

# Mobile Forms of Radionuclide $^{137}\text{Cs}$ in Sandy Soils in Northeastern Poland

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*Received 6 June, 1999*

*Accepted, 8 October, 1999*

## Abstract

Mobile forms of radionuclide  $^{137}\text{Cs}$  in different soils (natural pastures) of northeastern Poland were evaluated. An attempt was made to show if and what mobile forms of  $^{137}\text{Cs}$  are related to different soil properties. For this reason 108 soil samples from 0 to 10 cm in depth were measured for mobile forms of  $^{137}\text{Cs}$  activity and analyzed for clay fraction, pH-value, exchangeable potassium (Kex.), exchangeable calcium (Caex.), magnesium (Mgex.), sodium (Naex.) content, organic matter and organic carbon content (C org.), and cation exchange capacity (CEC). Samples of soils were collected in the period from June 1995 to July 1996. The radiocaesium and mobile forms of  $^{137}\text{Cs}$  activity were determined by gamma spectrometry. The mobility of  $^{137}\text{Cs}$  was studied by means of sequential extraction. Mobile forms of radionuclide  $^{137}\text{Cs}$  were related to physicochemical parameters of soils.

**Keywords:** radiocaesium, mobile forms of  $^{137}\text{Cs}$ , soil properties.

## Introduction

The bioavailability of radionuclide  $^{137}\text{Cs}$  derived from Chernobyl is discussed in terms of its speciation in soils and the influence of soil properties on this speciation. From literature there is evidence that retention and migration of radionuclides depends on the chemical forms under natural conditions and their interaction with the soil [1, 2, 3, 4].

It is generally accepted that the most appropriate way to understand the mechanism of transport, mobilization, trapping and transformation of radionuclides in soils is based on solid speciation. The most widely used technique for soils is speciation by a single extractant, which is useful to predict plant uptake for a specific element but having limitations in particular soil types or in particular elements [4]. Sequential extraction schemes using a series of single reagents in a defined sequence tries to quantify elements in specific phases of the soil and are normally used with speciation purposes. From the more elaborate speciation schemes the one proposed by Tessier has received most attention for metal speciation [5]. This

scheme includes five fractions: exchangeable metal, metal bound to carbonates, metal bound to iron and manganese oxides, metal bound to organic matter and residual fraction. As far as radiocaesium is concerned. In literature are reported the different procedures to determine the speciation of  $^{137}\text{Cs}$  in soils.

Sequential extraction procedures Tessier Method with some modification [6] includes five fractions:

1. Readily exchangeable ions:  $\text{NH}_4\text{COOCH}_3$  (1M, pH 7) was added to the soil with a ratio 1:10, at room temperature for 1 hour while stirring from above. Subsequently, the suspension was first passed through a paper filter, and finally a membrane filter (0.45  $\mu\text{m}$ ). The soil was then rinsed with distilled water. After filtration, this rinse water was added to the above solution phase for analysis.

2. Bound to Fe-Mn oxides: the residue from the above was extracted with 0.004 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% (v/v) acetic acid at 80°C for 6 hours with occasional agitation. The subsequent separation of the liquid phase and rinsing of the soil was performed as above.

3. Bound to Organic Matter: the residue from above

was resuspended in water stirred and heated to 80°C. Then, H<sub>2</sub>O<sub>2</sub> (30%), adjusted to pH 2 with HNO<sub>3</sub>, was added very slowly. At the end, in 6 hours the ratio soil: H<sub>2</sub>O<sub>2</sub> is about 1:8. After cooling, 250 ml of 3.2 M NH<sub>4</sub>AC in 20% (v/v) HNO<sub>3</sub> was added and the samples were agitated for 30 m.

4. Persistently bound: the fraction contains mainly primary and secondary minerals, which might hold the radionuclides extremely tightly. The above fractions were treated with HNO<sub>3</sub> (1:1), and stirred for 6 hours at 80°C.

5. Residual: the amount of radiocaesium not extracted by any of the above steps was determined by direct gamma spectrometry of the sample.

Sequential extraction procedures Pavlotskaya Method [7] includes five fractions.

1. Water soluble ions: distilled water was added to the soil with ratio liquid: soil = 10:1 (peaty and peaty gley soils) and 5:1 (soddy-podzolic and podzolic soils) at room temperature. The sample is incubated for 1 day, with shaking each 0.5 hours. Following water and soluble form are separated by filtering with 0.45 µm filter.

2. Exchangeable ions: NH<sub>4</sub>COOCH<sub>3</sub> (1M, pH 7) was added to the soil with a ratio 1:10 (peaty and peaty gley soils) and 5:1 (soddy-podzolic and podzolic soils) at room temperature for 1 day, with shaking each 0.5 hours. Following liquid and soluble form are separated by filtering with 0.45 µm filter.

3. Bound to Fe-Mn oxides: hydrochloric acid 1 M with ratio liquid: solid = 10:1 (peaty and peaty gley soils) and 5:1 (soddy-podzolic and podzolic soils) at room temperature. The sample is incubated for 1 day, with shaking each 0.5 hours. Following liquid and soluble form are separated by filtering with 0.45 µm filter.

4. Unexchangeable form: hydrochloric acid 6 M with ratio liquid: solid = 10:1 (peaty and peaty gley soils) and 5:1 (soddy-podzolic and podzolic soils) at room temperature, twice 0.5 hours boiling.

5. Residual: the amount of radiocaesium not extracted by any of the above steps was determined by direct gamma spectrometry of the sample.

Maubert et al. [8] have studied the radiocaesium speciation in soils after the Chernobyl accident applying several schemes. The first one includes five steps: water soluble fraction, 1M NH<sub>4</sub>COOCH<sub>3</sub> exchangeable fraction, 0.1M Cu(COOCH<sub>3</sub>)<sub>2</sub> exchangeable fraction, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> plus 0.1M NaOH extractable fraction, and residual fraction. Other schemes that have been studied by this author are based on:

- a) acid extractions with 0.1M HCl and 0.05M HCl plus 30% H<sub>2</sub>O<sub>2</sub>;
- b) lipidic fraction extraction;
- c) interstitial water fraction.

## Materials and Methods

Samples of soil (10 cm diameter) were collected in northeastern Poland (Fig. 1 - location of sampling spots) twice a year from June 1995 to July 1996. Soil samples were dried at room temperature, then sieved through a 1-mm mesh to remove the roots of plants and stones and homogenized prior to analysis and sequential extraction studies. The <sup>137</sup>Cs activity concentrations were deter-

mined by gamma spectrometry. The gamma spectrometer consisted of a high purity germanium detector with an energy resolution of 1.88 keV for Co (1332 keV). The detector was connected to a multichannel Livius analyzer (Silena, Italy).

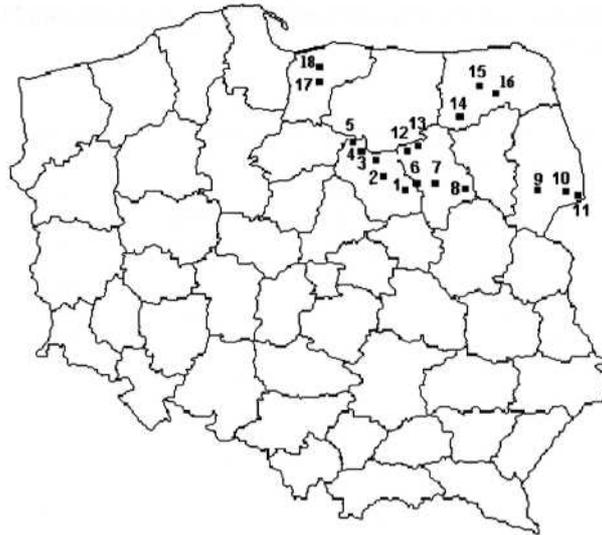


Fig. 1. Location of sampling spots.

Physicochemical characteristics of soils were recorded. Soil parameters: pH, content of organic matter, cation exchange capacity (CEC), and organic carbon (C org.) of the soils were determined by standard techniques. Exchangeable calcium (Caex.), magnesium (Mgex.), sodium (Naex.) and potassium (Kex.) were determined using AAS.

To the samples of the soils (250 g) distilled water (1:5) was added to separate the water-soluble fraction of the radionuclide <sup>137</sup>Cs. Then the residue was treated with 1 M NH<sub>4</sub>COOCH<sub>3</sub> (pH 7). Later the residue was treated with 1 M HCl. Mobile forms, according to Pavlotskaya method, are defined as sum of radionuclides extracted from water, ammonium acetate and hydrochloric acid [6]. The fraction of radionuclides extracted by water, NH<sub>4</sub>COOCH<sub>3</sub> and HCl thought is to represent a more mobile or bioavailable fraction and can be used to calculate the mobility factor, i.e. the percentage of radionuclide present in mobile forms.

The mobile forms of <sup>137</sup>Cs activity was calculated as the difference between total caesium content and <sup>137</sup>Cs activity in samples after tree extractions, because it can be observed that radiocaesium content in the some extracts is very low and is not measurable (< LLD). Statistical estimations and other computations were made by using Statgraphics procedures.

## Results and Discussion

The study of radiocaesium and mobile forms of <sup>137</sup>Cs activity was performed on 108 sandy soils. Due to the large number of studied soils only the highest medium and lowest values of radiocaesium activity are demonstrated in Table 1. In the author's previous work more

results are presented [4]. Physicochemical characteristics of studied soils is given in Table 2. The acidity in water (pH) ranged from 4.74 to 7.92. The content of organic matter varied from 3.17% to 13.26%. The highest cation exchange capacity (CEC) parameter was 26.91 cmol/kg and the lowest CEC parameter was 5.21 cmol/kg. The highest exchangeable potassium content was 0.89 cmol/kg and the lowest exchangeable potassium content - 0.05 cmol/kg.

Table 1. The radiocaesium activity of soil (n = 108). The sum of counting errors was less then 10%.

|         | Cs-total (Bq/kg) | Cs-mobile (Bq/kg) | Cs-mobile (%) |
|---------|------------------|-------------------|---------------|
| Medium  | 29.22            | 1.04              | 3.56          |
| Minimum | 5.95             | 0.03              | 0.53          |
| Maximum | 59.85            | 7.54              | 12.59         |

On the basis of those data, single correlations were studied between mobile forms of <sup>137</sup>Cs as the dependent variables and the corresponding soil parameters from Table 2 as the independent variables.

The soil parameters were correlated with mobile

forms of <sup>137</sup>Cs in an attempt to identify those parameters that influence radiocaesium availability. No high correlation coefficients have been found (Table 3) although a few points do arise. Mobile forms of <sup>137</sup>Cs are positively correlated with organic carbon content and organic matter content. Better correlations exist with with organic carbon content (0.64) than with organic matter content (0.50). Interestingly, there are negative correlations between mobile forms of <sup>137</sup>Cs and pH value (-0.63), exchangeable potassium content (-0.49) and clay content (-48).

The obtained correlations are shown in Figs. 2-5. This certainly does not mean that the other parameters cannot participate in the functional relationships. The figures indicate that more or less close relationships can be found between the mobile forms of <sup>137</sup>Cs and the pH value, the clay content, exchangeable potassium content and organic carbon content.

According to Fig. 2, with decreasing pH value, i.e. with increasing H<sup>+</sup> concentration, the mobile forms of <sup>137</sup>Cs increase. A closer relation is found between clay content and the dependent variables as demonstrated in Fig. 3. With increasing clay content, the mobile forms of <sup>137</sup>Cs decrease. The low clay content has an effect, because clay content has a selectivity for radiocaesium. The same is true for exchangeable potassium content. A decreasing exchangeable potassium content entails in-

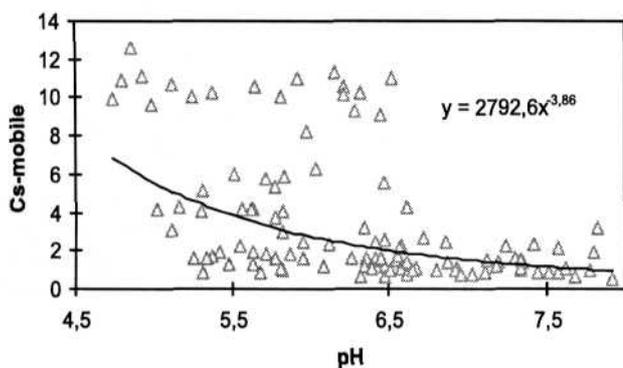


Fig. 2. Mobile forms of Cs-137 in soils in relation to the ph-value.

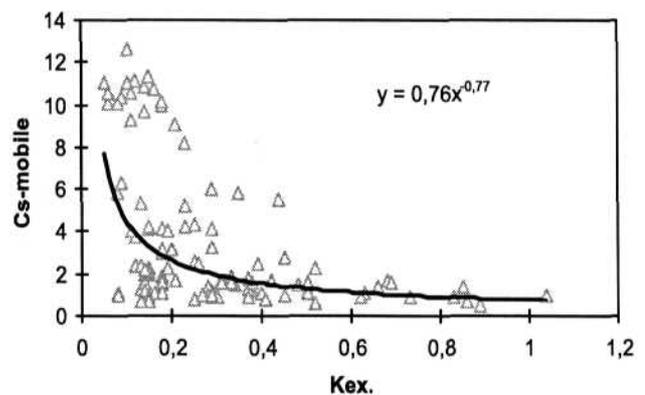


Fig. 4. Mobile forms of Cs-137 in soils in relation to the K ex. content.

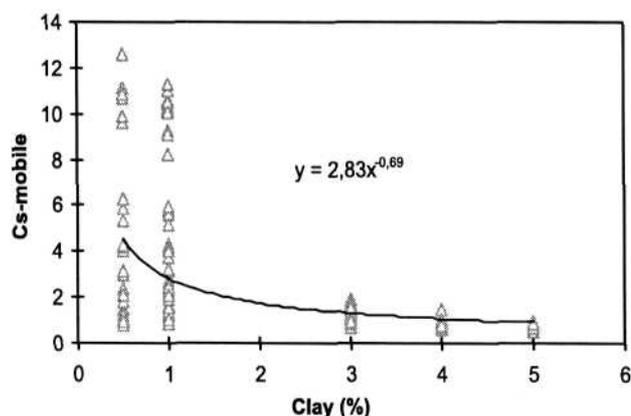


Fig. 3. Mobile forms of Cs-137 in soils in relation to the clay content.

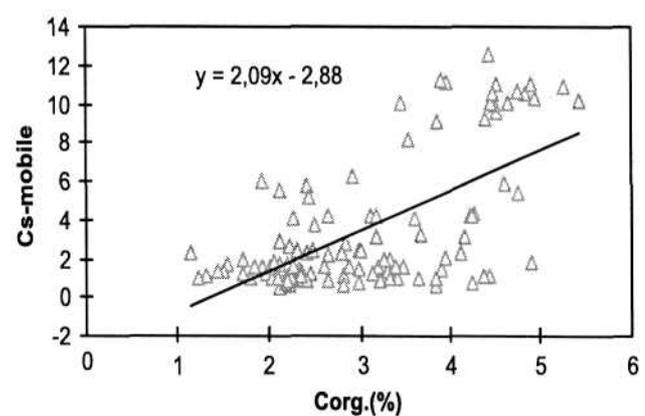


Fig. 5. Mobile forms of Cs-137 in soils in relation to the C org. content.

Table 2. Physicochemical properties of the soils (n = 108).

|         | Clay (%) | pH   | Org. mat. (%) | C org. (%) | CaCO <sub>3</sub> (%) | Ca ex. (cmol/kg) | Mg ex. (cmol/kg) | Na ex. (cmol/kg) | K ex. (cmol/kg) | CEC (cmol/kg) |
|---------|----------|------|---------------|------------|-----------------------|------------------|------------------|------------------|-----------------|---------------|
| Medium  | 2.00     | 6.24 | 8.24          | 3.08       | 1.52                  | 6.75             | 1.93             | 0.32             | 0.28            | 11.81         |
| Minimum | 0.50     | 4.74 | 3.17          | 1.14       | 0.10                  | 1.84             | 0.30             | 0.16             | 0.05            | 5.21          |
| Maximum | 4.00     | 7.92 | 13.26         | 5.42       | 5.20                  | 20.60            | 6.49             | 0.58             | 0.89            | 26.91         |

Table 3. Correlation coefficients (r) between selected soil parameters and mobile forms of Cs-137 (P &lt; 0.05).

|           | Clay  | pH    | C org. | K ex. |
|-----------|-------|-------|--------|-------|
| Cs-mobile | -0.48 | -0.63 | 0.64   | -0.49 |

creasing mobile forms of <sup>137</sup>Cs, as shown in Fig.4. Finally, an increase of the mobile forms of <sup>137</sup>Cs is connected with an increase of the organic carbon content, according to Fig. 5.

### Conclusion

1. Physicochemical properties of soils influence radiocaesium availability. Good correlations between mobile forms of <sup>137</sup>Cs and soil parameters have been found.

2. Negative correlations between mobile forms of <sup>137</sup>Cs and pH values, exchangeable potassium and clay content have been found.

3. Mobile forms of <sup>137</sup>Cs are positively correlated with organic carbon content and organic matter content.

4. Organic carbon content, pH value, exchangeable potassium and clay content are the dominant factors responsible for bioavailability radiocaesium.

5. Exchangeable potassium, clay content and pH value control the availability of free ions and govern the transfer from soil to liquid phase.

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