Short communication

DEPTH DISTRIBUTION OF ^{137}Cs IN ANTHROSOL FROM THE EXPERIMENTAL FIELD "RADMILOVAC" NEAR BELGRADE, SERBIA

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This is a preliminary study of the depth distribution of ^{137}Cs radionuclides in cultivated anthrosol soil of a 15-year old peach tree plantation at the experimental field "Radmilovac" near Belgrade. Before planting, the soil was ploughed at the depth of 1 m. The soil had not been annually ploughed, irrigated and treated with mineral fertilizers for three years before sampling. Activity concentration for ^{137}Cs ranged from 1.8 Bq kg^{-1} to 35 Bq kg^{-1}. Along the soil depth it varied highly, reaching as high a total variation coefficient as 83 %. Radiocaesium distribution patterns depended on the extent of soil mixing in the plough layer, as it was mechanically transferred from the surface to the lower soil layers during cultivation. [137]Cs was associated with humus content and fixation to clay fractions in the soil. Our results single out soil's hygroscopic water as a valuable parameter for ^{137}Cs behaviour that could be used commonly if the measurement is standardised.

KEY WORDS: *cultivated soil, fruit trees, hygroscopic water, radiocaesium, soil properties*

The source of most of ^{137}Cs is the radioactive fallout of nuclear fission products from the Chernobyl accident in 1986 (1). Until the accident, it had been the global fallout from atmospheric nuclear weapon tests (1-2). [137]Cs has a physical half-life of 30.23 years and enters easily into biological systems. As current radionuclides mainly enter food chains from soil, many studies have focused on ^{137}Cs behaviour in soil, cultivated soil in particular (3-13).

It is well known that ^{137}Cs is not uniformly distributed along soil depth in undisturbed soil profiles (4-5, 8-10). After atmospheric deposition, radiocaesium is believed to rapidly migrate into the soil, and soon after contamination there is a high activity in the upper layers that decreases exponentially with depth (4-5). Subsequent progress of ^{137}Cs into the deeper layers is much slower, as vertical migration mechanisms depend on the physico-chemical interactions with the soil matrix (4-7).

A non-uniform distribution pattern has also been observed in cultivated soil. Tilling however perturbs soil and redistributes radiocaesium (5, 8). Therefore, radiocaesium depth distribution in cultivated soils depends on the extent of mechanical manipulation of soil (such as tillage) in the plough layer. Regular tilling over several years results in a uniform ^{137}Cs depth distribution throughout the plough layer (5, 8, 13).

In soil, radiocaesium binds to solid particles (mineral part of the soil) or makes part of a solution. Its mobility in the soil is affected by: a) soil matrix and moisture determining its retention, b) biological elements and processes in the soil (e.g. plant roots, soil microbiota activity), and c) downward migration dependent on soil properties (e.g. pH level, particle

size distribution, organic matter content) (2-3, 6-10). Although the solubility of radiocaesium is considered very high, radiocaesium is essentially non-exchangeable and 95 % of ^{137}Cs was irreversibly sorbed onto the soil even under conditions that theoretically increase the release (3).

^{137}Cs in soil can adsorb onto organic particles (humus substances), clay, silt, and sand (2-4, 8-10). The ability of clay minerals to fix ^{137}Cs is the most important retention process that keeps caesium from being taken up by root or to migrate downward (11). On the other hand, little is known how soil moisture affects radionuclide mobility, because models that simulate radionuclide movement in soils usually do not take into account soil moisture changes but assume constant mean water content (12).

The mobility of radiocaesium in soils is greatly affected by frayed edge sites (FES) of clay minerals that strongly fix Cs ions. FES governs the mobility of trace Cs in the rhizosphere and its transfer from soil to plant. However, caesium is not an essential plant nutrient, as K^+ ions, normally present in field conditions, compete for FES (11). The uptake of Cs by roots is therefore affected by the concentration of K in the root zone (9, 11).

Natural potassium is composed of three isotopes: ^{39}K, ^{40}K, and ^{41}K. Approximately 0.012 % of total potassium occurs as ^{40}K, radioactive isotope with a long half-life (1.28x10^9 years). Like most potassium, ^{40}K is contained in mineral components of soil, and as it is distributed homogeneously within a soil horizon, it has been used as a reference nuclide to determine the behaviour of ^{137}Cs in soil over time (4, 13).

The aim of this preliminary study was to determine the activity of anthropogenic radiocaesium and its depth distribution in soil deeply transformed by cultivation. As radiounuclide content in every soil layer depends on soil properties, we wanted to investigate the impact of some main soil characteristics on ^{137}Cs distribution in soil to better understand its behaviour in the environment.

MATERIALS AND METHODS

Soil was sampled from a 2 ha experimental field "Radmilovac" (property of Agricultural Faculty, Belgrade University), in the vicinity of the Vinča Institute of Nuclear Science located near Belgrade (l=44° 45' N, F=20° 35' E, H=135 m). According to the 2006 International Union of Soil Sciences Working Group World Reference Base, the soil of this field belongs to the anthrosol class of anthropogenic soils (14). Our soil was used for growing peach trees and was formed from natural chernozem soil by ploughing at the depth of 1 m to form the Ap-horizon. The soil was deep ploughed in 1992 to prepare it for planting peach trees. The plantation had been cultivated and treated with mineral fertilisers for 12 years, followed by a 3-year pause from fertilisation, ploughing, and irrigation.

At the end of the 3-year pause, soil samples were collected at four randomly selected points from the Ap horizon depth of 80 cm with a step of 20 cm [upper layer of (0 to 20) cm, layers from the root zone of (20 to 40) cm and (40 to 60) cm, and layer below the root zone of (60 to 80) cm]. Three soil profiles (P_1, P_2, and P_3) were taken from near the root of three randomly selected peach trees to see if the distribution of ^{137}Cs was even across the plantation. The fourth profile (P_4) was taken from a soil area covered with grass in the same field.

These 16 soil samples were air-dried and ground to pass a 2-mm sieve. Standard analytical techniques used to determine physical and chemical properties of the soil included the Tjurin method modified by Simakov for the content of humus (15) and the pipette method for mechanical composition (16). Hygroscopic water content was determined through gravimetric loss of water by drying pre-weighed soil samples in an oven at 105 °C.

Samples for gamma spectrometry were packed in 500 mL Marinelli beakers and kept sealed for four weeks to attain radioactive equilibrium. ^{137}Cs activity was measured using a computer-controlled, high-purity germanium (HPGe) detector (Canberra Industries, Inc., Meriden, CT, USA) with 20 % relative efficiency and energy resolution of 1.8 keV at 1332 keV ^{60}Co gamma-ray energy. The detector was calibrated using reference soil material (MIX-OMH-SZ, National Office of Measures (Budapest, Hungary) in the same geometry as measured samples (500 mL Marinelli beaker). The activity of ^{137}Cs were determined from its 661.66 keV gamma energy. The spectra were recorded and analysed using the Canberra Genie 2000 software. The background spectrum was recorded immediately after or before gamma sample counting and subtracted from each sample spectrum. Counting time was around 70,000 s and the combined standard uncertainty of the method was approximately 10 %.

RESULTS AND DISCUSSION

Soil properties

Originally natural chernozem, the sampled soil had been significantly altered by deep ploughing and by 12 years of annual (less deep) ploughing, irrigation, and treatment with phosphate mineral fertilisers. After a three–year pause, soil structure was sufficiently stable to determine the properties and ^{137}Cs activity concentration of the obtained anthrosol (Table 1).

A detailed description of soil properties has been reported in our previous article (18). Chararacteristic of all the profiles was the leaching of clay (particle sizes of less than 0.002 mm) out of the root zone layer (20 cm to 60 cm) and their accumulation in deeper layers. The proportion of clay (across all layers and profiles) varied from 33.08 % to 43.33 %. All profiles exhibited the same decreasing trend in humus content with the depth, varying from 37 % to 47 %. Hygroscopic water content varied with depth up to 18 % within each profile.

Radioicesium activities varied from below the minimum detectable activity (MDA) to 35 Bq kg^{-1} across the profiles and layers and were within the range reported for the region (17, 19).

^{137}Cs variability with soil depth

Figure 1 shows similar variability in ^{137}Cs activity between layers of single profiles, including P4 that was sampled away from the root zone. This variation was lower (CV ~60 %) in P1 and P2 compared P3 and P4 (~80 % and ~100 %, respectively). In the (60 to 80) cm layer of P4, radiocaesium activity was below MDA, so we roughly assumed that it would be below MDA in all soil profiles at depths over 85 cm (data not shown). We did not measure radiocaesium activity in the (80 to 100) cm soil layer because the (60 to 80) cm layer was already 20 cm below the tree roots.

We also found that radiocaesium content across anthrosol layers differed from the one found in undisturbed soil profiles, in which most of caesium was concentrated in the topmost 20 cm (4, 12, 13) only to exponentially decrease with depth. A similar difference can be noticed in radiocaesium distribution between our anthrosol and undisturbed chernozem reported by Dragović et al. (19).

To compare the distribution of ^{137}Cs activity at a given depth z (cm) in our anthrosol soil profiles, we
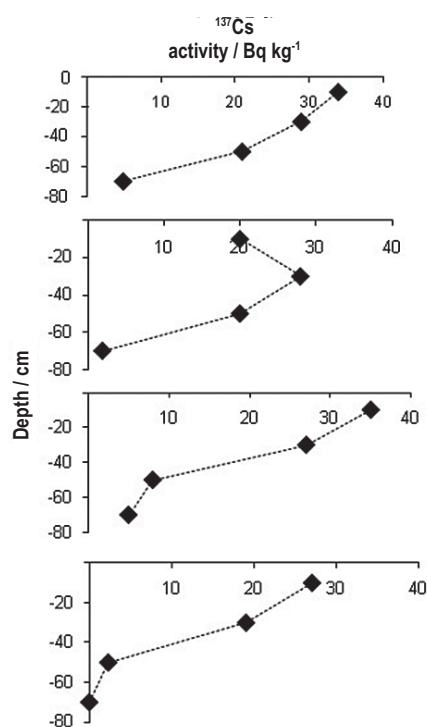

Figure 1 *Activity concentration variation of ^{137}Cs at (0 to 80) cm depth.*

used the equation recommended by Du et al. (8) for cultivated soils, with coefficients $a>1$ and $0<b<1$, as follows:

$$Cs = a\,(1 - z/H)^b \qquad [1]$$

where H (cm) is the threshold depth at which ^{137}Cs can still be detected (85 cm). The coefficients obtained from fitting equation [1] to the experimental data were a=38 and b=0.81, and the coefficient of determination of the fit was R^2=0.76 ($p≤0.05$). Equation [1] not only provides a slightly better fit to data than linear equation, but it also shows that caesium depth distribution in cultivated soils depends on ploughing, because if ploughing continues over time, soil would be thoroughly mixed and even caesium depth distribution ($b→0$, $Cs→a$).

Effects of soil properties on ^{137}Cs depth distribution

We used linear regression to analyse the effects of single soil properties on radiocaesium activity. Humus content affected ^{137}Cs distribution along the soil depth, with medium correlation (r=-0.51), which accounted for 27 % of its variability ($p≤0.05$). Similar correlations

Table 1 *Soil properties and ^{137}Cs activity concentration at 20-cm depth intervals*

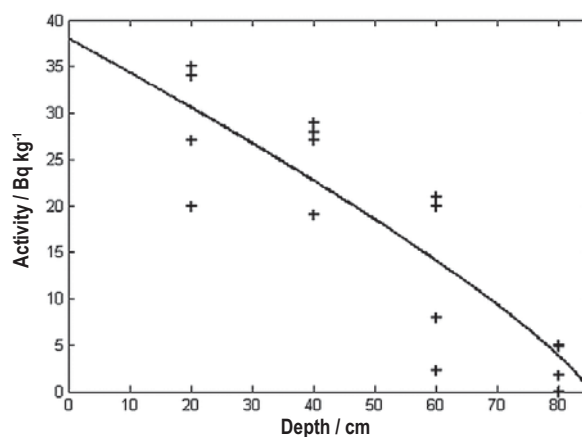| Soil depth / cm	Humus / %	Clay / %	Hygroscopic water / %	^{137}Cs / Bq kg^{-1}
Profile 1 (P$_1$)				
0 to 20	2.12	43.02	3.21	34±3
20 to 40	1.36	41.63	4.31	29±3
40 to 60	1.19	41.62	3.33	21±2
60 to 80	0.92	43.33	3.60	4.9±0.7
Profile 2 (P$_2$)				
0 to 20	1.27	34.71	2.82	20±2
20 to 40	1.10	33.15	2.90	28±2
40 to 60	0.75	33.19	2.90	20±2
60 to 80	0.48	33.36	2.92	1.8±0.4
Profile 3 (P$_3$)				
0 to 20	1.42	34.67	3.06	35±4
20 to 40	1.06	33.08	3.11	27±3
40 to 60	0.67	33.28	3.28	8.0±1.0
60 to 80	0.46	33.51	3.28	5.0±0.6
Profile 4 (P$_4$)				
0 to 20	2.80	38.75	1.38	27±3
20 to 40	1.97	37.79	0.98	19±2
40 to 60	1.64	38.32	1.22	2.3±0.4
60 to 80	1.05	35.48	0.94	<MDA*

The results are presented as measured value ± combined standard uncertainty.
*MDA=minimum detectable activity (1.5 Bq kg^{-1})

Figure 2 *Depth distribution of ^{137}Cs activity concentration in anthrosol profiles*

were found for other types of soil (9, 13, 19), confirming that humic substances in clayey soils facilitate interaction between soluble radiocaesium and soil particles (4-7).

However, the amount of radionuclides which would be incorporated in or onto soil particles depends primarily on the mineralogical properties of soil. In our earlier study of the same anthrosol, we established that illite and smectite minerals prevailed (approximately 70 %) in the total clay content (20). It is well documented that illite FES strongly fixes radiocaesium ions in soil (4, 9, 11, 21).

Our multiple linear regression analysis showed that radiocesium distribution across the profiles correlated positively with humus and hygroscopic water content and negatively with clay content, accounting for 81 % of radiocaesium behaviour (p≤0.0001) (Table 2). The negative relationship with clay can be explained by the higher concentration of this isotope in the upper layers and low concentration in deeper layers that have a slightly higher clay content.

Hygroscopic water is part of soil moisture that holds tightly to the surface of soil particles without evaporating at normal atmospheric temperatures, which is why it is considered unavailable to plants. The amount of hygroscopic water in soil depends on environmental conditions such as temperature, relative air humidity, pressure (22, 23), and on the specific surface area of a soil particle. Coarser particles like sand have small surface areas per gram (about 1 m^2 g^{-1}), whereas clay can have an area as large as several hundred square meters per gram and a high capacity to adsorb water and other substances including hygroscopic water (22).

Most clay minerals (such as illite and smectite) have negative charges, and a negatively charged clay mineral surface attracts water molecules to form several monomolecular layers of hygroscopic water (24). This suggests that variation in hygroscopic water content in anthrosol corresponds to illite/smectite distribution in soil. The ability of these minerals to bind hygroscopic water is similar to their ability to include caesium in their lattice structure. This is in accordance with the results of Wudivira et al. (25) who used hygroscopic water measurements at 50 % atmospheric relative humidity to estimate site-specific clay mineral content. All this suggests that hygroscopic moisture is an important and useful soil parameter that deserves further investigation, but it cannot serve as a fundamental soil characteristic unless multiple environmental factors are eliminated by standardised measurement (23, 25).

Table 2 *Correlation between soil properties taken together and ^{137}Cs activity concentrations*

	Humus / %	Clay / %	Hygroscopic water / %	Constant	R² / %
^{137}Cs / Bq kg^{-1}	23.3	- 1.8	11.6	21.5	81*

R²=coefficient of determination
*Multiple regression analysis, significance level: p≤0.0001

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Sažetak

RASPODJELA ^{137}Cs U ANTROSOLU OGLEDNOG POLJOPRIVREDNOG DOBRA "RADMILOVAC" KOD BEOGRADA

Ovo je preliminarno istraživanje dubinske raspodjele radionuklida ^{137}Cs u kultiviranome zemljištu tipa Antrosol 15 godina starog voćnjaka pod zasadom breskvi koje pripada oglednom poljoprivrednom dobru "Radmilovac" u blizini Beograda. Dubokim oranjem do dubine od 1 m zemljište je pripremljeno za postavljanje zasada breskvi. Tri godine prije uzorkovanja zemljišta prekinuta je obrada voćnjaka odnosno godišnje oranje (do 40 cm dubine), navodnjavanje i unos mineralnoga gnojiva. Koncentracija aktivnosti ^{137}Cs kretala se od 1,8 Bq kg^{-1} do 35 Bq kg^{-1} i bitno varirala s povećanjem dubine zemljišta te dostigla ukupni koeficijent varijacije od 83 %. Obrasci raspodjele radiocezija po dubini zavisili su od stupnja obrade zemljišta u prethodnom razdoblju, s obzirom na to da je mehanička manipulacija zemljišta dovela do njegove prisutnosti i u nižim slojevima. ^{137}Cs izravno je korelirao sa sadržajem humusa i bio je fiksiran za glinovitu frakciju zemljišta, što upućuje na njegovu povezanost s česticama zemlje. Unatoč tome što se sadržaj higroskopske vlage u zemljištu pokazao korisnim parametrom za opis ponašanja cezija, za njezino određivanje još uvijek nije utvrđena standardna metoda mjerenja.

KLJUČNE RIJEČI: *higroskopska vlaga, kultivirano tlo, radiocezij, svojstva tla, voćke*

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