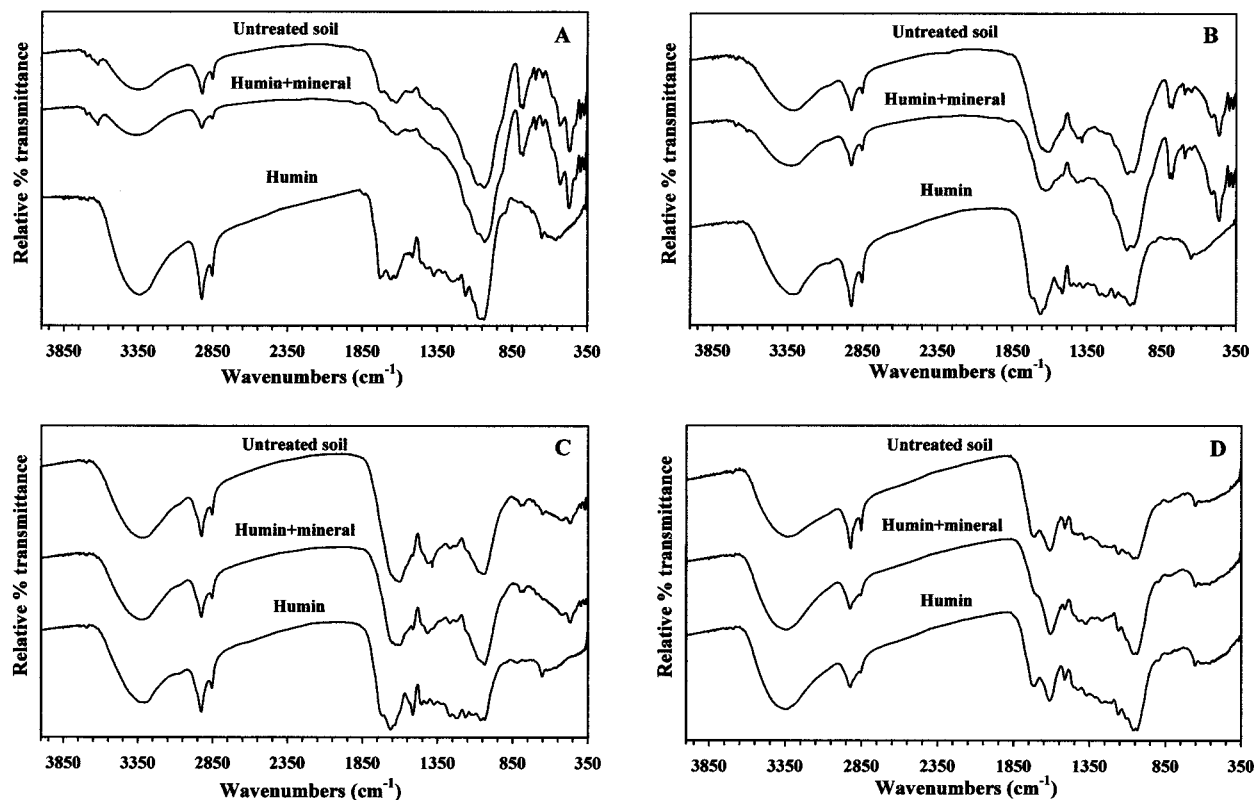


FIGURE 1. Infrared spectra of the four soils and their derived fractions: (A) Birnie, (B) Bragin, (C) Komsomoletz, (D) Hatton.

also noted in humin + mineral fractions and was taken into account in drawing conclusions about interaction of radiocesium (RCs) in these soils.

Effectiveness of Mineral Matter Removal. The decrease in the content of Fe, Al, and Si on transforming humin + mineral to humin for each of the four soils was used as an indicator of the mineral matter removed by the HF treatment.

Table 3 shows the total amount of Fe, Al, and Si in humin + mineral and humin fractions for the four soils. The percentage of decrease of these elements, calculated on the basis of the mean values, allows the evaluation of the effectiveness of the HF treatment. Within these results, the decrease in the Si content can be considered as the best indication of the removal of the structural mineral matter. This element was almost completely eliminated from all humin + mineral fractions. The decrease in Fe and Al content was around 87–100% in Bragin, Komsomoletz, and Birnie samples. Hatton samples, in which the mineral content was initially relatively small, seemed to behave differently from the other soils since smaller percentages of decrease were obtained for these two elements. However, final amounts in the humin fractions were similar to those in the rest of the soils. Therefore, it can be concluded that the procedure was effective in removing structural mineral matter from the organic soils.

Infrared Spectroscopy. Figure 1 shows the infrared spectra of the four soils and their respective humin + mineral and humin fractions. The spectra shown are those obtained after treatment at 150 °C since there was better resolution of the peaks associated with mineral matter. Besides, heating results in the removal of water bands.

For the initial soils, differences could be observed according to the OM content. Soils with a high OM content (Bragin, Komsomoletz, and Hatton) presented strong absorption bands at 1650 and 1550 cm^{-1} assigned to proteinaceous material and at 1600 and 1400 cm^{-1} assigned to carboxylate, these bands being less significant for Birnie. On the other hand, all soils showed a strong absorption at 1000–

1100 cm^{-1} related to carbohydrate. Most of the inorganic components such as quartz and feldspar were clearly present from absorption bands in the 900–350 cm^{-1} region for all the soils, except Hatton because of its negligible mineral matter content.

If the spectra for the fractions derived from the same soil are compared, they are seen to be quite similar for initial soil and humin + mineral fractions, whereas some variations were observed in the humin fractions (Figure 1). The spectra of humin fractions demonstrated that inorganic components were almost totally removed by HF, as shown by the absence of bands in the 900–350 cm^{-1} region. Furthermore, as a result of the acid treatment, a decrease in the carbohydrate band was observed for Bragin and Komsomoletz humin fractions, accompanied by an enhancement of the C=O stretching band of free carboxyl groups at 1730–1710 cm^{-1} , the latter also being observed for Birnie humin fraction. However, Hatton and Birnie retained the same intensity for the carbohydrate band after HF treatment, suggesting the presence of a more inert material such as cellulose. Finally, lignin bands (1600–1000 cm^{-1} region) were more evident for Bragin and Komsomoletz humin samples. In conclusion, infrared spectra show that treatment with HF decreases the structural mineral matter content with relatively little influence on the OM phase.

Adsorption Behavior of Radiocesium. The RCs solid-liquid distribution coefficients ($K_D(\text{Cs})$) were obtained in different Ca–K– NH_4 scenarios for the set of fractions generated from each soil (results were calculated as the mean of three replicates with RSD < 2%, except for $K_D < 3 \text{ mL g}^{-1}$, for which RSD was lower than 8%).

If radiocesium was associated with frayed edge sites (FES) in illite, K_D should be quite sensitive to changes of NH_4 concentrations since NH_4 is much more competitive than K at these sites, with values of the trace selectivity coefficient that may be around 5–8 (2). In this case, the ratio of K_D can be expressed as

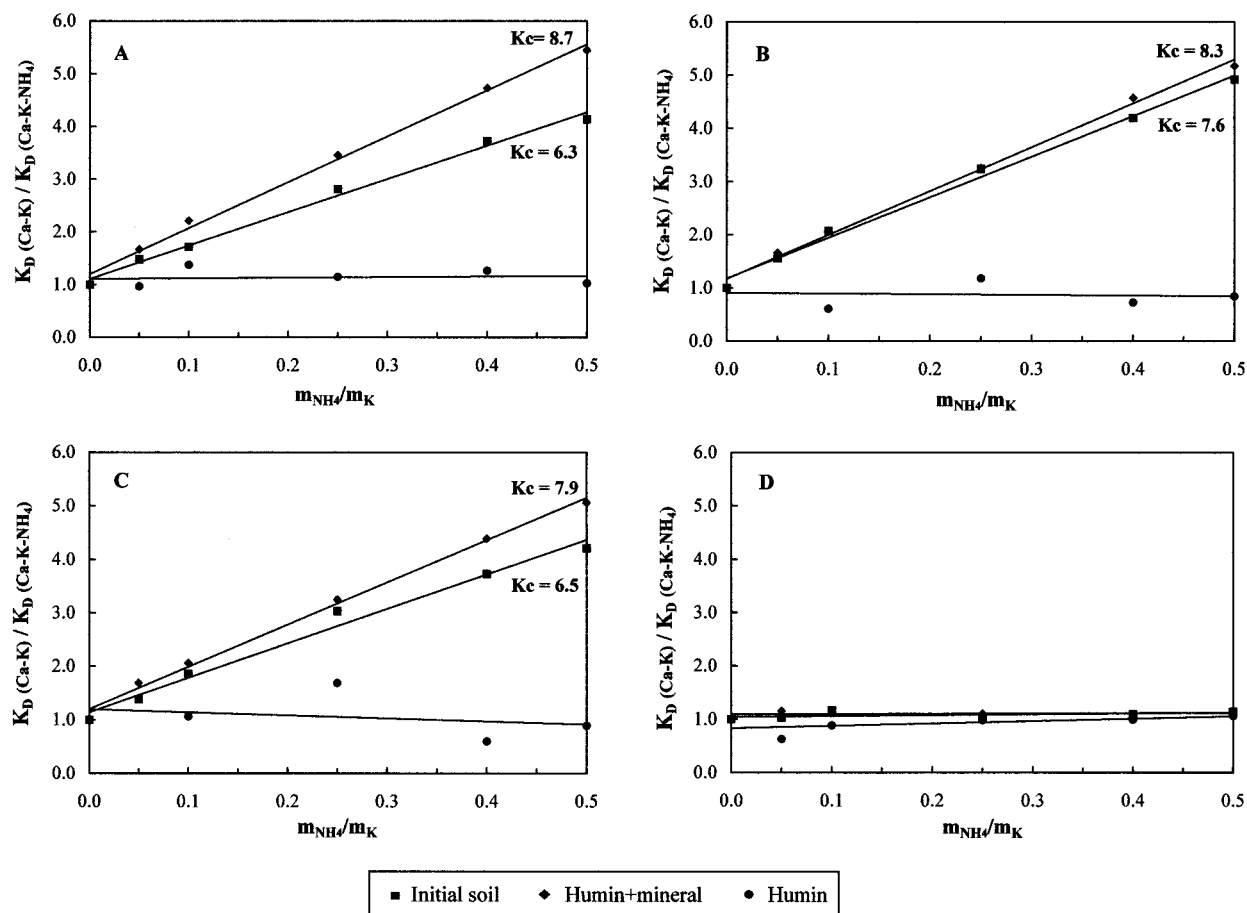


FIGURE 2. Response of radiocesium solid-liquid distribution coefficient (K_D) to increasing NH_4 concentrations in a Ca-K- NH_4 scenario for (A) Birnie, (B) Bragin, (C) Komsomoletz, and (D) Hatton soils and their derived fractions.

$$\frac{K_D(\text{Ca-K})}{K_D(\text{Ca-K-NH}_4)} = 1 + K_C^{\text{FES}}(\text{NH}_4/\text{K}) \frac{m_{\text{NH}_4}}{m_K}$$

where m_K and m_{NH_4} are the concentrations of K and NH_4 in mmol L^{-1} , $K_D(\text{Ca-K})$ is the K_D in a Ca-K scenario at zero loading of NH_4 , $K_D(\text{Ca-K-NH}_4)$ is the K_D in a Ca-K- NH_4 scenario, and $K_C(\text{NH}_4/\text{K})$ is the NH_4 -to-K selectivity coefficient in FES.

On the other hand, if radiocesium is related to the regular exchange sites, K_D should not change since NH_4 and K at these sites are equally competitive (18, 19), and the ratio $K_D(\text{Ca-K})/K_D(\text{Ca-K-NH}_4)$ tends to unity (12). Therefore, the response of the K_D to the changes of NH_4 concentrations may indicate if RCs is either associated with REC or FES sites. If it were the former, K_D would be unaffected by changes in NH_4 concentration. But if RCs is associated with FES sites, there would be a clear decrease in K_D as NH_4 concentrations increased. The response of this coefficient to changes of NH_4 concentration may be evaluated by plotting the ratio of the distribution coefficients at zero loading of NH_4 ($K_D(\text{Ca-K})$) and in a NH_4 -K scenario ($K_D(\text{Ca-K-NH}_4)$) against the ratio of the concentrations of NH_4 and K in mmol L^{-1} (m_{NH_4}/m_K), the slope being related to the NH_4 -to-K trace selectivity coefficient ($K_C(\text{NH}_4/\text{K})$), as shown in Figure 2.

As can be seen in Figure 2, two behavior patterns were observed; the Hatton set of samples behaving in a different way from Bragin, Birnie, and Komsomoletz samples. In these latter soils, initial soil and humin + mineral fractions clearly showed an interaction of RCs with the specific sites since a decreased response of the K_D with an increase in NH_4 concentration was observed, also represented by slopes ranging from 6.3 to 7.6 for initial soil samples and from 7.9

to 8.7 for humin + mineral fractions, thus showing the clear domination of illite in RCs partitioning. Furthermore, the higher trace selectivity coefficients observed after removing the organic acids in soil samples suggest an indirect role of these organic acids in RCs adsorption by blocking the specific sites (20), although it has also been shown in a previous study that there is no relationship between humic acid content and RCs desorption (14). The RCs adsorption behavior changed drastically for humin as compared to other fractions since no variations of K_D were noticed after increasing NH_4 concentrations in the solution. Therefore, after the HF treatment and thus the removal of the mineral phase, the RCs adsorption seemed to be determined by the regular exchange complex, mainly OM sites.

The adsorption pattern of RCs in Hatton soil and humin + mineral fractions was identical with that observed in the humin fractions. Hatton samples did not show an interaction with specific sites since there was no response of the K_D to changes in NH_4 concentration. Therefore, it can be concluded that only in soils with an extremely low mineral content and with no illite present will the partitioning of RCs be controlled by sites in the regular exchange complex. A comparison of the K_D values obtained at zero loading of NH_4 , included in Table 4, allows similar conclusions to be drawn. In Komsomoletz, Bragin, and Birnie soils, the relative sequence of K_D values was the same for all the soils: with highest values for humin + mineral, lower values for initial soil, and much lower values for humin fractions. The higher values of K_D after the extraction of the organic acids may also indicate a blocking effect of these in mineral sites, thus decreasing the specific adsorption properties in the untreated initial soil samples. For Hatton soil, the adsorption pattern

TABLE 4. K_D and Desorption Yield Values of Radiocesium for the Initial Soil, Humin + Mineral, and Humin Fractions Obtained from the Adsorption Experiment

soil		K_D (mL g ⁻¹) ^a	desorption yield (%) ^b	
			CH ₃ COONH ₄	CaCl ₂
Birnie	initial soil	180.6	49.6	5.8
	humin + mineral	696.6	33.4	0.7
	humin	2.6	94.2	84.2
Bragin	initial soil	164.0	46.1	3.3
	humin + mineral	644.0	41.3	1.1
	humin	1.9	86.1	86.3
Komsomoletz	initial soil	61.0	49.4	10.7
	humin + mineral	239.7	49.5	3.3
	humin	1.4	86.8	94.5
Hatton	initial soil	4.3	88.8	88.2
	humin + mineral	4.4	80.3	83.4
	humin	3.8	80.2	86.2

^a Calculated in 0.1 mol L⁻¹ CaCl₂ and 0.01 mol L⁻¹ KCl. ^b Soil samples come from the adsorption experiment in a Ca-K scenario.

was the same for the three fractions: the K_D values were low and similar to those of humin fractions of the other soils, clearly showing that the organic component of humin does not play a key role in RCs retention in organic soils. However, it has been suggested that OM, which could be removed by extraction and oxidation, could play a role in RCs partitioning by hindering adsorption at specific sites of illite (7) just as humic and fulvic acids appear to do.

Desorption Behavior of Radiocesium. To complete the information about the partitioning of RCs in organic soils, two parallel extractions were carried out with all the samples derived from the initial soils, using NH₄ and Ca as extractant solutions. In previous studies, the contrasting capacity of monovalent and divalent cations for desorbing exchangeable RCs has been shown (13, 14). NH₄ is able to extract RCs associated with both REC and FES sites, whereas Ca, because of its greater hydrated ratio, cannot enter into the specific sites and can only desorb RCs from the regular exchange complex. Therefore, the comparison between the desorption yields obtained with the two reagents allows conclusions to be drawn about RCs partitioning between REC and FES sites.

Table 4 shows the RCs desorption yields in samples resulting from the adsorption experiment after applying 1 mol L⁻¹ CH₃COONH₄ and 1 mol L⁻¹ CaCl₂. The desorption yields obtained with CaCl₂ in Komsomoletz, Bragin, and Birnie samples show a similar sequence for all the fractions derived from the same soil. The desorption yields were greatest for the humin, much lower for the initial soil, and even lower for the humin + mineral. This was exactly the opposite sequence to that for the distribution coefficients, showing the highest rate of fixation in the humin + mineral; RCs remaining, in contrast, exchangeable in the humin. If a similar comparison was carried out with CH₃COONH₄ desorption yields, a similar sequence could be established. The comparison between the desorption yields of NH₄ and Ca in Komsomoletz, Bragin, and Birnie samples sheds light on partitioning aspects. NH₄ desorption yields were much higher than those of Ca in the initial soil and humin + mineral fractions, whereas similar, high values were obtained for the humin. This behavior means that for the initial soil and humin + mineral fractions the RCs were mainly associated with FES. The desorption with Ca in these samples was less than 10%, with the exception of the values for the Komsomoletz initial soil. Furthermore, comment should be made on the magnitude of desorption yields for all samples, particularly for humin fractions. The lack of a total extraction in these latter samples should not be taken to indicate an irreversible fixation in the humin, but simply show the inefficiency of a single extraction to desorb all the exchangeable RCs. Nevertheless, for comparative purposes, values

from single extractions have been used. Moreover, if all the desorption yields for the Hatton fractions are compared, it can be observed that similar large values are obtained regardless of the sample and of the extractant reagent used. This behavior pattern was again in agreement with that found for K_D , showing the lack of specificity of this soil in its interaction with RCs, which remained in an easily exchangeable form in the REC sites. The high availability of RCs in organic soils may therefore not be related to an association with OM sites but related to the fact that OM partially inhibits irreversible Cs adsorption at FES, possibly by preventing the collapse of the clay lattice.

On the other hand, it must be considered that adsorption-desorption experiments in this work were conducted for a fixed an relatively short time period and that some changes could be expected for longer periods depending on the sample. Thus, for samples in which the mineral phase (illitic materials) controls the sorption, an increase in fixation could be expected in a scale of months (4, 8, 9), whereas for samples in which mineral matter does not rule the sorption (negligible content or no presence of illitic minerals), no increase should be observed; radiocesium being present in an available form for longer than in the former samples (8, 9).

Finally, the conclusions drawn from adsorption-desorption experiments allow us to postulate that, for organic soils with low sorption properties and low fixation capacity, the addition of soil amendments with a high illitic content could be a promising countermeasure strategy.

Acknowledgments

This work was part funded by the Scottish Office Agriculture, Environment and Fisheries Department and by DGICYT (AMB-96-0950). The authors thank S. Hillier (MLURI) and X. Alcobé (SCT-UB) for XRD analyses and A. R. Fraser (MLURI) for IR analyses. A.R. thanks MEC for the grant received.

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Received for review July 31, 1997. Revised manuscript received December 2, 1997. Accepted December 4, 1997.

ES970672Y