Plutonium as a tracer for soil erosion assessment in northeast China

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HIGHLIGHTS

- The potential for the use of Pu as a soil erosion tracer was investigated.
- Pu would be a good tracer given its long half-life.
- Depth profiles of Pu in soils were systematically studied and compared to ^{137}Cs.
- Pu is an effective soil erosion tracer with behavior similar to that of ^{137}Cs.
- Thus, Pu provides a means of investigating soil erosion.

GRAPHICAL ABSTRACT
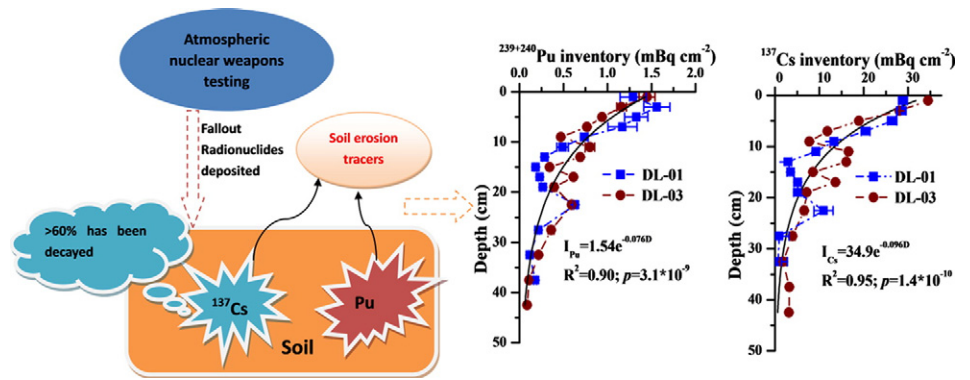
ABSTRACT

Soil erosion is one of the most serious environmental and agricultural problems faced by human society. Assessing intensity is an important issue for controlling soil erosion and improving eco-environmental quality. The suitability of the application of plutonium (Pu) as a tracer for soil erosion assessment in northeast China was investigated by comparing with that of ^{137}Cs. Here we build on preliminary work, in which we investigated the potential of Pu as a soil erosion tracer by sampling additional reference sites and potential erosive sites, along the Liaodong Bay region in northeast China, for Pu isotopes and ^{137}Cs. ^{240}Pu/^{239}Pu atomic ratios in all samples were approximately 0.18, which indicated that the dominant source of Pu was the global fallout. Pu showed very similar distribution patterns to those of ^{137}Cs at both uncultivated and cultivated sites. $^{239\,+\,240}$Pu concentrations in all uncultivated soil cores followed an exponential decline with soil depth, whereas at cultivated sites, Pu was homogenously distributed in plow horizons. Factors such as planted crop types, as well as methods and frequencies of irrigation and tillage were suggested to influence the distribution of radionuclides in cultivated land. The baseline inventories of $^{239\,+\,240}$Pu and ^{137}Cs were 88.4 and 1688 Bq m^{-2} respectively. Soil erosion rates estimated by $^{239\,+\,240}$Pu tracing method were consistent with those obtained by the ^{137}Cs method, confirming that Pu is an effective tracer with a similar tracing behavior to that of ^{137}Cs for soil erosion assessment.

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1. Introduction

Soil erosion is one of the most serious environmental and agricultural problems faced by human society (Pimentel et al., 1995; Pimentel, 2006; Montgomery, 2007). It is a global concern that is particularly

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severe in developing countries including China. Soil erosion causes degradation of soil quality and downstream deposition in fields and floodplains, thereby affecting water quality and consequently reducing the productivity of natural, agricultural, forest, and aquatic ecosystems (Pimentel et al., 1995; Pimentel, 2006). To efficiently control and alleviate the loss of soil by erosion and reduce its environmental impact, comprehensive data that integrate the magnitude of soil erosion spatially and temporally are necessary (Mabit et al., 2013).

Based on its close association with soil particles (mainly minerals), global fallout ^{137}Cs that originated from nuclear weapons testing (NWT), mainly conducted in the 1950s to 1960s, has been validated as a powerful and extensively used tracer for soil erosion assessment in the past few decades (cf. Zapata, 2002; Mabit et al., 2013). However, given a relatively short half-life (30.17 years), about 70% of the global fallout ^{137}Cs deposited in the environment has already disappeared through radioactive decay. This property makes ^{137}Cs less sensitive for investigating soil erosion, a situation that will worsen in the near future. In recent years, Pu isotopes have been suggested as new tracers to replace ^{137}Cs in soil erosion investigation (Schimmack et al., 2002; Zapata, 2002; Zapata and Nguyen, 2010; Everett et al., 2008). Pu isotopes have the same dominant global fallout source as ^{137}Cs, but have much longer half-lives (24,110 years for ^{239}Pu and 6561 years for ^{240}Pu), and have higher radioactive intensity and low mobility in soils, and are relatively easy to determine using highly sensitive mass spectrometric measurement techniques (Hoo et al., 2011; Xu et al., 2013). However, few efforts have been devoted to the application of Pu in soil erosion assessment; limited applications have been performed only in Australia (Tims et al., 2010; Hoo et al., 2011; Lal et al., 2013) and in areas affected by the Chernobyl nuclear accident (Schimmack et al., 2002; Alewell et al., 2014). No such applications regarding Chinese soil erosion have been performed, except for our previous preliminary study in northeast China (Xu et al., 2013).

Similar to ^{137}Cs, the requirements for Pu as a fallout tracer for soil erosion studies include (i) $^{239+240}$Pu should be dominantly derived from the global fallout of NWT, which occurred intensively from 1954 to the mid-1960s; (ii) the global fallout of $^{239+240}$Pu is locally spatially uniform; and (iii) $^{239+240}$Pu was quickly and strongly absorbed by soil particles after being deposited onto the soil surface, and the subsequent redistribution in soils is mainly ascribed to the physical movement process of soil particles during soil erosion and sedimentation. Based on the above criteria, our previous work (Xu et al., 2013) preliminarily demonstrated that Pu can be applied as a substitute of ^{137}Cs to trace soil erosion along the Liaodong Bay region in northeast China. However, given the limited soil cores (only two) with a lack of representation, soil erosion in the study area was not quantified using Pu as a tracer with erosion models. In the current work, we extended the sampling sites including additional reference sites and potentially erosive sites along the Liaodong Bay region in northeast China, and analyzed all soil core samples for ^{239}Pu, ^{240}Pu, and ^{137}Cs. These analyses aim to further investigate the suitability and practical applicability of $^{239+240}$Pu as a tracer for quantification of soil erosion in the study area by comparing the obtained erosion rates from the two tracers. Depth distribution characteristics of $^{239+240}$Pu in both uncultivated and cultivated soil cores were also investigated and compared with those of ^{137}Cs.

2. Materials and methods

2.1. Soil sampling

Soil core samples were collected in October 2009, May 2013, and July 2013 from Dalian (DL) and Jinzhou (JZ), which are located in the coastal region of Liaodong Bay in northeast China (Fig. 1). The sampling area is located in a typical temperate zone dominated by a monsoonal climate with an annual precipitation amount of 600 to 800 mm (Li et al., 2006) and an annual mean temperature of 8.4 to 9.7 °C (Sun, 2005). Low hills and coastal plains are the major topographic characters in this region.

Aside from the reference soil core DL-01 and the study soil core DL-02, the ^{137}Cs and Pu isotope concentrations of which have been published elsewhere (Xu et al., 2013) and were applied for quantification of soil erosion, two other flat reference sites with permanent native vegetation cover and without obvious disturbance as well as potential sediment input or erosion (according to the field observation and interviews with local residents) were selected in DL to obtain additional reference soil cores (DL-03 and DL-04). It is worthy of note that the DL-04 site is located at the top of a hill that is surrounded by forest with very fine brown soil, and many stones were observed to be distributed throughout the soil core during the sampling process. Five other potentially erosive sites, including uncultivated and cultivated lands, were selected in DL and JZ to obtain study soil cores, among which the uncultivated sites of JZ-01 and JZ-02 were situated on an unculturedland with very low vegetation coverage. All uncultivated soil cores, including the reference soil cores, were sampled to a total depth of 50 cm with the same sampling strategy implemented in our previous study (Xu et al., 2013). By interviewing local farmers, we learned that cultivation histories of the three cultivated sites were generally more than 40 years, and the long-term planted crop type for the DL-C01 and JZ-C01 sites was corn while the sampling site DL-C02 was used for vegetables such as potatoes and cabbages, which were planted in rotations. The sampling depth of the three cultivated soil cores was 30 cm since plow layers of the cultivated lands were generally 20 to 30 cm thick, and each soil core was sliced at 5 cm intervals to determine the Pu isotopes and ^{137}Cs.

2.2. Analysis of ^{137}Cs and Pu isotopes in soil samples

Except for the soil cores DL-01 and DL-02, the analyses of ^{137}Cs and Pu isotopes on all other soil core samples (Table 1) were conducted by the authors in the laboratory of the Division of Radioecology and Tracer, Center for Nuclear Technologies, Technical University of Denmark.

The activities of ^{137}Cs in soil samples were determined by gamma spectrometry using HPGe (High-purity Germanium) detectors with 10% to 40% relative counting efficiency. To reach acceptable levels of detection limit and measurement error, the counting time of each sample (ca. 50 g of dry soil) was set at around 20 h. The measurement uncertainties for ^{137}Cs in most soil samples were lower than 10% (measurement error at 1-sigma), except for those deep soil samples in which the activity concentrations of ^{137}Cs were close to the detection limit of the equipment.

Pu isotopes in all soils were analyzed using the method described in Xu et al. (2013, 2014). The flow chart of the analytical procedure for the determination of Pu isotopes is presented in Fig. 2. Briefly, an aliquot of ca. 10 g of prepared soil was first ashed at 550 °C overnight to decompose the organic matter (as well as to obtain the organic matter content by calculating the mass loss in this procedure). After spiking with 5 to 10 mBq of ^{242}Pu as a chemical yield tracer (the ^{242}Pu tracer added to the ashed aliquot does not cover the losses during the mineralization, but they should be negligible) and acid leaching with aqua regia for 2 h at 200 °C, Pu in the leachate was co-precipitated with iron hydroxides to remove the major matrix components. After centrifugation, the precipitate was dissolved with a few milliliters of concentrated HCl, and about 300 mg of $K_2S_2O_5$ was used to reduce Pu to Pu(III). And then Pu(III) was further oxidized to Pu(IV) with conc. HNO_3. The prepared sample solution in 8 mol L^{-1} HNO_3 medium was then loaded to an AG1-×4 anion-exchange column (1 cm in diameter and 15 cm in length). After rinsing the column with 70 mL of 8 mol L^{-1} HNO_3 to remove most uranium and matrix elements, followed by 50 mL of 9 mol L^{-1} HCl to remove thorium, Pu was eluted with 70 mL of 0.1 mol L^{-1} $NH_2OH \cdot HCl$ in 2 mol L^{-1} HCl. To obtain better decontamination of uranium, the separated Pu was further purified using a 2 mL TEVA column (0.7 cm in diameter and 5.0 cm in length). The procedure of TEVA column separation is closely similar to the anion exchange chromatographic separation. Prior to TEVA column purification, Pu in