Plutonium distribution in sequentially extracted phases of arable and uncultivated soils

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Received: 19 January 2022 / Accepted: 16 July 2022 / Published online: 12 August 2022
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Abstract
The aim of this study was to determine the distribution of alpha-emitting plutonium isotopes from arable and uncultivated soils. The effect of soils cultivation on plutonium fractionation and mobility was studied using the sequential extraction technique (modified Tessier’s method). Soil samples were collected from the surface layer in the selected points. By means of reagents with increasing leaching power, the fractions were separated: readily available, carbonate bound, sesquioxide (Fe/Mn) bound and organically bound as well as residual. The content of $^{239+240}$Pu in the fractions was determined by alpha spectrometry. The sequential analysis showed that in the case of uncultivated soils, 67% of Pu was combined with organic matter, 15% was permanently bound to the matrix, but only 4% was associated with the available fraction, and 2% with the carbonate one. Arable soils revealed a different distribution: 36% of Pu was combined with the organic fraction, only 7% was bound permanently but as much as 9% was bound with the available fraction, and 11% with the carbonate one. It was proved that plutonium is bound mostly by organic matter (67% Pu—uncultivated and 36%—arable soils), however, the amounts of Pu combined with the labile fractions (ion-exchange and carbonate) are approximately 4 times higher for the arable soils than for uncultivated ones. This proves that soil cultivation can lead to the launch of plutonium in soil and its transition to more accessible forms which can cause a radiological risk.

Keywords Fallout plutonium isotopes · Plutonium fractionation · Sequential extraction · Alpha spectrometry · Arable and uncultivated soil

Introduction

The chemical form of an element is one of the most important factors influencing its mobility in environmental matrixes (e.g. soil) and accessibility to plants (Lieser 1995). Determination of chemical speciation is often complicated, especially if a concentration of the element is small. This is of particular difficulty for anthropogenic radionuclides whose concentrations in the soil are very small, many times lower than the concentration of natural radionuclides. The source of plutonium was the global fallout, resulting mainly from the nuclear weapon testing in the previous century. Plutonium concentrations in Polish soils ranged from 0.1 to 1 Bq/kg (Rudzinski and Komosa 2011; Orzel and Komosa 2014) which corresponds to $4\times10^{-8}$–$4\times10^{-7}$ mg/kg, and what is also 50–100 times less than $^{137}$Cs fallout and about 400 times less than natural $^{40}$K concentration in soil. Such small concentrations practically preclude from the speciation analysis method involving the isolation and identification of certain species. In such a case the so called fractionation method of analysis was preferred (Templeton et al. 2000; Hall 1998). This method is based on the extraction of various geochemical fractions from a soil sample by applying solutions of the extended extraction power (see below). Such procedure is especially useful for environmental anthropogenic...
radionuclides, usually present in trace amounts. Determination of radionuclides in each extracted fraction allows establishing which part of the radionuclide is bound to a particular fraction of specific chemical character. Therefore, in spite of the lack of information on a defined chemical form of radionuclide, the chemical behavior of this radionuclide can be confirmed. In practice, extraction of geochemical fractions can be performed by the so-called selective leaching (extraction) of the sample by the extractants of various capabilities to transfer given compounds into the solution, as presented below (Tack and Verloo 1995; Ure et al. 1995; Zimmerman and Weindorf 2010; Almazán-Torres et al. 2016; Rosado et al. 2016; Luo et al. 2018; Mizerna and Król 2018; Lemonsa et al. 2018; Rzhevskaia et al. 2021). The procedure was developed first by Tessier et al. (1979) and is still considered as the basic one, however, numerous modifications were also made by others, mainly to match the procedure to the specific sample. Such procedures differ generally in: solid/extractant ratio, temperature of extraction, kind of extractant, time of contact between a solid and liquid phase etc., (Komosa 2002, 2006; Rosado et al. 2016). The Tessier sequential extraction procedure is based on the isolation of the following phases: exchangeable or adsorbed ion fraction (released by neutral salts such as MgCl2 or CaCl2), carbonate bound fraction (extractable with acetic acid or acetic buffer), organic matter bound fraction (separated by the oxidizing destruction with H2O2 or complexing with the alkaline solution of sodium pyrophosphate), fraction bound to hydrous oxides of Fe and Mn (released by means of ammonium oxalate complexation or by reduction with hydroxylamine hydrochloride), and residual fraction. The sequential extraction method provides information about the accessibility of a given element without further knowledge of its chemical form (Tessier et al. 1979; Rauret 1998).

The bioavailability can be inferred by studying the relative proportion of trace elements in various soil fractions (Harmsen 2007; Kim et al. 2015; Rosado et al. 2016; Petruzelli et al. 2020). There is no strict definition of the term bioavailability and it is often used interchangeably with bioaccessibility. Harmsen (2007) proposed to define bioaccessibility as the fraction of a compound that is released from its matrix in the gastrointestinal tract. The term bioavailability means also the quantity of metals (also radionuclides) present in the soil solution and/or the most readily releasable from the solid phase (e.g. with a mild extractant such as water or alkaline earth solutions). Our research concerns the term bioavailability in the above defined meaning. However, it should be underlined that the radionuclides present in the soil may reach plants through their root system or be present in drinking water. Plants can obtain elements from soils, even if they are in the form of complexes. Therefore, we can also consider the released part with the complexing agents as bioavailable. On the other hand, it should be remembered that Pu is mainly tetravalent, which is not a common feature of biogenic elements. However, radionuclides present in soil in the form of cations, after getting into the soil solution, most often undergo hydrolysis, hydration and condensation reactions (Lieser 1995).

Apart from the Tessier method there are various extraction procedures developed for fractionation. One of the most important procedures was that proposed by Rauret (1998) and Davidson et al. (1998) which includes three stages. This simplified extraction procedure was called the BCR (Community Bureau of Reference) procedure Rosado et al. 2016. It comprises isolation of: (i) the physically adsorbed and exchangeable fraction (extracted with 0.1 mol dm−3 acetic acid), (ii) the Fe and Mn sesquioxide bound fraction (extracted with 0.1 mol dm−3 hydroxylamine hydrochloride at pH 2), (iii) the organically bound fraction (extracted with 8.8 mol dm−3 hydrogen peroxide at pH 2–3 followed by 1 mol dm−3 ammonium acetate at pH 2).

The other researchers proposed different modifications of the original Tessier’s procedure. For example Laleter and Probst (1999) and Aubert et al. (2004) used the additional stages dividing the Fe/Mn sesquioxide fraction into three parts (Mn oxide, amorphous Fe oxide and crystalline Fe oxide). Significant studies comprising optimization of some parameters of extraction (such as reagent concentrations, conditioning time or temperature) were carried out by Outola et al. (2009) and Faye et al. (2017). For successive extraction of five fractions of lake and oceanic sediment samples the authors suggested the following reagents and parameters: (i) 0.1 mol dm−3 MgCl2 at 25 °C for 1 h, (ii) 1 mol dm−3 NH4Ac in 25% HAc at 50 °C for 2 h, (iii) 0.1 mol dm−3 HN2OH-HCl in 25% HAc at 70 °C for 6 h, (iv) H2O2 in 0.05 mol dm−3 HNO3 at 70 °C for 3 h and (v) 4 mol dm−3 HNO3 at 90 °C for 4 h.

The sequential extraction method was largely used in analytical practice, especially during heavy metal studies. Since the nineties of the previous century this method has been more frequently applied for assessment of radionuclides bioavailability, particularly from the areas contaminated due to nuclear accidents such as Palomares (Antón et al. 1994), Chernobyl (Amano et al. 1997; Oughton et al. 1992; Beresford et al. 2020), Mayak (Rozhikova et al. 2021) and the work of the nuclear fuel reprocessing plant in Rocky Flat (Iggy Litaor and Ibrahim 1996), Dounreay NPP (Cook et al. 1984), or Sellafield (Schultz et al. 1998). Next, the less contaminated areas in Finland, Italy and Russia were subjected to investigations (Puhakainen et al. 2001; Blanco et al. 2004; Desideri et al. 2006; Aubert et al. 2004; Testa et al. 1998; 1999). The soil and sediment samples were the most frequently analyzed (Testa et al. 1999; Desideri et al. 2001; 2002; Skipperud et al. 2009). Concerning radionuclides,
the $^{137}\text{Cs}$ (present in sample as the result of fission reactions taking place in nuclear reactors and during nuclear tests) was the most studied because of its easy determination by gamma spectrometry. In the case of plutonium whose average environmental concentration is very small, it is difficult to determine its small activity by the means of the fractionation method. Moreover, plutonium emits the alpha radiation which demands a thorough radiochemical sample treatment before measurements. Therefore, only few papers report using fractionation of plutonium (Nagao et al. 1999; Haque and Nakanishi 1999; Bunzl et al. 1995; Komosa 2002; Hirose et al. 2017; Santschi et al. 2017a, b; Lin et al. 2019a, b; Rozhkova et al. 2020; Sáez-Muñoz et al. 2020).

Plutonium, an artificial radioactive element, is considered as one of the most toxic elements (Agency for Toxic Substances and Disease Registry 2010). It does not play a biological role but it retains in the body, mainly in the bones and liver. The organ distribution pattern shows that plutonium was accumulated at 54–60% in bones and 34–43% in liver. Only 3–6% was found in lung including lymph nodes, kidney, spleen, thyroid, and gonads together contained around 1% (Singh et al. 1983).

Moreover, the alpha radiation emitted by plutonium ($^{239+240}\text{Pu}$) has a large carcinogenic effect (Jensen et al. 2011). Plutonium, as a residue from the nuclear testing, is rather homogeneously distributed all over the globe (Eisenbud and Gesell 1997). It is assumed to be permanently bound to the organic matter not posing a threat to human health. However, changes in the chemical composition of the soil or changes in physicochemical conditions caused by external factors, such as fertilization, may cause the transition of plutonium from an insoluble form to a more mobile one. As follows from the investigation the long-term soil fertilization increases the contribution of the soil organic carbon and the total nitrogen but the soil pH decreases (e.g. Ge et al. 2018; Dong et al. 2012; Lin et al. 2019a, b).

The aim of the research was to find out whether there are differences in the plutonium distribution combined with different soil fractions in the arable and uncultivated soils. As the test method there was chosen the sequential extraction which enables determination of plutonium bioavailability by specifying the contribution of Pu combined with easily dissolved fractions. The ion-exchange fraction is most often combined with the carbonate one, and the total analyte content is treated as an indicator of the bioavailable part of the analyte (Rosado et al. 2016; Harmsen 2007; Petruzzelli et al. 2020). The study of the plutonium bioavailability is of scientific importance because it is possible to predict the conditions under which its release into the environment can take place, which may pose a threat to human health. Currently, the concentration of plutonium in soil is traceable, however, it can increase resulting in emergency release or nuclear accidents. The analysis of the radionuclides migration in the environment is important for many reasons. The presence of radionuclides in soil and groundwater may cause them to penetrate into plants, animals and humans. This situation has a direct impact on the exposure of the population to contamination. The reason for that is the possibility of consuming food contaminated with soil (fruit, vegetables) through the alimentary tract and absorption of air contaminated with soil dust (resuspension phenomenon) through the respiratory tract. Assuming that each person is in contact with the surface layer of soil (0–5 cm), on the basis of the results obtained in this manuscript, it is possible to estimate the radiation doses that a person could theoretically receive if he was exposed to the absorption of plutonium contained in the soil. Moreover, pluton, as the alpha radioactive isotope with the highest ionizing capacity, shows high toxicity to living organisms. Therefore, research on its migration and presence in the environment as well as bioavailability are both interesting and fully justified.

### Materials and methods

#### Study area and sampling

The samples subjected to the fractionation studies were collected in seven points of Leczna-Wlodawa Lake District in the eastern part of Poland (Table 1) in the following

| Table 1 Location of sampling points | Geographical coordinates | Height (MASL) | Type of soil$^a$ |
|------------------------------------|--------------------------|--------------|-----------------|
| Ludwig (LUD)                       | 51°20′38″N 22°54′04″E    | 172          | Histi-mollis gleysols |
| Kulczyn (KUL)                      | 51°23′48″N 23°21′49″E    | 165          | Histi-mollis gleysols |
| Turno (TUR)                        | 51°32′40″N 29°09′59″E    | 168          | Histi-mollis gleysols |
| Krzczyn (KRZ)                      | 51°24′41″N 22°55′26″E    | 157          | Terric histosols  |
| Swierszczow (SWI)                  | 51°19′10″N 23°11′24″E    | 173          | Terric histosols  |
| Wola Wereszczyńska (WOW)           | 51°26′19″N 23°07′34″E    | 164          | Mollic gleysols   |
| Pieszowola (PIE)                   | 51°29′34″N 23°09′42″E    | 170          | Fluvisols        |

$^a$According to Kabala et al. (2019); Food and agriculture organization 2015. Type of soil presents the mean characteristics of soil
locations: Swierszczow (SWI), Krzczen (KRZ), Kulczyn (KUL), Wola Wereszczynska (WOW), Turno (TUR), Ludwin (LUD) and Pieszowola (PIE). In each location point the places in the nearby area of arable and uncultivated soils were chosen and the samples were collected from a soil surface layer (0–5 cm). Sampling from the 0–5 cm layer is typical of the monitoring studies and determining contamination by the radioactive and heavy metal fallout (IAEA 1989; Petruzelli et al. 2020).

Six cores of soil were collected (according to IAEA 1989) along the circumference with a 1-m radius circle and seven samples were taken (six from the circumference and one from the center). Samples were taken using specially made cylindrical sampler, 5 cm high and 8.3 cm in diameter (3¼ inch), with a cutting edge on one side. All samples were pooled and the soil material was homogenized after drying (at 80 °C for 48 h) and sieved below 2 mm. Twenty grams of such prepared dry material was used for the sequential extraction study.

Classification of soil was made according to the World Reference Base for soil resources (Kabala et al. 2019; Food and Agriculture Organization 2015). Most of them were Gleysols which are a wetland soil of blue–grey color (anaerobic conditions), abundant in Fe (II) and organic matter being slightly aerated. Terric histosols are the soils with a large clay content and evenly distributed carbonates, containing organic carbon and being saturated with water. Fluvisols are poor soils with a diversified structure developed on the alluvial deposits.

The mean content of organic matter (OM, %) in soil samples was determined from the difference in mass of sample before and after burning at 450 °C for 24 h (Lacrainard furnace). Soil samples were conducted to elemental analysis, determination of carbonate content and exchangeable pH after sieving through a 1-mm sieve to remove organic residues (grass, turf, root debris). The elemental analysis were conducted using the EuroEA3000 CHNS-O Analyser, EuroVecor) and pH measurements were carried out in KCl solution. The exchange acidity derived from $\text{H}^+$ ions displaced from the sorption complex by neutral salt cations was estimated. For this purpose 10 g of dried and homogenized soil was poured over with 50 cm$^3$ of 1 M KCl solution, vigorously mixed for 3 min and set aside for 24 h. After this time, pH of the tested systems was measured with a pH meter (pHi 360, Beckman). The carbonate content was determined using the Scheibler method (Bąk 1992).

The characteristics of the examined soils are presented in Table 2. As can be seen from the presented data, the content of the organic matter differs depending on the type of soil. However, it can be noticed that in arable soils the average content of organic matter is about 20% lower than in uncultivated ones. This is due to the fact that the surface uncultivated soil is covered usually with turf and collect organic matter from soil-forming processes. It was also noticed that the percentage of carbonates is closely related with the exchangeable pH. Pearson correlation coefficient is 0.99 and 0.95, respectively for uncultivated and arable soils.

Another conclusion resulting from the data analysis is that arable soils are characterized by a higher content of all analyzed soil parameters as: carbonate content (average of about 24%), organic carbon (37%), nitrogen (36%) exchangeable hydrogen (33%) in comparison with uncultivated soils. Also exchangeable pH has in average a higher value of about 0.5 unit in arable soils than in uncultivated ones. In our opinion, this is due to the use of various chemical fertilizers and liming on arable soils. Unfortunately, we cannot precisely

| Location point               | Mean OM content (%) | Carbonate content (%) | C (%)  | N (%)  | H (%)  | pH    |
|------------------------------|---------------------|-----------------------|--------|--------|--------|-------|
| Ludwin (LUD) arable          | 12.1                | 0.2                   | 2.821  | 0.315  | 0.517  | 5.54  |
| Ludwin (LUD) uncultivated    | 19.9                | 0.1                   | 2.226  | 0.233  | 0.456  | 5.24  |
| Kulczyn (KUL) arable         | 23.4                | 2.0                   | 3.812  | 0.349  | 0.665  | 6.49  |
| Kulczyn (KUL) uncultivated   | 26.2                | 0.5                   | 1.715  | 0.169  | 0.367  | 5.73  |
| Turno (TUR) arable           | 3.8                 | 1.7                   | 1.931  | 0.165  | 0.321  | 5.46  |
| Turno (TUR) uncultivated     | 4.3                 | 1.0                   | 1.801  | 0.105  | 0.212  | 5.25  |
| Krzczen (KRZ) arable         | 17.7                | 4.8                   | 11.24  | 0.831  | 1.70   | 7.02  |
| Krzczen (KRZ) uncultivated   | 18.6                | 3.8                   | 4.822  | 0.382  | 0.762  | 6.89  |
| Swierszczow (SWI) arable     | 18.3                | 5.2                   | 5.267  | 0.515  | 0.869  | 7.66  |
| Swierszczow (SWI) uncultivated| 20.4              | 4.8                   | 4.765  | 0.368  | 0.713  | 7.22  |
| Wola Wereszczynska (WOW) arable| 6.6              | 2.4                   | 4.187  | 0.331  | 0.658  | 6.73  |
| Wola Wereszczynska (WOW) uncultivated| 11.4| 1.9              | 3.836  | 0.345  | 0.672  | 6.02  |
| Pieszowola (PIE) arable      | 22.7                | 1.3                   | 2.182  | 0.228  | 0.495  | 6.61  |
| Pieszowola (PIE) uncultivated| 28.6                | 1.0                   | 1.990  | 0.229  | 0.369  | 6.38  |
determine the type of fertilizers used on individual soils as well as their doses.

Sequential extraction procedure

The sequential extraction procedure was based on the Tessier’s method (1979) modified by Haque and Nakanishi (1999) and consisted in extraction of the following fractions: ion-exchange, carbonate bound and specifically adsorbed, Fe/Mn oxides bound, organically bound and residual one (Komosa 2002). The performed experiments were as follows: twenty grams of dry sample was mixed with a proper volume of a given extracting solution. The suspension was mechanically mixed during a given time (Table 3) and then the phases were separated by centrifugation. The required temperature of extraction was maintained by means of a hot plate. Before the addition of the successive extracting medium, the sample was washed with 2 cm$^3$ of distilled water and centrifuged. The reagents and conditions of the sequential extraction procedure used in our study are presented in Table 3.

Alpha spectrometric determination of plutonium

Due to the small specific activity, determination of Pu isotopes in the environmental samples using the alpha spectrometry requires a special care in sample preparation for precise separation of Pu from other matrix components. The solutions obtained after the sequential extraction (the fractions) were traced by $^{242}$Pu standard (AEG Fuel Services, UK, of specific activity 0.73 Bq·g$^{-1}$) and then the trace elements were co-precipitated with iron hydroxide(III) using ammonia (if necessary, a small amount of ferric nitrate was added). The precipitate was dissolved in 6 mol dm$^{-3}$ HCl and then separated from Fe and other alpha-emitting nuclides by co-precipitation with calcium oxalate. Next, oxalates were thermally decomposed and dissolved in acid. Then co-precipitation with a weighed amount of Fe(OH)$_3$ was conducted. After dissolution and oxidation of plutonium into Pu$^{4+}$ (by adding a small amount of sodium nitrite) the anion exchange separation (using 10 cm$^3$ column filled with Dowex 1x8) was performed in the nitric acid medium. Finally, Pu was eluted from the column using the HCl/HI solution and evaporated. Then, Pu was electrodeposited onto the stainless steel discs from 0.4 mol dm$^{-3}$ ammonium oxalate/0.3 mol dm$^{-3}$ HCl and measured by the alpha spectrometry. The detailed separation procedure, based on the IAEA guidebook (IAEA 1989) was described earlier (Orzeł and Komosa 2014).

Four Canberra 7401 alpha spectrometers (equipped with the PIPS silicon detector of 450 mm$^2$ area) connected with a mixer-router 1520 and the S-100 multichannel analyzer PC card were used to measure an alpha radiation. The spectrum analysis was performed with Genie 2000. The purity of the standard $^{242}$Pu solution was below 0.1 % of $^{238}$Pu and $^{241}$Am, and <0.01 % of $^{239+240}$Pu. The background measured with a blank source amounted to about 0.005 cpm in the $^{239+240}$Pu region. The samples were usually measured for 10,000 min. The average minimum detectable amount of $^{239+240}$Pu, estimated according to Boecker et al. (1991) was equal to 0.2 mBq per sample.

For validation of our analytical procedure for plutonium determination, two standard reference materials from IAEA were analyzed. Our result of total $^{239+240}$Pu concentration in the IAEA 384 sample was 111 ± 13 Bq·kg$^{-1}$ at the certified value 108 ± 13 Bq·kg$^{-1}$ and in the Soil-6 sample it was 1.065 ± 0.131 Bq·kg$^{-1}$ at the certified value of 1.04 ± 0.07 Bq·kg$^{-1}$ (IAEA Soil-6 Report 2000; IAEA-384 2000) which confirmed the proper quality of plutonium determination in our laboratory.

Results

To test correctness of our sequential analysis procedure and the reliability of the results, the reference material IAEA Soil-6 was examined according to the above procedure. This material was chosen because of the same plutonium origin (global fallout) and a similar level of activity compared to the analyzed arable and non-crop soil samples analyzed. The IAEA Soil-6 was taken in 1984 near the town of Ebensee (Austria) at an altitude of 1100 m ASL from the surface layer (0–10 cm). There are the ortic rendzina soils in this area (Bodenkarte 2000), formed on limestone rocks containing large amounts of carbonates. The basic composition

| Table 3 | Conditions of the sequential leaching procedure applied for the soil sample and reagents |
|---------|-------------------------------------------------------------------------------------|
| Fraction               | Extracting conditions                                                                 | Solid/ solution ratio |
| Ion-exchange fraction  | 1 mol dm$^{-3}$ MgCl$_2$, 20 °C, 1 h                                              | 1:20                 |
| Carbonate bound        | 1 mol dm$^{-3}$ acetic acid/1 mol dm$^{-3}$ sodium acetate, 20 °C, 5 h              | 1:20                 |
| Fe/Mn oxides bound     | 0.04 mol dm$^{-3}$ NH$_2$OH·HCl/25% acetic acid, 96 °C, 6 h                         | 1:20                 |
| Organically bound      | 0.02 mol dm$^{-3}$ HNO$_3$ /30% H$_2$O$_2$, 85 °C, 2 h; 3.2 mol dm$^{-3}$ ammonium acetate / 20% HNO$_3$, 20 °C, 0.5 h | 1:32, 1:12 |
| Residual               | 6 mol dm$^{-3}$ HCl, 95 °C, 1 h                                                   | 1:5                  |
of this material was 22.9% CaO, 38.5% SiO₂, 8.9% Al₂O₃, 3.7% Fe₂O₃, 2.9% K₂O and 1.9% MgO (IAEA Soil-6 Report 2000). The obtained results of plutonium distribution in the fraction of the above reference material are presented in Table 4.

The concentrations of plutonium in the extracted soil fractions (layer 0–5 cm) are presented in Table 5 and Fig. 1 for the uncultivated soils and in Table 6 and Fig. 2 for the arable ones. Moreover, the data show the percentage distribution of plutonium in the individual fractions for each soil samples. The values presented in Tables 5, 6 were obtained analyzing individual samples from each location (collected according to the procedure described earlier). The tables present also the measurement uncertainties obtained from the alpha spectrometric measurements.

### Discussion

The large content of carbonates in the IAEA reference soil (Soil-6) is probably why plutonium isotopes from the global fallout bind with the carbonate fraction to the greatest extent (slightly exceeding 40%) as it can be seen in Table 4. The remaining amount of plutonium in almost equal amounts (just above 20%) was combined with the organic and water soluble (very readily available) fractions. It is generally accepted that plutonium binds to the organic fraction (Santschi et al. 2017). However, as our measurements proved a significant amount of plutonium was bound with available

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**Table 4** ²³⁹+²⁴⁰Pu contents and percentage distribution among the sequentially extracted fractions of the IAEA Soil-6 reference material

| Fraction                | ²³⁹+²⁴⁰Pu [Bq·kg⁻¹] | ²³⁹+²⁴⁰Pu [%] |
|-------------------------|--------------------|--------------|
| Water soluble           | 0.22 ± 0.043       | 24.4         |
| Ion-exchange fraction   | 0.031 ± 0.009      | 3.5          |
| Carbonate               | 0.36 ± 0.057       | 40.8         |
| Fe/Mn oxides            | 0.049 ± 0.012      | 5.5          |
| Organic                 | 0.21 ± 0.040       | 23.6         |
| Residual                | 0.018 ± 0.005      | 2.1          |
| Total                   | 0.88 ± 0.083       | 100          |

**Table 5** ²³⁹+²⁴⁰Pu content [Bq·kg⁻¹] in the sequentially extracted fractions of uncultivated soils (layer 0–5 cm)

| Fraction                | KUL            | KRZ            | SWI            | LUD            | WOW            |
|-------------------------|----------------|----------------|----------------|----------------|----------------|
| Ion-exchange fraction   | 0.0025 ± 0.00065 | 0.007 ± 0.007  | 0.011 ± 0.006  | 0.004 ± 0.007  | 0.013 ± 0.011  |
| Carbonate               | 0.013 ± 0.004  | 0.005 ± 0.011  | 0.0005 ± 0.005 | 0.0005 ± 0.005 | 0.001 ± 0.004  |
| Fe/Mn oxides            | 0.052 ± 0.009  | 0.005 ± 0.007  | 0.010 ± 0.005  | 0.016 ± 0.005  | 0.011 ± 0.005  |
| Organic                 | 0.23 ± 0.029   | 0.21 ± 0.023   | 0.039 ± 0.023  | 0.068 ± 0.011  | 0.091 ± 0.022  |
| Residual                | 0.0075 ± 0.0025 | 0.039 ± 0.006  | 0.019 ± 0.015  | 0.016 ± 0.004  | 0.014 ± 0.004  |
| Total                   | 0.30 ± 0.032   | 0.26 ± 0.028   | 0.080 ± 0.028  | 0.11 ± 0.014   | 0.14 ± 0.026   |

*Value lower than MDA with alpha spectrometric determination

**Table 6** ²³⁹+²⁴⁰Pu content [Bq·kg⁻¹] in the sequentially extracted fractions of arable soils (layer 0–5 cm)

| Fraction                | KUL            | KRZ            | SWI            | LUD            | WOW            | TUR            | PIE |
|-------------------------|----------------|----------------|----------------|----------------|----------------|----------------|-----|
| Ion-exchange fraction   | 0.026 ± 0.011  | 0.12 ± 0.074   | 0.019 ± 0.027  | 0.11 ± 0.026   | 0.001*         | 0.079 ± 0.018  | 0.001* |
| Carbonate               | 0.033 ± 0.013  | 0.010 ± 0.011  | 0.020 ± 0.017  | 0.027 ± 0.011  | 0.51 ± 0.055   | 0.56 ± 0.084   | 0.023 ± 0.016 |
| Fe/Mn oxides            | 0.017 ± 0.009  | 0.080 ± 0.020  | 0.069 ± 0.019  | 0.035 ± 0.010  | 0.17 ± 0.034   | 0.051 ± 0.018  | 0.024 ± 0.013 |
| Organic                 | 0.20 ± 0.036   | 0.045 ± 0.023  | 0.14 ± 0.030   | 0.11 ± 0.069   | 0.074 ± 0.024  | 0.030 ± 0.022  | 0.16 ± 0.035 |
| Residual                | 0.022 ± 0.004  | 0.026 ± 0.007  | 0.050 ± 0.016  | 0.014 ± 0.014  | 0.075 ± 0.010  | 0.026 ± 0.006  | 0.010 ± 0.004 |
| Total                   | 0.30 ± 0.041   | 0.28 ± 0.081   | 0.30 ± 0.050   | 0.29 ± 0.076   | 0.82 ± 0.070   | 0.75 ± 0.090   | 0.22 ± 0.041 |

*Value smaller than MDA as follows from the alpha spectrometric determination
and carbonate fraction what can be considered as “easily available”. Undoubtedly, this is related to the chemical composition of the soil. The large content of silica is probably responsible for retaining plutonium which can get readily into the solution together with the hydrated forms of silica.

Silicates are present in soil in relatively high concentration. During the aging of their surface, cations such as: K\(^+\), Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) are washed out. Instead, hydroxyl groups are formed on the surface which, depending on the pH, can accept or donate protons. The most frequently formed groups are: ≡SiOH, ≡AlOH, ≡FeOH, which bind radionuclides present in the form of hydroxy complexes or bivalent oxanions through the formation of surface complexes. Much weaker interactions of these groups were recorded with radioactive elements present in the form of other inorganic complexes, complexes with organic ligands and in the form of colloidal solutions (Lieser 1995).

As it was found during the sequential extraction of this reference material the total (cumulative) concentration of \(^{239+240}\text{Pu}\) in the fractions was 0.883 Bq·kg\(^{-1}\). Knowing the certified value of plutonium content (1.04 ± 0.07 Bq·kg\(^{-1}\)), the yield of the sequential extraction procedure was calculated to be about 85%. This confirms that the sequential extraction method combined with the alpha spectrometric analysis of the plutonium concentration in the separated fractions provides sufficiently accurate results to assess the plutonium distribution among individual fractions.

The results of plutonium distribution in the uncultivated soil fractions presented in Fig. 1 and Table 5 are consistent with the generally accepted view that plutonium binds mainly to the organic fraction. The average plutonium content in the organic phase of uncultivated soil was 67 ± 11\% (range 49–78\%). Plutonium combined with the Fe / Mn oxide fraction is in the range of 2–17\% (average (11 ± 6) \%; median 13\%), and with ion-exchange fraction average fraction (6.2 ± 5.3) \% (range 0.9–13\%, median 4.3\%). A very small amount of plutonium combined with the average carbonate fraction (in two cases the amount of Pu was below the detection limit), (2.2 ± 2.2) \%, median 2\%, range 0–4.5\%) is due to the soil composition containing carbonate minerals (as shown in Table 1) being organic soils (Histosols and Mollisols) or carbonate soil (Terrisols). Plutonium bound permanently to the matrix was found in an average amount (13 ± 7.8) \%, median 15\% and range of median 2.5\% to 24\%.

From the point of view of plutonium bioavailability, its content in the relatively easily accessible fractions (ion-exchange fraction and carbonate ones) is very important because it can pass into soil solution readily under the neutral and slightly acidic conditions, often found in the environment. The average plutonium content in these fractions was on the average (8.4 ± 5.0) \% in the range 4.3–14 \%, median 5.2 \%. These values are relatively small, thus plutonium in the organic soils is rather strongly bound to the soil organic matter.

The distribution of plutonium in the separated fractions in the arable soils is different from that in the uncultivated soil. As given in Fig. 2 and the data presented in Table 6, the distribution of plutonium in individual fractions is diverse. Although the largest share of Pu in the average organic fraction is still observed (median 36 \%, range 4–73 \%), the share of Pu in the residual, ion-exchange fraction, carbonate and Fe/Mn oxides fractions is comparable with each other (median values 7\%, 9\%, 11\% and 12\%, respectively).

The comparison of the results presented in Table 5 and Fig. 1 with those in Table 6 and Fig. 2 indicates significant differences in plutonium distribution in the arable and uncultivated soils. The amount of Pu bound rigidly to the soil matrix (organic and residual fraction) decreases, and the amount of Pu bound in a less stable way (the Fe/Mn oxides fraction) or completely available increases in the case of arable soil in comparison with uncultivated one. The comparison of the obtained results clearly shows that the amount of plutonium in the available and carbonate bound fractions is much larger (about 4 times) in the case of arable soils as compared to the uncultivated areas from the same locations. Thus there is also an increase in the bioavailability of plutonium. The sequential extractions are the commonly used methods for estimation of the mobility of metals closely related to bioavailability (Rosado et al. 2016). It is probable that the reason for the observed increase in the share of Pu in the ion-exchange fraction and carbonate fractions of arable soils is their cultivation. As mentioned in the introduction, the literature data indicate that long-term fertilization changes the soil chemical composition. The research by Shunfeng et al. (2018) and Dong et al. (2012) carried out in apple orchard and the rice field proved that intensive fertilization with various substances causes the increase of the amount of organic carbon and total nitrogen with a simultaneous decrease of the carbon and nitrogen ratio as
The authors would like to thank the unknown reviewers for their detailed and valuable comments that allowed us to improve our manuscript.

Conclusions

The research showed that the sequential extraction method is a useful tool for estimation of plutonium presence in labile or binding form in arable and uncultivated soils from the region of eastern Poland. The sequential extraction procedure used in combination with the alpha spectrometry to determine plutonium allowed to study the distribution of this element in the separated geochemical fractions. The modified Tessier sequential extraction was applied. The results show that arable soils contain more bioavailable (accessible and carbonate bound fractions) plutonium in comparison to the uncultivated soils collected from the same locations. It was demonstrated that in the studied soils with the intact structure 67% Pu (median value) is combined with the organic fraction, 13% with the Fe/Mn oxide fraction, and only 5% with the ion-exchange and carbonate fractions. In the arable soil more plutonium is bound with the ion-exchange and carbonate soil fractions. Moreover, that in the case of arable soils, the largest amount of Pu is combined with the organic fraction (36%) but about 20% of Pu is combined with the fractions relatively easily accessible for plants (ion-exchange fraction and carbonate) which is the fourfold larger value compared to that of the uncultivated soils. This is important because food is grown on arable soils. In this way, plutonium can enter the food chain through absorption in plants.

Acknowledgements The authors would like to thank the unknown reviewers for their detailed and valuable comments that allowed us to improve our manuscript.

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