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Correspondence and requests for materials should be addressed to X.L.H. (xiho@dtu.dk) or S.M.P. (span@nju.edu.cn)

Plutonium in Soils from Northeast China and Its Potential Application for Evaluation of Soil Erosion

Yihong Xu[1,2], Jixin Qiao[2], Xiaolin Hou[2,3] & Shaoming Pan[1]

[1]The Key Laboratory of Coastal and Island Development of Ministry of Education, Nanjing University, Nanjing 210093, China, [2]Center for Nuclear Technologies, Technical University of Denmark, Risø Campus, Roskilde 4000, Denmark, [3]Xi'an AMS Center, SKLLQG, Institute of Earth Environment, CAS, Xi'an 710075, China.

Surface and soil core samples from northeast China were analyzed for Pu isotopes. The measured ^{240}Pu/^{239}Pu atomic ratios and $^{239+240}$Pu/^{137}Cs activity ratios revealed that the global fallout is the dominant source of Pu and ^{137}Cs at these sites. Migration behavior of Pu varying with land type and human activities resulted in different distribution of Pu in surface soils. A sub-surface maximum followed by exponential decline of $^{239+240}$Pu concentrations was observed in an undisturbed soil core, with a total $^{239+240}$Pu inventory of 86.9 Bq/m^2 and more than 85% accumulated in 0 ∼ 20 cm layers. While only half inventory of Pu was obtained in another soil core and no sub-surface maximum value occurred. Erosion of topsoil in the site should be the most possible reason for the significantly lower Pu inventory, which is also supported by the reported ^{137}Cs profiles. These results demonstrated that Pu could be applied as an ideal substitute of ^{137}Cs for soil erosion study in the future.

Since the 1940s, plutonium isotopes have been produced and released into the environment due to human nuclear activities, including nuclear weapons testing (NWT), operation and accidents of nuclear power plants (NPPs), e.g. Chernobyl accident in 1986 and Fukushima accident in 2011[1–4], production and reprocessing of nuclear fuel, as well as other nuclear accidents, e.g. Kyshtym accident in Russia in 1957; aircraft accidents in Thule, Greenland in 1968 and in Polomares, Spain in 1966; and satellites SNAP-9A in 1964[5–7]. Among the 20 isotopes of Pu, ^{239}Pu and ^{240}Pu with half-lives of 24110 yr and 6561 yr, respectively, are the most important ones due to their highly radiological toxicities and long-term persistence in the environment.

In the past decades, most researches on environmental Pu have focused on the evaluation of radiation risk in contaminated areas[1–7], migration of Pu in the environment related to nuclear activities and waste repository[8], dispersion of Pu in the contaminated aquatic system[9,10], as well as the environmental behavior of Pu in the ecosystem for radioecology studies[11–13]. Based on the significantly different isotopic composition of Pu related to its production and releases, the measurement of isotopic ratios and decay products of Pu in the environmental materials can be used to identify its source term and age. For instance, ^{240}Pu/^{239}Pu atomic ratios for weapon-grade Pu are very low (0.01 ∼ 0.07)[5–7,10,13,14] while much higher values are expected in spent fuel of nuclear power plants (up to 0.2 ∼ 0.8, depending on reactor type and burn-up of the fuel)[2–4,10], as well as in atmospheric weapons testing fallout (0.14 ∼ 0.24, with an average of 0.18)[15–17].

The deteriorated soil erosion and associated sedimentation arising from human activities have become a serious problem in many developing countries including China, which causes land degradation, downstream sedimentation in fields, floodplains and water bodies, consequently affects water quality. Since the 1960s, radionuclides have been proven to be powerful tracers for soil erosion investigation[18]. Based on high association of ^{137}Cs to soil particles (mainly minerals), global fallout ^{137}Cs from NWT mainly conducted in later 1950s and beginning of 1960s has been widely used for soil erosion studies in the past decades[18]. However, due to its relatively short half-life (30.2 yr), the concentrations of global fallout ^{137}Cs in the environment have decreased by a factor of more than 2 comparing to the levels in the 1970s due to its radioactive decay, and this declined trend will continue. This makes the applications of ^{137}Cs for investigations of soil erosion, transportation and sedimentation less sensitive at present and will become difficult in the future. Because of the long half-lives of ^{239}Pu and ^{240}Pu, their dominating source of nuclear weapons testing fallout worldwide, as well as their high retention and low mobility in soil, they were therefore suggested as ideal substitutes of ^{137}Cs for investigation of soil erosion[19–22]. Especially, with the rapid development of sensitive measurement techniques using mass spectrometry including inductively coupled

plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS) in the recent years, application of Pu isotopes for this investigation becomes more attractive and competitive. Nonetheless, quantification of soil erosion using Pu isotopes has not yet been well established up to date, and very few baseline data of Pu isotopes have been reported[22–25]. Although concentrations of Pu isotopes in surface soils have been measured in many sites worldwide in the past 40 years[23,26,27], a few works on Pu distribution in Chinese soils (less than 15 sampling sites, mainly surface soils) have been reported[28–30] and no data of Pu isotopes in soils from northeast China is available.

In the past years, nuclear activities including NWT in North Korea have caused a high concern on the radiation exposure to inhabitants in northeast China, where is close to North Korea. However, no observations regarding anthropogenic radionuclides including Pu in northeast China have been reported. With the rapid development of nuclear energy in China in the past 10 years, there are 4 NPPs with 11 units in operation, and 7 NPPs with 20 units under construction. Among them, Hongyanhe NPP with 4 units located in Dalian, Liaodong Bay region, is going to be operated in 2014, and the first unit has already started to operate from February 2013. Releases of radioactive materials from NPPs are also a major concern of the local inhabitants, in this case monitoring radionuclides in the surrounding environment can provide necessary information to the authorities and public.

Liaodong Bay, located in northeast China, is an inner bay of Bohai Sea. Major rivers flowing through this region, include Liao, Daliao, Fudu, Lianshan, Yantai, Liugu, Xingcheng, and Daling River. Through these rivers, a large amount of surface soil removed from their catchments is transported to and deposited in the Liaodong Bay[31], which degrades the soil quality of the coastal region for agriculture purpose. The high sedimentation of the eroded soil in the Bay

is indeed a big concern related to the ecosystem of the Liaodong Bay. Understanding the soil erosion processes and dynamics is a vital issue for controlling soil erosion and improving eco-environmental quality of the region.

In this work, surface soil samples and soil cores were collected in the Liaodong Bay region (Fig. 1) and analyzed for ^{239}Pu and ^{240}Pu, in order (1) to provide basic information for environmental risk monitoring and evaluation related to the nuclear activities in North Korea and the Hongyanhe NPP; (2) to investigate the distribution, source term and environmental behavior of Pu in northeast China; (3) to establish Pu depth profile and inventory baseline, as well as to explore the feasibility of applying Pu in soil erosion studies in the region.

Results

The results of activity concentrations of $^{239 + 240}$Pu and ^{137}Cs, the atomic ratios of ^{240}Pu/^{239}Pu and the activity ratios of $^{239 + 240}$Pu/^{137}Cs in all surface soil samples and two soil core samples were summarized in Supplementary Table S1 and Table S2 online, respectively. Data of ^{137}Cs activity for all samples were cited from He et al[32]. A large variation of $^{239 + 240}$Pu concentrations from 0.023 to 0.938 mBq/g was observed in these surface soil samples (Fig. 2 and Supplementary Table S1 online). The statistical analysis (ANOVA) showed that Pu concentrations in surface soil from cultivated land (from 0.023 to 0.223 mBq/g with an average of 0.136 mBq/g) were significantly lower ($p = 0.049 < 0.05$) than those from grass land (from 0.027 to 0.938 mBq/g with an average of 0.361 mBq/g); whereas differences of Pu concentrations between cultivated and saline land, as well as saline and grass land, respectively, were not statistically significant, although their average Pu values followed the order of grass land (0.361 mBq/g) > saline land (0.211 mBq/g) > cultivated land (0.136 mBq/g). Figure 3 shows vertical distribution of
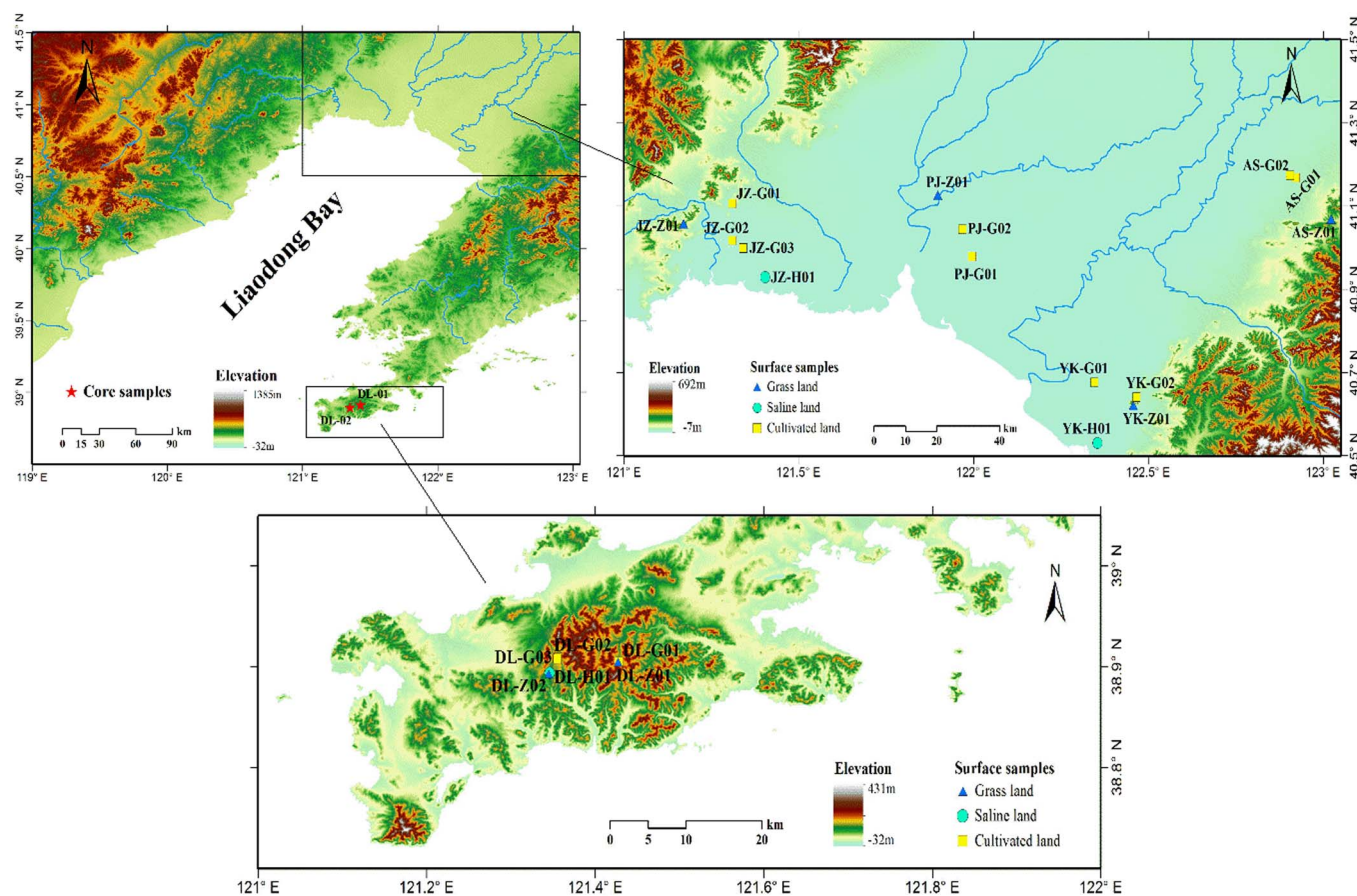

Figure 1 | Map showing the soil sampling locations along the Liaodong Bay, northeast China. Generated using ArcGis 10.0 (ESRI).
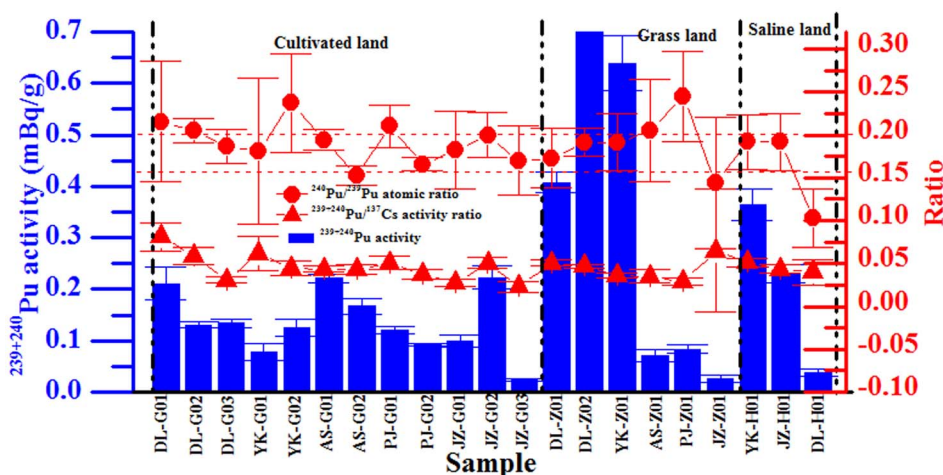
Figure 2 | Distribution of $^{239+240}$Pu activity concentration, ^{240}Pu/^{239}Pu atomic ratios and $^{239+240}$Pu/^{137}Cs activity ratios in surface soils along the Liaodong Bay. ^{137}Cs activities were cited from He et al.[32] and decay corrected to 1st Sept. 2009. The horizontal dashed lines indicate the global fallout ^{240}Pu/^{239}Pu atomic ratio range of 0.18 ± 0.02. Vertical error bars correspond to analytical uncertainty (1σ).

$^{239+240}$Pu in the two soil cores (DL-01 and DL-02) collected in Dalian, Liaodong Bay. A sub-surface maximum of Pu concentration at 2 ~ 4 cm depth followed by exponentially decrease with depth until 16 cm was observed in the DL-01 soil core, while merely exponentially decreased Pu concentration from surface to 8 cm depth was observed in the DL-02 core. Similar depth profiles as DL-01 have also been reported in soil cores from Japan and South Korea[11,24]. The total $^{239+240}$Pu inventories in sampling sites of DL-01 and DL-02 were calculated by integrating the content of Pu in each layer of soil cores. The results (Table 1) indicated that about double $^{239+240}$Pu inventory (86.9 Bq/m^2) in the sampling site of DL-01 compared to the sampling site of DL-02 (44.1 Bq/m^2) was obtained. Since the two sampling sites are < 20 km distance, atmospheric deposition of Pu in these two sites should be similar. The difference in the total Pu inventory might only be attributed to different retention of Pu in these two sites.

The measured ^{240}Pu/^{239}Pu atomic ratios in this work varied from 0.144 to 0.245 with an average of 0.192 ± 0.020 (1σ) in all surface samples, while in the two soil cores, the values ranged from 0.162 to 0.213 with an average of 0.187 ± 0.012 (1σ) in DL-01 core, and from

0.146 to 0.209 with an average of 0.180 ± 0.021 (1σ) in DL-02 core, respectively, which were relatively constant and similar to those measured in the surface soils. Clearly, the measured ^{240}Pu/^{239}Pu ratios in all soil samples agreed very well with the value of 0.18 for the integrated global atmospheric fallout[17], indicates that the major source of Pu in soils in northeast China might be the global atmospheric fallout.

Discussion

The sampling sites in this work located in northeast China (Fig. 1). There were no nuclear facilities operated in this region (<100 km to the sampling locations) before the sampling date (Oct. 2009). The nearest nuclear facilities were those located in Korea, which was more than 300 km far from the sampling sites. The atmospheric releases from nuclear activities in the North Korea including the nuclear reprocessing and underground NWT might have negligible contribution to Pu in the soil samples analyzed in this work. In addition, as a refractory element, Pu is not easily to be released to the atmosphere during underground NWT. Actually no radionuclide (even for volatile ^{85}Kr, ^{133}Xe, ^{131}I) dispersion from the NWT
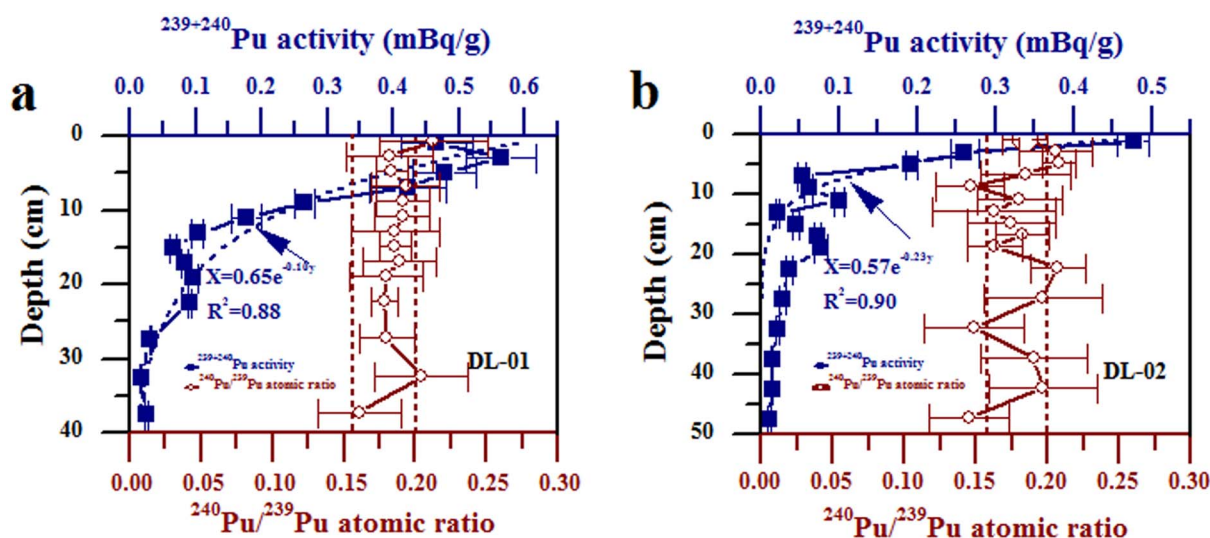

Figure 3 | Vertical distributions of $^{239+240}$Pu activity concentration and ^{240}Pu/^{239}Pu atomic ratios in soil cores ((a). DL-01 and (b). DL-02) from Dalian, northeast China. The vertical dashed lines indicate the global fallout ^{240}Pu/^{239}Pu atomic ratio range of 0.18 ± 0.02. Horizontal error bars correspond to analytical uncertainty (1σ).

Table 1 | The inventories of Pu and ^{137}Cs in soil cores[a]

Depth (cm)	$^{239+240}$Pu (Bq/m^2)	$^{239+240}$Pu inventory distribution (%)	^{137}Cs[b] (Bq/m^2)	^{137}Cs inventory distribution (%)
DL-01				
0–6	41.8 ± 2.5	48	916 ± 19	54
6–20	33.6 ± 1.9	39	650 ± 25	38
> 20	11.5 ± 0.3	13	138 ± 40	8
Total	86.9 ± 3.1		1704 ± 40	
DL-02				
0–6	24.5 ± 0.6	56	426 ± 17	56
6–20	11.3 ± 0.4	26	175 ± 22	23
> 20	8.2 ± 0.4	18	163 ± 46	21
Total	44.1 ± 0.9 (51%)[c]		764 ± 47 (45%)[c]	

[a]All given uncertainties are overall analytical uncertainty (1σ).
[b]^{137}Cs activities were cited from He et al.[32] and decay corrected to 1st Sept. 2009.
[c]Numbers in parentheses indicate percentages relative to the inventory of the reference core DL-01.

in the North Korea has been observed in South Korea, Japan and China. As for the Chinese atmospheric NWT conducted in Lop Nor site (located in the Kumtag Desert, northwest China) during 1964 ~ 1980, the long distance between our sampling sites and Lop Nor (> 2600 km) probably made the close-in fallout Pu contribution from these NWTs insignificant to the Pu in soil samples analyzed in this work. Atmospheric release of Pu from NPPs in normal operation is very limited since almost all Pu isotopes are produced and captured in the fuel elements in the NPPs, therefore the contribution from the NPPs in remote areas in South Korea and South China (Tianwan, Qinshan and Dayawan NPPs, >550 km from the sampling locations) to the Pu in the soil samples investigated in this work is negligible. The dominant source of Pu in northeast China might be the global fallout of atmospheric NWT.

The measured ^{240}Pu/^{239}Pu atomic ratios in all soil samples in this work agreed very well with the reported values of the global fallout as well as those in similar latitude in China, such as soil samples from Gansu province (40°N, 97° E) of 0.169 ~ 0.192 with an average of 0.182 ± 0.008 (1σ)[29], and from Hubei province (31°N, 112°E) of 0.172 ~ 0.220[30]. Similar ^{240}Pu/^{239}Pu atomic ratios of 0.157 ~ 193 with an average of 0.182 ± 0.012 (1σ) have also been reported in a sediment core collected in Lake Sihailongwan, northeast China (42°20′N, 126°50′E)[33]. In addition, the measured $^{239+240}$Pu/^{137}Cs activity ratios (Supplementary Table S1 online) in all surface soil samples (~0.045, decay corrected to 1st Sept. 2009) agreed well with the reported values (0.030 ~ 0.043) in soils contaminated only by global atmospheric fallout[34].

^{240}Pu/^{239}Pu atomic ratios of 0.403 ~ 0.412 of close-in fallout Pu derived from Chernobyl accident have been reported in soil samples heavily contaminated by Chernobyl accident collected in 30 km zone of Chernobyl[2], the measured ^{240}Pu/^{239}Pu atomic ratios in all soil samples investigated in this work were about 2 times lower than these values. During the Chernobyl accident, most released radionuclides were deposited in the local area, some fraction of volatile radionuclides dispersed and deposited in the Europe, and very small amount of radionuclides dispersed to other regions[1,2,8,12,35–37]. The inventory of ^{137}Cs in the soil core DL-01 has been estimated to be 1.7 kBq/m^2[32] which was more than 10 times lower than that in Germany (20 ~ 40 kBq/m^2)[37], while no measurable Chernobyl-derived Pu in the soil from west Europe has been reported. The $^{239+240}$Pu/^{137}Cs activity ratios in surface soil samples in this work (~0.045, decay corrected to 1st Sept. 2009) were also 3 times higher than those measured in the Chernobyl contaminated soil (0.010 ~ 0.015, decay corrected to 2010)[2]. Based on these facts, it might be concluded that the direct contribution of the close-in fallout from Chernobyl accident to the Pu in soils in the northeast China should be negligible. Moreover, the

reported ^{240}Pu/^{239}Pu atomic ratios of close-in fallout Pu in the Semipalatinsk NWT (0.04 ~ 0.07)[14] (more than 3400 km distance to the present sampling locations), the Chinese NWT (0.08 ~ 0.103)[33,38] and from the Kyshtym accident (0.0282 ± 0.0002)[4,5] were all obviously lower than those (around 0.18) observed in this work, indicating that any close-in fallout contribution from these two NWT sites as well as from Kyshtym site could also be negligible in our sampling sites.

All above results suggested that Pu in the soils of northeast China should be primarily originated from the integrally global stratospheric fallout of the atmospheric NWT, and the close-in fallout from any NWT sites and accidents is insignificant. The Hongyanhe NPP (39°47.5′N, 121°28.5′E) has just started in operation of its first unit from Feb. 2013. The measurement results in this work will provide a background data for the monitoring and evaluation of environmental impact of this NPP in the future.

A large variation in Pu concentrations (Fig. 2, Supplementary Table S1 online) was observed in the surface soil samples. Since the analyzed soil samples were collected within a relatively small area (100 × 300 km) where no local input of Pu has been reported, the total input of Pu or the integral input of Pu from the global fallout should not vary significantly due to their similar climate and latitude. Therefore distinct retention, migration and removal behavior of Pu in different type of soil, as well as disturbance of soil column with varying degrees, should be major reasons causing high variation of Pu concentrations among surface soils collected from different sites. In the cultivated land, soils were heavily disturbed due to periodic cultivation activities; consequently, Pu from the atmospheric deposition to the surface soil was mixed with the soil in the deeper layer, which might cause a homogenized distribution of Pu in the plough horizon, and decreased Pu concentration in the top soil. Meanwhile, irrigation of the cultivated land might leach and remobilize some Pu (water soluble fraction) from the soil thus reducing Pu levels in the surface soil. In addition, the cultivated land was seasonally covered by vegetation, and a relatively high removal of the newly deposited Pu by wind was expected in a certain period of a year with lower vegetation coverage. All these factors contributed to lower Pu concentrations in surface soil from the cultivated land. Among these factors, the turnover of soil during the cultivation process causing the dilution of Pu by mixing the surface soil with deep soil might be the dominated reason. Similar observations have also been reported that Pu and ^{137}Cs concentrations in the cultivated soil column were significantly lower than those found in undisturbed soil cores, meanwhile their distributions were rather constant in 0 ~ 10 cm layer in the cultivated soil column[24]. In grass land, grass roots reinforced the soil strength withstanding water flow flush and wind blow, thus effectively preventing surface soils from erosion, consequently Pu deposited on the soil could be effectively retained. In addition, the large surface area of vegetation leaves could also retain the Pu deposited from the atmosphere, which would be further transferred to the underneath soil by precipitation flushing or decomposition of the vegetation after death. The well retention and less removal of Pu in the grass land resulted in high Pu concentrations in its surface soil. As for the saline land with very low vegetation coverage, Pu deposited on the surface soil could be quickly removed by wind blow and runoff of precipitation, especially for small grains, resulting in Pu loss with varying degrees. Hence, different distribution of Pu in surface soil within a relatively small area might be mainly influenced by the pattern of land utilization. This phenomenon has also been reported for other fallout radionuclides including ^{7}Be and ^{210}Pb[39].

Besides the high erosion of the surface soil in the low coverage land (such as saline land) and disturbance of the soil by agriculture activity in the cultivated land, the soil properties such as particle sizes, clay contents, and organic matter contents might also influence the behavior of Pu in soils[26,27], thus contribute to the variation of Pu concentrations. The surface soil samples analyzed in this work were

collected from 5 different areas with distinct soil properties (Supplementary Table S3 online). However, regression analysis did not show any significant correlations between Pu concentrations and either grain size distributions or organic matter contents in these surface soil samples, implying that no single factor such as one parameter of soil properties but the joint-effect of many environmental factors is responsible for the variation of Pu concentrations in surface soils along the Liaodong Bay. Among all those factors, land utilization patterns resulting in somewhat changes of soil properties could be the dominated one.

Further insight into the environmental behavior of Pu in soils was provided by the distribution of Pu in the two soil cores. The sequential fractionation of radionuclides in soil has shown that Pu was mainly associated with organic matter and metal oxides, while ^{137}Cs was mainly in minerals[12,40]. Therefore Pu might be relatively mobile in the soil, especially when Eh/pH of the soil was changed and decomposition of organic matter occurred. In addition, the relatively higher proportion of exchangeable and carbonate associated Pu compared to ^{137}Cs has also been reported[12,40]. In the DL-01 soil core, although 80% ~ 90% of $^{239 + 240}$Pu and ^{137}Cs accumulated in the top 20 cm soils, the relative inventory of $^{239 + 240}$Pu in the upper 6 cm soil (48%) was slightly lower than that of ^{137}Cs (54%) (Table 1), and no sub-surface maximum of ^{137}Cs in this soil core could be observed (Fig. 4a)[32], agreeing well with the fractionation observation that Pu had a relatively higher mobility in soil compared to ^{137}Cs[40]. Considering that the sampling site of the DL-01 core situated on the top of a broad hill with low possibilities of runoff or flowing, negligible erosion or deposition would be expected at this site. Possible reasons for the sub-surface maximum of Pu concentration at 2 ~ 4 cm in the DL-01 soil core (Fig. 3a, Fig. 4a) might include migration of Pu associated fine particles[24] from surface to the sub-surface; accumulation of Pu associated organic matters (mainly humic or fulvic material) in the sub-surface layer and downwards migration of Pu caused by rainfall. However, clay contents and mean grain sizes in the two soil cores (Supplementary Fig. S1 online) varied slightly from layer to layer. Besides, the organic matter content in the sub-surface layer (2 ~ 4 cm) of the DL-01 core was not higher than that in the top layer (0 ~ 2 cm), although significant correlations (based on the regression analysis of ANOVA) were observed between organic matter contents and the concentrations of Pu and ^{137}Cs, respectively (Fig. 5), indicating that fine particles and organic matter might not be responsible for the sub-surface maximum of Pu concentration in the DL-01 soil core. Therefore, the migration of Pu from the surface to the sub-surface should be induced by the adsorption and desorption process of Pu in the soil core driven by rain fallout.

In the DL-01 soil core, the activity ratios of $^{239 + 240}$Pu/^{137}Cs tended to increase slightly with the increasing soil depth. An average $^{239 + 240}$Pu/^{137}Cs activity ratio of 0.045 in the upper 6 cm layer agreed very well with the reported values (0.042 ~ 0.043, decay corrected to 1st Sept. 2009) in sites of a similar latitude (40° N) in USA[34]. However, the $^{239 + 240}$Pu/^{137}Cs activity ratio increased to 0.079 (average) in deep layer (6 ~ 40 cm), which might resulted from a higher downwards migration of Pu compared to ^{137}Cs due to the higher mobility of Pu. While in the DL-02 core, the $^{239 + 240}$Pu/^{137}Cs activity ratios (0.038 ~ 0.109) throughout the soil core were generally higher than those reported values. In addition to the higher migration of Pu as mentioned above, another possible explanation for this might be linked to the out-flowing loss of fine particles enriched clay or materials absorbing higher amount of ^{137}Cs in the surface layer, which was confirmed by lower inventory of ^{137}Cs (45%) than Pu (51%) in the DL-02 core compared to the DL-01 core (Table 1).

Although the migration of Pu in the soil cores was higher than ^{137}Cs, it was still a slow process and almost all Pu currently still remained in upper 50 cm (Fig. 3). As a consequence, strong correlations (based on the regression analysis of ANOVA) between the ^{137}Cs and Pu isotopes in the two soil cores (R^2 = 0.98, P = 1.8 × 10^{-10} for DL-01 core and R^2 = 0.95, P = 6 × 10^{-10} for DL-02 core) were observed (Supplementary Fig. S2 online). High correlations between the concentrations of Pu and ^{137}Cs were also observed in all surface samples in this work (Supplementary Fig. S3 online), especially in grass land (R^2 = 0.95, P = 6 × 10^{-4}), where the soil was less disturbed by human activities. The relatively low correlation between ^{137}Cs and $^{239 + 240}$Pu concentrations in the cultivated land (R^2 = 0.51, P = 0.005) might be attributed to high disturbance during cultivation activities. High correlation between ^{137}Cs and Pu concentrations has also been reported in soils from other locations[24,26,27]. These results indicated that the physical transport of $^{239 + 240}$Pu and ^{137}Cs in soils should be very similar despite their different chemical behaviors. Consequently, $^{239 + 240}$Pu and ^{137}Cs could convey similar information about soil erosion and redistribution of soils in a small area.

Investigation of soil erosion using radionuclides is based on the principle that the radionuclides deposited on the soil surface are quickly and strongly adsorbed on the soil particles and then follow the physical processes of soil particles to be redistributed during soil erosion and sedimentation. To implement quantitative estimation of soil erosion and sedimentation rate from the measurement of radionuclides, it is critical to establish the baseline or reference inventory of radionuclides in the investigated area. In the present work, the DL-01 soil core was collected at a stable and undisturbed site, where neither significant erosion nor additional deposition has been
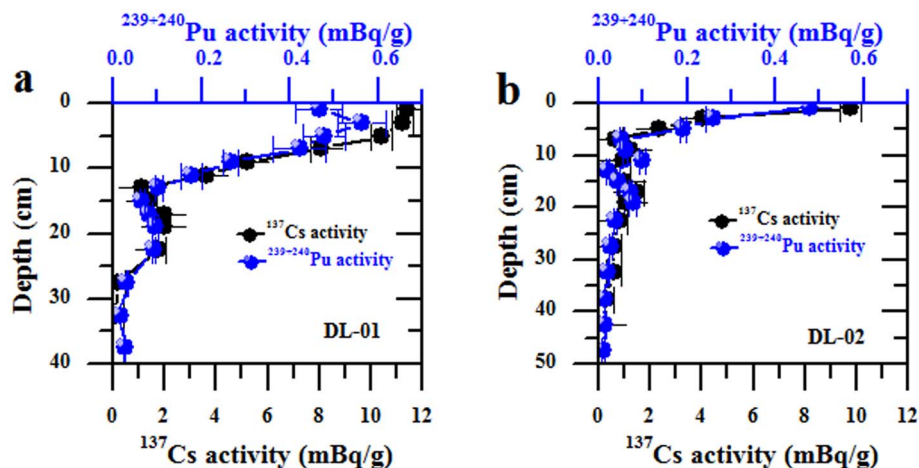

Figure 4 | Comparison between the profiles of $^{239 + 240}$Pu and ^{137}Cs in the two soil cores ((a). DL-01 and (b). DL-02). ^{137}Cs activities were cited from He et al.[32] and decay corrected to 1st Sept. 2009. Horizontal error bars correspond to analytical uncertainty (1σ).

recorded. Based on the depth profile of Pu in the DL-01 soil core, the estimated total inventory of $^{239+240}$Pu of 86.9 ± 3.1 Bq/m^2 (Table 1) agreed very well with those reported values in soil profiles in similar latitude (30 ~ 40°N) in Korea (84 ~ 88 Bq/m^2)[24]. A slightly higher $^{239+240}$Pu inventory (101.8 Bq/m^2) in Euiwang, Korea[24], lower values in Hubei (44.9 ~ 54.6 Bq/m^2)[30] and Lanzhou (32.4 Bq/m^2)[29] in China have also been reported. The deviation of $^{239+240}$Pu inventory in the DL-01 core from those values might be attributed to the differences in the locations and climate of specific location. For example, the much higher precipitation rate in Dalian (600 ~ 800 mm)[41] compared to that in Lanzhou (235 ~ 238 mm)[29] could cause a relatively higher deposition of Pu and thus a higher inventory of $^{239+240}$Pu. In any case, the depth profile and total inventory of Pu in the soil core DL-01 could serve as reference inventory or baseline for further investigations in the sampling area.

The total inventory of $^{239+240}$Pu in the DL-02 core was measured to be 44.1 ± 0.9 Bq/m^2 (Table 1), only half of the value in the DL-01 core. Since the distance between the two sampling sites are < 20 km, the atmospheric deposition of Pu in the two sites should not be significantly different. The erosion of soil at the DL-02 site might be the most possible reason for the significantly lower Pu inventory in this core. Comparing the Pu profiles in the two soil cores, the loss of Pu in the DL-02 core corresponded to the Pu in the first ~6 cm layer in the reference core (DL-01) (Table 1, Fig. 6a), deducing that the top ~6 cm soil at the site of DL-02 might be eroded. A similar conclusion could be also deduced based on the ^{137}Cs profiles in the two soil cores (Table 1, Fig. 6b). This demonstrated that Pu could be used as a satisfied substitute of ^{137}Cs for the investigation of soil erosion.

The obvious spatial variation of Pu concentrations in the upper 5 cm soils (Fig. 2, Supplementary Table S1 online) demonstrated that the surface soil was redistributed in different extents by erosion, transport and re-deposition processes in the studied area. However, to estimate the intensity of the erosion in a specific site of the area, more comprehensive work involving analyzing Pu profiles in a series of soil cores and modeling of downwards migration of Pu has to be carried out.

This is the first report of the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios in soils in the northeast China. The present work demonstrated that fallout Pu could be an ideal substitute of the relatively short-lived fallout ^{137}Cs for evaluation of soil erosion and redistribution in the future. The data sets provided background baseline for further monitoring and evaluation of anthropogenic Pu contamination in the area in case any unexpected releases of radionuclides from the Hongyanhe NPP or other NPPs in adjacent areas occur, as well as for quantitative studies on soil erosion in the region and the source identification of sediments in the Liaodong Bay in the following work.

Methods

Soil sampling. Soil samples were collected in Oct. 2009 in the coastal region of Liaodong Bay (Fig. 1), including five districts of Dalian (DL), Jinzhou (JZ), Panjin (PJ), Yingkou (YK) and Anshan (AS), which locate in a typical temperate zone dominated by a monsoonal climate with annual precipitation rate of 600 ~ 800 mm[41] and annual mean temperature of 8.4 ~ 9.7°C[42]. Low hills and coastal plain are the major topographic characters in this region.

According to the vegetation coverage and utilization of the land at the sampling sites, all surface soil samples (0 ~ 5 cm) (Fig. 1, Supplementary Table S3 online) collected can be sorted to three types, i.e. cultivated land (12 samples), grass land (6 samples) and saline land (3 samples). Soil cores collected in this region were analyzed for Pu isotopes, among them two cores (DL-01 and DL-02) up to 50 cm depth collected from Dalian were selected for investigating the feasibility of applying Pu isotopes for soil erosion studies. DL-01 sampling site (brown soil) situated on the top of a broad hill which was covered by native vegetation with dense bushes, without
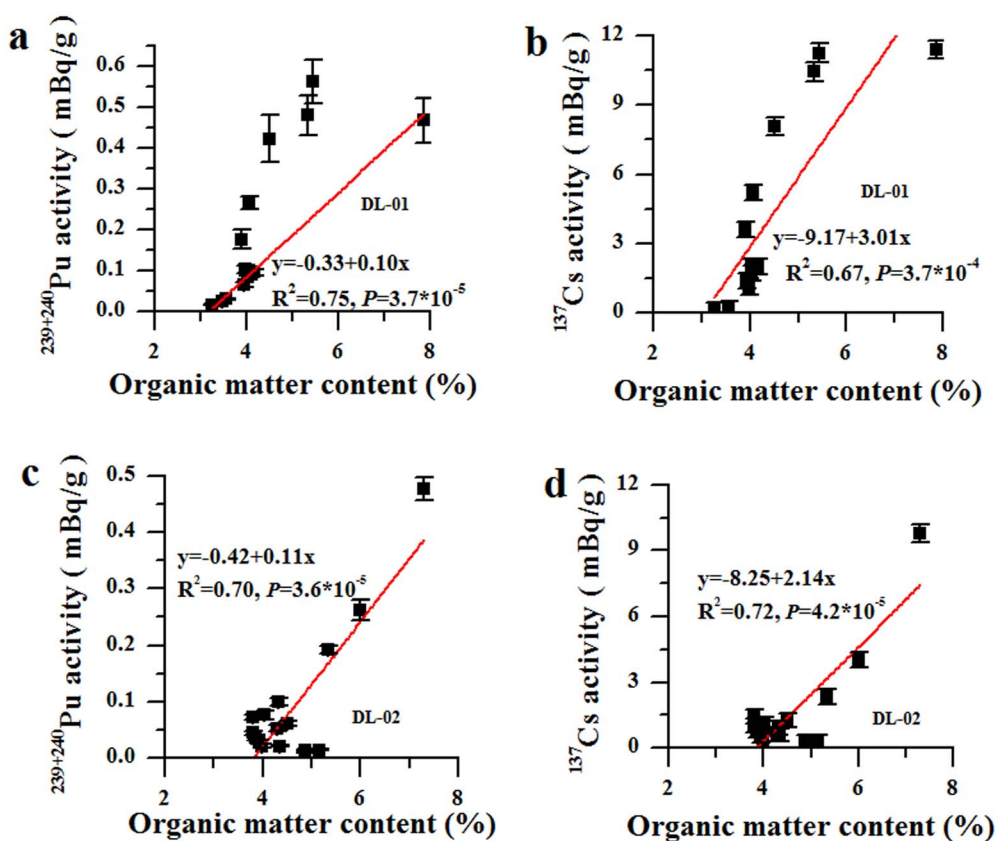

Figure 5 | Correlation between the concentrations of Pu and ^{137}Cs and organic matter contents in the two soil cores ((a). Pu ~ organic matter for soil core DL-01; (b). ^{137}Cs ~ organic matter for soil core DL-01; (c). Pu ~ organic matter for soil core DL-02; (d). ^{137}Cs ~ organic matter for soil core DL-02). ^{137}Cs concentrations were cited from He et al.[32] and decay corrected to 1st Sept. 2009. Vertical error bars correspond to analytical uncertainty (1σ).
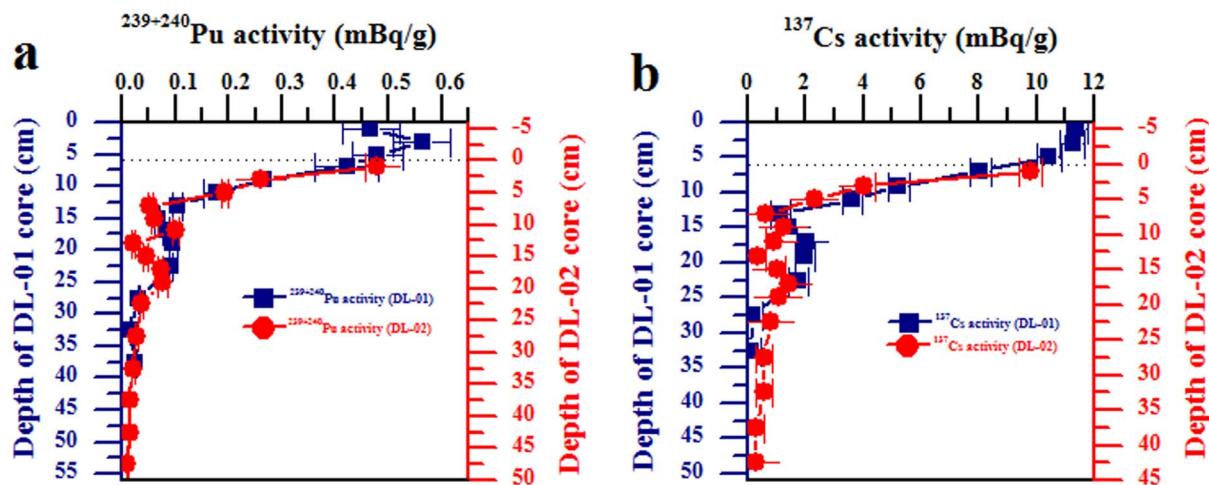
Figure 6 | Comparison of $^{239+240}$Pu and ^{137}Cs profiles between the two soil cores ((a). DL-01 and (b). DL-02). ^{137}Cs activities were cited from He et al.[32] and decay corrected to 1st Sept. 2009. Horizontal error bars correspond to analytical uncertainty (1σ).

receiving obvious human disturbance. DL-02 sampling site was an un-cultured land with lower vegetation coverage. In the DL-01 soil core, lots of vegetation roots were observed distributing in the layer up to 35 cm, while fewer roots were observed in the DL-02 core. The two sampling sites are about 10 ~ 20 km distance from each other. The top 0 ~ 20 cm depth of the soil cores were sliced at 2 cm intervals and 20 ~ 50 cm depth at 5 cm intervals.

Soil analysis for Pu isotopes. Pu isotopes in all soils were determined using a modified method based on the method reported by Qiao et al.[43] at the Center for Nuclear Technologies, Technical University of Denmark. An aliquot of 10 g 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 ^{242}Pu as a chemical yield tracer and acid leaching with aqua regia for 2 hours under 200°C, Pu in the leachate was co-precipitated with iron hydroxides to remove major matrix components. After centrifugation, the precipitate was dissolved with a few milliliters of concentrated HCl, then redox pair of $K_2S_2O_5$-$NaNO_2$ was used to adjust overall Pu to Pu(IV). The final sample solution prepared in 8 mol/L HNO_3 medium was loaded to an AG 1-×4 anion-exchange column (1 cm in diameter and 15 cm in length). After rinsing the column with 70 mL of 8 mol/L HNO_3 to remove most uranium and matrix elements, followed by 50 mL of 9 mol/L HCl to remove thorium, Pu was eluted with 70 mL of 0.1 mol/L $NH_2OH\cdot HCl$ in 2 mol/L HCl. The separated Pu was further purified using a 2-mL TEVA column (0.7 cm in diameter and 5 cm in length) to get better decontamination of uranium. Prior to the TEVA column purification, Pu was co-precipitated with $Fe(OH)_2$ after adding 100 mg of Fe, then the precipitate was dissolved with 1.0 mL of concentrated HCl, and concentrated HNO_3 to oxidize Pu to Pu(IV), the sample was then diluted to 1 mol/L HNO_3 and loaded to the TEVA column. After rinsing the column with 60 mL of 1 mol/L HNO_3 and 60 mL of 6 mol/L HCl, Pu was finally eluted with 20 mL of 0.1 mol/L $NH_2OH\cdot HCl$ in 2 mol/L HCl. The eluate was evaporated to dryness on a hot-plate followed by the addition of concentrated nitric acid and heating to decompose the hydroxylamine and eliminate the hydrochloric acid. The residue was finally dissolved in 5 mL of 0.5 mol/L HNO_3 for measurements of Pu isotopes (^{239}Pu, ^{240}Pu, ^{242}Pu) by an ICP-MS system (X Series II, Thermo Fisher Scientific, Waltham, MA) equipped with an Xs- skimmer cone under hot plasma conditions. A high efficiency ultrasonic nebulizer (U5000AT+, CETAC, USA) was used for sample introduction to the ICP-MS. The detection limits were calculated as three times of the standard deviation (3σ) of the procedure blank to be 0.3 ~ 0.5 pg/L for ^{239}Pu, ^{240}Pu and ^{242}Pu.

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Author contributions

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