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Distinctive distributions and migrations of $^{239+240}$Pu and ^{241}Am in Chinese forest, grassland and desert soils

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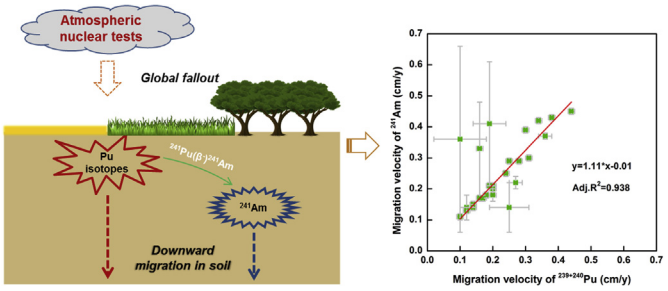
HIGHLIGHTS

- Distributions of Pu and Am in diverse types of Chinese soils were investigated.
- Higher apparent dispersion coefficients were observed for soils with lower pH.
- Mean migration velocities of Pu and Am were similar, being less than 0.3 cm/y.
- Migration results were compatible with short-term simulation studies in China.

GRAPHICAL ABSTRACT



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ABSTRACT

The vertical distributions and downward migrations of the global fallout derived $^{239+240}$Pu and ^{241}Am in diverse types of Chinese soils (forest, grassland and desert) were studied. The mean $^{239+240}$Pu and ^{241}Am activity concentrations in the investigated soil cores were 0.28–0.69 mBq/g and 0.13–0.37 mBq/g, respectively, while the accumulative inventories were 61.53–138.99 Bq/m^2 for $^{239+240}$Pu and 28.29 –61.05 Bq/m^2 for ^{241}Am. The convection-dispersion equation (CDE) was used to calculate the migration parameters of $^{239+240}$Pu and higher apparent dispersion coefficients (D) were observed for the acidic forest soils compared with the alkaline grassland and desert soils; meanwhile a compartment model was employed to compare the migration of $^{239+240}$Pu and ^{241}Am in successive soil layers which showed that the migration behaviors of $^{239+240}$Pu and ^{241}Am were rather similar; both velocities were less than 0.3 cm/y in diverse types of soils and these findings were compatible with those of short-term laboratory simulation experiments in China.

1. Introduction

Plutonium (Pu) has been released to the environment worldwide mainly as a result of nuclear weapon tests in the last century, by which the total amount of $^{239+240}$Pu was approximately 11 PBq

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(UNSCEAR, 2000). Unlike the fallout $^{239+240}$Pu that was directly deposited to the earth's surface during the atmospheric nuclear weapon tests, ^{241}Am ($T_{1/2} = 432.2$ y) (Hou and Roos, 2008) has been steadily increasing in the environment as a consequence of the beta-decay of ^{241}Pu ($T_{1/2} = 14.4$ y) (Hou and Roos, 2008) produced concurrently with other Pu isotopes during the nuclear explosions. The produced ^{241}Am content in the environment is expected to reach its maximum in the year 2042 (Zheng et al., 2012). On the one hand, considering their long half-lives and high radiotoxicities, the levels of $^{239+240}$Pu and ^{241}Am in the environment are of scientific concern regarding their long-term radiation risk assessments; on the other hand, since the ^{240}Pu/^{239}Pu atom ratio and ^{241}Am/$^{239+240}$Pu activity ratio vary from different sources, information on these characteristic ratios could be regarded as radioactive fingerprints to distinguish possible contamination once a nuclear accident happens (Zheng et al., 2012). Therefore, it is meaningful to enrich the database of $^{239+240}$Pu and ^{241}Am distributions in the diverse natural environments in China. Although many data have been reported on the distributions of $^{239+240}$Pu in several parts of China (Bu et al., 2014, 2015; Dong et al., 2010; Sha et al., 1991a, 1991b; Xu et al., 2013, 2017; Zheng et al., 2009), studies on ^{241}Am are very scarce. To our knowledge, only Sha et al. (1991a; 1991b) have reported the activity concentrations of $^{239+240}$Pu and ^{241}Am in soils collected in 1990 in northern and eastern China. Further investigations are necessary to renew the knowledge about the current status of ^{241}Am in Chinese environments.

Soil is a principal reservoir of radionuclides present in terrestrial environments. Information on their vertical migration in soil is valuable since this process controls the long-term behaviors of these radionuclides in ecosystems. Furthermore, comprehensive understanding of the environmental behaviors of long-lived radionuclides (such as ^{239}Pu, ^{240}Pu and ^{241}Am) is crucial for the management of highly radioactive waste disposal. Actually, simulation experiments under controlled field or laboratory conditions with artificially added Pu and Am tracers have been conducted in China to acquire valuable information on their mobility under specific scenarios (Guo et al., 2003; Li et al., 2004a, 2004b). Nevertheless, in spite of the advantages of the controlled experimental conditions, it is very difficult to ensure realistic environmental conditions in this way, especially for long-term investigations. For this reason, it is useful to study the behaviors of radionuclides that have been introduced into an actual environment for many years. Benefitting from having the same source of radionuclides, similar deposition density on regional scales and long migration times (decades) since their initial deposition onto the soil, the global-fallout-derived radionuclides are appealing tools for worldwide comparative studies on their migration behaviors in different environments and ecosystems.

Principally, the basic physical processes behind the migration of radionuclides in soil include convection through flowing pore water, dispersion caused by spatial variations of convection, diffusion of radionuclides within the fluid and physical-chemical interaction with soil particles (Kirchner et al., 2009). There are two models that have been widely used for modeling the migration of radionuclides, i.e. the convection-dispersion equation (CDE) and the compartment model. The CDE is established based on the actual physical processes of the radionuclides in the soil cores and has analytical solutions for specific initial and boundary conditions (Bossew and Kirchner, 2004). It has been widely employed to obtain the migration parameters of ^{137}Cs and ^{90}Sr which have been compiled by the IAEA in the technical report series IAEA TRS-472 (IAEA, 2010). However, the application of CDE for Pu migration is seriously limited by the lack of field data (Strebl et al., 2009). The application of CDE for ^{241}Am is much more complicated than that for Pu because not only the migration of ^{241}Am is involved, but also its ingrowth from ^{241}Pu should be considered. As a way out, the migration of ^{241}Am could be roughly evaluated by the compartment model without taking into account detailed migration mechanisms. The compartment model is a black-box approach described by a series of linear first-order differential equations with which the residence times of the radionuclides in each soil layer can be calculated (Boone et al., 1985; Kirchner, 1998). To date, reports on the migration of Pu isotopes and ^{241}Am in Chinese field environments are rather limited. To our knowledge, only Bu et al. (2014) have calculated the migration parameters of Pu in forest soils in southwestern China with CDE, while no results of ^{241}Am migration in undisturbed Chinese soils have been reported yet. On account of the large diversities of Chinese environment, it is informative to compare the migration parameters of Pu and Am in different environments to check whether the environmental difference could lead to distinct migration behaviors of Pu and Am.

In this work, we investigated the vertical distributions and downward migrations of $^{239+240}$Pu and ^{241}Am in four areas in China. These areas were chosen for their large diversities in environmental condition such as precipitation, soil pH, plantation coverage etc. Sources of $^{239+240}$Pu and ^{241}Am in these areas were identified. The migration of Pu was quantified by the physically based CDE. Besides, for the first time, the migration behaviors of $^{239+240}$Pu and ^{241}Am in Chinese soils in diverse environments (forests, grassland, and desert) were compared with the compartment model.

2. Materials and methods

2.1. Sample collection

Four soil cores were collected from diverse environments (two forests, one grassland and one desert) in different areas of China more than 1000 km from each other. The two core samples from Guiyang (GY) city (106°40′1″E, 26°39′23″N) and Guazhou (GZ) city (95°44′57″E, 40tyincepl) were collected in the previous work of Bu et al. (2014, 2015) in 2011 while the other two were sampled in 2014 (QS) from Qinshan (120°56′42″E, 30°26′17″N) and in 2015 from Chengde (CD) city (117°13′52″E, 42°24′13″N), respectively. The sample information and locations are presented in Table 1 and Fig. A.1. For GY, GZ and QS cores, the depth interval was 2 cm for the initial 10 cm and 5 cm for the subjacent soils. For the CD sample that was collected in another sampling campaign, the whole soil core was divided into 2 cm intervals. Before further analysis, soil samples were dried and passed through 2 mm sieve to remove gravels and plant roots.

2.2. Chemical separation and analysis of Pu isotopes and ^{241}Am

Pretreated soil samples were firstly ashed in an oven at 450 °C for 4 h to decompose organic matter (Wang et al., 2015). A HNO_3 leaching method was used to release Pu and Am from soil samples. The Pu and Am analysis procedures were described in Appendix A and more details can be referred to our previous work (Wang et al., 2016, 2017). Both Pu isotopes and Am fractions were analyzed by SF-ICP-MS. The IAEA-soil-6 reference material was used for quality control of the analytical methods and results were presented in Table A.1.

2.3. Model fitting

The migrations of Pu isotopes in these soil cores were quantified by two models, viz. the CDE and the compartment model. The CDE

Table 1
Sample information of the soils used in this study.[a].

Sample ID	Sample location	Sampling year	Plant type	Precipitation (mm/y)	Bulk density (g/cm^3)	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	pH (H_2O)
GY[b]	Guiyang	2011	Forest	1130	1.3	11.3	4.9	81.2	13.8	4.8
QS	Qinshan	2014	Forest	1189	1.5	4.9	35.9	56.9	7.2	4.4
GZ	Guazhou	2011	Desert	88	1.3	5.8	51.2	37.7	11.1	8.1
CD	Chengde	2015	Grassland	512	1.0	8.0	24.3	69.8	5.9	8.7

[a] The values of the soil characteristics are the mean values of the whole soil cores.
[b] The information of the GY sample was from Bu et al. (2014).

is deduced by the fundamental physical processes, while the compartment model is a black box model that only cares about the residence times of radionuclides in successive soil layers without detailed knowledge about the migration dynamics (Coughtrey, 1988). For $^{239+240}$Pu vertical distribution data, both CDE and the compartment model were employed for fitting; while, for ^{241}Am, since there is no analytical solution is available for the CDE, we did not use CDE for the ^{241}Am case, only the compartment model was used for ^{241}Am fitting. As the CDE and compartment model have been already established and are among the most widely employed models in this field, detailed descriptions of these models were not given in the text but provided in the Appendix A.

3. Results and discussion

3.1. Current distributions of ^{241}Am and $^{239+240}$Pu in different Chinese areas

The vertical distribution data of ^{241}Am and $^{239+240}$Pu are presented in Table A.2 and Fig. 1. The accumulative inventory of ^{241}Am and $^{239+240}$Pu at each site could be estimated by the following Eq. (1).

$$I = \sum_{i=1}^{N} B \times d_i \times C_i \quad (1)$$

Where I (Bq/m^2) stands for the accumulative inventory of ^{241}Am or $^{239+240}$Pu; B (g/cm^3) is the soil bulk density as provided in Table 1; d_i is the depth of each layer and C_i represents the activity concentration of ^{241}Am or $^{239+240}$Pu in each layer. The mean ^{241}Am activity concentration in our four soil cores ranged from 0.13 mBq/g to 0.37 mBq/g and the accumulative inventories at the QS, CD, GY and GZ sites were 52.92 Bq/m^2, 61.05 Bq/m^2, 28.29 Bq/m^2, 42.88 Bq/m^2, respectively. To date, information on the levels and distribution characteristics of ^{241}Am in Chinese environments is rather limited. We found only two papers by Sha et al. (1991a; 1991b) that determined $^{239+240}$Pu, ^{241}Am and ^{137}Cs activity concentrations in soil cores from four cities (Beijing, Jinan, Taiyuan and Shijiazhuang) in northern and eastern China in the early 1990s. The ^{241}Am activity concentrations of our samples were systematically higher than those (0.01 mBq/g to 0.12 mBg/g) in their samples and our ^{241}Am inventories (28.29–61.05 Bq/m^2, mean 46.28 Bq/m^2) were approximately 3 times of the inventories (5.9–19.9 Bq/m^2, mean 12.3 Bq/m^2) of their sites after decay correction to Jan. 2018. Besides, the $^{239+240}$Pu inventories in the four cities were only 10.1–36.4 Bq/m^2, further illustrating that the results of Sha et al. (1991a; 1991b) might be somewhat underestimated. Apart from the difference in environmental conditions, another important reason for this discrepancy might be, we think, the inhomogeneity of the soil samples in the earlier studies of Sha et al. (1991a; 1991b) since vertical soil cores were sampled as only two rough layers (0–5 cm and 5–20 cm) and a large sample size (50–100 g) was required to satisfy the detection limit of alpha spectrometry. As an illustration, in their study, the mean $^{239+240}$Pu and ^{241}Am activity concentrations in the 5–20 cm soil layers were close to or even higher than those in the 0–5 cm soils, which was more or less arguable on account of the slow migration velocity of ^{241}Am and its persistence in the surface or subsurface soils (Bunzl et al., 1992, 1995). In contrast, our results were more comparable to the ^{241}Am activity concentration in Japanese rice-field soils (0.04 mBq/g to 0.50 mBq/g, decay corrected to January 2018) (Yamamoto et al., 1983). Lee et al. (2013) also reported the ^{241}Am activity concentration in Korean soils collected between 2006 and 2008. Large variation of ^{241}Am activity concentration in the surface soils was observed, ranging from 0.23 mBq/g to 2.04 mBq/g and the accumulative ^{241}Am inventories in three soil cores varied from 30.9 Bq/m^2 to 72.1 Bq/m^2 (decay corrected to January 2018) (Lee et al., 2013). In summary, the ^{241}Am activity concentrations and inventories in the investigated Chinese soils were in good agreement with those in the Japanese and Korean soils across the similar latitude region, indicating the ^{241}Am in these studies might have the same source, i.e. global fallout. Since the ^{241}Am was produced from ^{241}Pu, a further discussion of the sources of these radionuclides was provided in the section 3.2.

The accumulative inventories of $^{239+240}$Pu were 138.99 Bq/m^2, 138.37 Bq/m^2, 61.53 Bq/m^2 and 109.98 Bq/m^2 for QS, CD, GY and GZ sites, respectively. The Pu data of the GY and GZ sites were previously reported by Bu et al. (2014, 2015), while the results of the QS and CD soil cores were newly measured in this study. Compared with ^{241}Am, reports on the Pu distribution in Chinese environment are more abundant. Current $^{239+240}$Pu activity concentrations as well as $^{239+240}$Pu inventories in these soil samples were comparable to the literature values for Chinese soils reported by other researchers. For example, Xu et al. (2017) investigated the $^{239+240}$Pu levels in Lianyungang city in east China which lies relatively close to our QS sampling site. The $^{239+240}$Pu activity concentration in the two 5 cm surface forest soils were 0.540 mBq/g and 0.604 mBq/g, respectively. These results were quite close to our QS profile results. The $^{239+240}$Pu inventory in the QS site was 138.99 Bq/m^2 in the undisturbed forest soil, which was, however, about 3 times higher than the reported mean deposition inventory of $^{239+240}$Pu (42 Bq/m^2) in the 30–40°N region (UNSCEAR, 2000). Since the inventory recommended by the UNSCEAR report is a rough estimation of the average level across the wide latitude region, it might be unsuitable to represent a specific area that has characteristic environmental conditions. For example, the accumulative deposition inventories of radionuclides including ^{238}Pu, $^{239+240}$Pu, ^{241}Am and ^{137}Cs in soils of forest and grassland were suggested to have positive correlations with the mean annual precipitation in Germany (Bunzl and Kracke, 1988). However, for the four sites in this study that locates more than 1000 km away from each other, direct correlations of both ^{241}Am and $^{239+240}$Pu inventories with the precipitation amount were not appreciable. In detail, at the coastal QS site that has the highest annual precipitation (1189 mm/y), the ^{241}Am and $^{239+240}$Pu inventories were the second highest among the four sites; however, for the GY site with similar abundant precipitation (1130 mm/y), the ^{241}Am and $^{239+240}$Pu inventories were the lowest compared with other sites. In comparison, for the CD soil core collected in

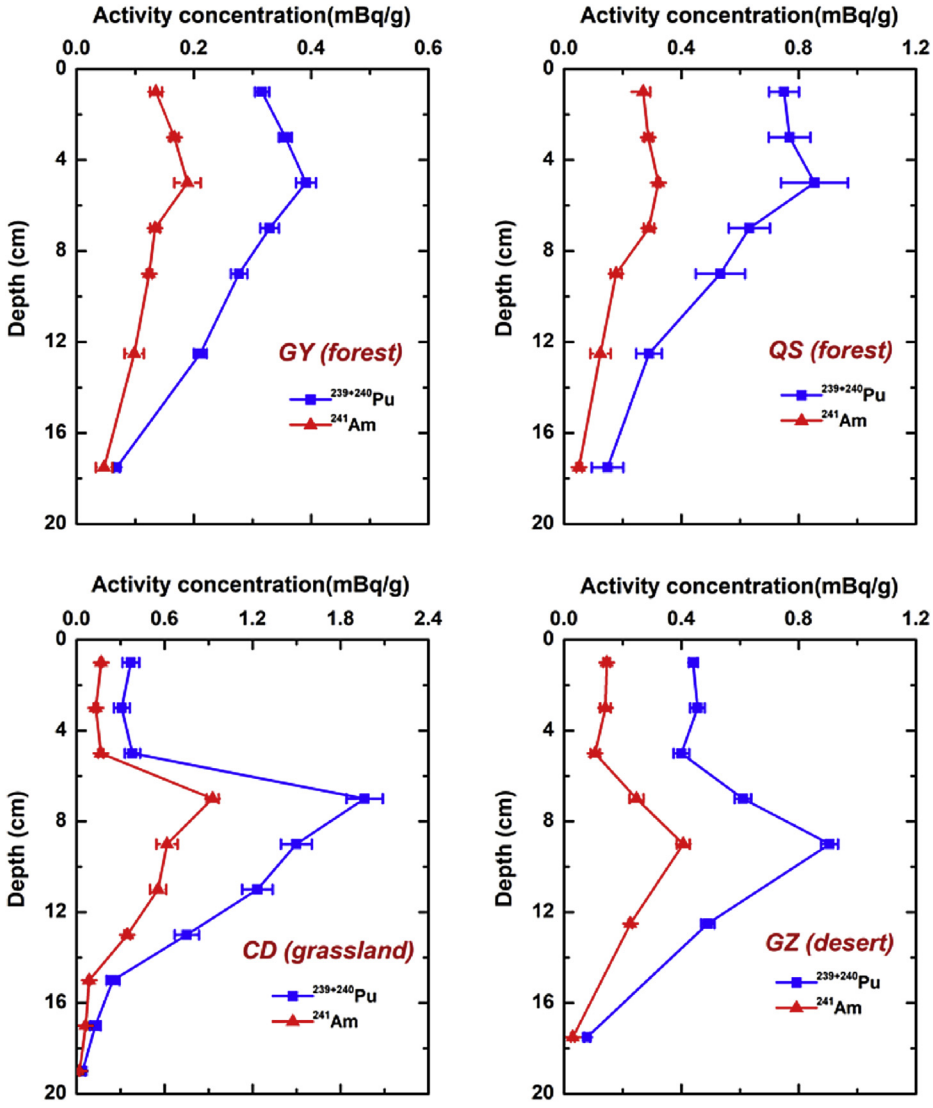

Fig. 1. Vertical distributions of $^{239+240}$Pu and ^{241}Am in four Chinese soil cores (the $^{239+240}$Pu data of GZ and GY cores were cited from Bu et al. (2014, 2015)).

northern China, despite the relatively low precipitation amount (512 mm/y) in that region, the $^{239+240}$Pu inventory (138.37 Bq/m^2) was very high. A similar high $^{239+240}$Pu inventory (106.9 Bq/m^2) in Beijing has also been reported by Dong (2010) where the sampling site was c.a. 350 km from CD site. Besides, the $^{239+240}$Pu inventories in soil cores around Liaodong Bay in northeast China have been determined to be 44.1–86.9 Bq/m^2 by Xu et al. (2013) which was lower than in our CD site, illustrating regional differences of the deposition inventory for these sites, even they are located in the similar latitude region (c.a. 39°N for vs. 42°N) and have similar precipitation (c.a. 700 mm/y vs. 512 mm/y). Therefore, the different depositions of ^{241}Am and $^{239+240}$Pu in these sites should be a result of the large environmental diversities as well as large spatial distances among these sites, which, in turn highlighted the necessity to conduct systematic site-specific studies under different environmental conditions.

3.2. Source identification with characteristic ^{240}Pu/^{239}Pu and ^{241}Am/$^{239+240}$ Pu ratios

The characteristic ^{240}Pu/^{239}Pu atom ratio and the ^{241}Am/$^{239+240}$Pu activity ratio can serve as radioactive fingerprints to identify their sources because these values vary with different manufacturing purposes and generation processes. As seen in Table A.2, the values of the mean ^{240}Pu/^{239}Pu atom ratio for the four sampling sites were from 0.17 to 0.21. Considering the large measurement uncertainties for the bottom layers (where the $^{239+240}$Pu activity concentration is low), the ^{240}Pu/^{239}Pu atom ratio in these cores corresponded to the typical global fallout value 0.180 ± 0.014 (Kelley et al., 1999), indicating that Pu in these areas originated from the atmospheric nuclear weapon tests in the last century. Because ^{241}Am is the decay product of ^{241}Pu, based on the serial decay theory, the ^{241}Am/$^{239+240}$Pu activity ratio derived from global fallout at a specific time t can be deduced by the following equation on account of $A_{239+240Pu(t)} \approx A_{239+240Pu(0)}$ (Zheng et al., 2012).

$$\frac{A_{241Am(t)}}{A_{239+240Pu(t)}} = \frac{A_{241Pu(0)}}{A_{239+240Pu(0)}} \times \frac{\lambda_{241Am}}{(\lambda_{241Am} - \lambda_{241Pu})} \left[e^{(-\lambda_{241Pu}t)} - e^{(-\lambda_{241Am}t)}\right] \quad (2)$$

The ^{241}Pu/$^{239+240}$Pu activity ratio at the peak time of global fallout (representatively, 1963) was reported to be 12.8 (Livingston et al., 1975). Based on these simplifications, the ^{241}Am/$^{239+240}$Pu

activity ratio of the global fallout was calculated to be 0.37 at the time of measurement (January 2018). The mean $^{241}Am/^{239+240}Pu$ activity ratios in the QS (0.38 ± 0.04) and GZ (0.37 ± 0.07) soil cores were very consistent with the theoretical value of global fallout. However, slightly higher $^{241}Am/^{239+240}Pu$ ratios were observed in the CD (0.44 ± 0.05) and GY (0.48 ± 0.09) soil cores. As noted by Yamamoto et al. (1983), there were two main periods for the atmospheric nuclear weapon tests, i.e. 1952–1958 and 1961–1962, and the $^{241}Pu/^{239+240}Pu$ in the first period was higher than in the second period, which could lead to different $^{241}Am/^{239+240}Pu$ activity ratios for specific areas if they received different amount of deposition; besides, after deposition, the environmental behaviors (such as downward migration and soil-to-plant transfer) of Pu and Am were not identical. For these reasons, the typical range of $^{241}Am/^{239+240}Pu$ activity ratio in soil sample for the global fallout showed relatively wider variation compared with the isotopic $^{240}Pu/^{239}Pu$ atom ratio. Therefore, although the $^{241}Am/^{239+240}Pu$ ratios in the CD (0.44 ± 0.05) and GY (0.48 ± 0.09) soils were slightly higher than those at the QS and GZ sites, they were all within the reported ranges of those in the global fallout influenced areas, i.e. 0.43–0.60 in northern China soils reported by Sha et al. (1991a); 1991b), 0.27–0.65 in Korean soils measured by Lee et al. (2013) and 0.33–0.62 in Japanese rice-field soils suggested by Yamamoto et al. (1983) (all values were decay corrected to January 2018). Therefore, both the $^{240}Pu/^{239}Pu$ atom ratio and the $^{241}Am/^{239+240}Pu$ activity ratios have illustrated that the Pu isotopes and ^{241}Am in these soils originated from global fallout.

3.3. Migration behaviors of $^{239+240}Pu$ and ^{241}Am in diverse types of Chinese soils

3.3.1. $^{239+240}Pu$

The $^{239+240}Pu$ activity concentrations in the four soil cores are listed in Table A.2. The mass concentration of $^{239+240}Pu$ should be converted into volumetric concentration (mBq/cm^3) before model fitting by multiplying the mass concentration (mBq/g) with the soil bulk density (g/cm^3) in Table 1. And the fitting time t was set as the time interval of the sampling year to the year 1963. The fitting curves of $^{239+240}Pu$ migration in soils by CDE are illustrated in Fig. 2 and the corresponding migration parameters are presented in Table 2. The Pu data of the GZ site were previously reported by Bu et al. (2015) but its migration has not been discussed. And Bu et al.

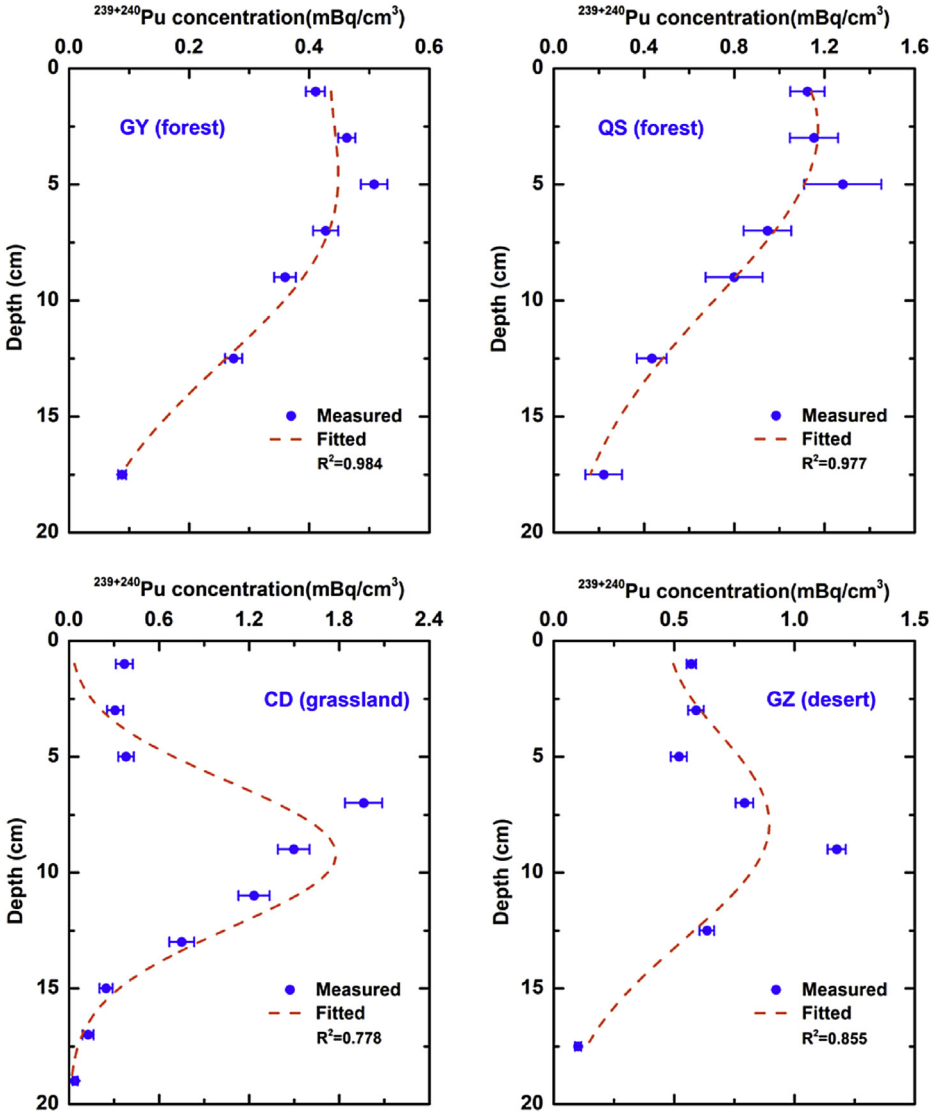

Fig. 2. Fitting curves of the $^{239+240}Pu$ migrations in different soils by the CDE.

Table 2
Migration parameters of Pu and Am in Chinese soils calculated with different models.

Sample ID	Soil type	v_c[a] (cm/y)	D[b] (cm^2/y)	$v_{m(Pu)}$[c] (cm/y)	$v_{m(Pu)}/v_c$	$v_{m(Am)}$[d] (cm/y)
GY	Forest	0.14 ± 0.01	0.39 ± 0.04	0.23 ± 0.08	1.6	0.29 ± 0.10
QS	Forest	0.03 ± 0.01	0.59 ± 0.10	0.21 ± 0.06	7	0.19 ± 0.06
GZ	Desert	0.17 ± 0.01	0.25 ± 0.05	0.23 ± 0.10	1.4	0.27 ± 0.10
CD	Grassland	0.17 ± 0.01	0.10 ± 0.02	0.21 ± 0.11	1.2	0.27 ± 0.12

[a] v_c—apparent convection velocity fitted by CDE.
[b] D—apparent dispersion coefficient fitted by CDE.
[c] $v_{m(Pu)}$—mean migration velocity of Pu in the whole core by the compartment model, the migration velocities in each soil layer are presented in detail in Table A.3.
[d] $\boldsymbol{v_{m(Am)}}$ —mean migration velocity of Am in the whole core by the compartment model, the migration velocities in each soil layer are presented in detail in Table A.3.

(2014) once studied the migration of Pu at the GY site, while only a simplified solution of the CDE was employed although it is an approximation for cases of t ≫ 20 y.

In all the investigated diverse types of soils (forests, grassland and desert), the apparent convection velocities (v_c) of Pu were low, being less than 0.2 cm/y, while the apparent dispersion coefficients (D) ranged from 0.10 cm^2/y to 0.59 cm^2/y. Interestingly, we found that slightly lower v_c occurred for the QS and GY forest soils compared with the grassland and desert soils. Additionally, activity concentration peak positions of $^{239+240}$Pu in the forest soils were shallower (ca. 4–6 cm) (Fig. 1). These results indicated that forest soils retained fallout Pu more efficiently than the grassland and desert soils after half century. Moreover, higher apparent dispersion coefficients of Pu were observed in the two forest soils (0.39 cm^2/y and 0.59 cm^2/y for GY and QS) compared with those in the grassland and desert.

The apparent convection velocities of fallout Pu in the four soil cores corresponded well with those (0.05–0.11 cm/y) in the southwestern Chinese forests reported by Bu et al. (2014) while the apparent dispersion coefficients in our study were slightly higher than the forest soils (0.09 cm^2/y to 0.29 cm^2/y) of Bu et al. (2014). In contrast, the apparent convection velocity and apparent dispersion coefficient of $^{239+240}$Pu in the four Chinese soil cores were comparable to that in the Korean soils where the v_c and D of $^{239+240}$Pu were reported to be 0.09–0.18 cm/y and 0.09–0.36 cm^2/y, respectively (Keum et al., 2013). But they were somewhat lower than those (v_c, 0.259–0.362 cm/y; D, 0.560–0.87 cm^2/y) in the Spanish forest soils calculated by Guillén et al. (2015) where pronounced dispersion processes were characterized.

In order to investigate factors that might influence the migration behavior of Pu, we compared some soil parameters and the migration parameters of the four soil cores. A clear trend was that the in the acidic forest soils (soil pH was 4.8 for GY and 4.4 for QS), the apparent dispersion coefficients were higher than the alkaline soils (soil pH was 8.1 for GZ and 8.7 for CD). Soil pH can influence the speciation of Pu and its partitioning with soil particles. It has been reported that the distribution coefficient (K_d) values for Pu were 30–50% lower for bentonite at pH 3 than they were at the natural pH, suggesting that at higher pH the Pu would likely to be more effectively associated with soil particles (Gillham and Sharma, 1989; Sharma and Oscarson, 1989). Therefore, a possible explanation of the lower apparent dispersion coefficients of Pu in GZ and CD sites might be that under these weak alkaline soil conditions, the hydrolysis of Pu was more significant and thus facilitated the association of Pu with soil particles, finally leading to less pronounced dispersion effect of Pu in these soils. Our guess was similar to that of Sharma and Oscarson (1991) where apparent dispersion coefficient D was greater at lower pH. However, in the regional studies of Guillén et al. (2015) and Bu et al. (2014) that studying the Pu migration in the forest soils, such trend was not observed, probably due to the small pH variation of these soils, i.e. 3.94–4.77 and 5.8–6.6, respectively.

Apart from soil pH, soil organic matter content and the soil texture might affect the behavior of Pu in the soils. For instance, it has been suggested that soil organic matter has high affinity for Pu while soil particles with different sizes present different bounding abilities for Pu, thus having influence on Pu migration in the soil (Lee and Lee, 2000; Xu et al., 2017). However, judged from our present results, the correlation of the migration parameters of Pu with these soil parameters was not illustrated. Nevertheless, taking into account the results of Guillén et al. (2015) and Bu et al. (2014) together with ours, we found that in the two Spanish forest soils that had low organic matter (2.7–3.5%), both the v_c and D of Pu were higher than the ever reported Chinese forest, grassland and desert soils by Bu et al. (2014) and our study with higher organic matters (4.0–12.9%). Since the migration of Pu is a multi-factorial process, further systematic studies at regional scale are suggested to control environmental variables so that to screen dominant factors effecting Pu migration.

Besides, we also calculated the migration velocities of $^{239+240}$Pu in successive vertical soil layers by the compartment model and results are presented in Table A.2. Considering the low activity concentrations and the measurement uncertainties of $^{239+240}$Pu and ^{241}Am in the bottom layers, we did not give the fitted results for these layers in the table as they were unreasonable. In general, the mean migration velocities of $^{239+240}$Pu in the four soil cores were very close to each other, being around 0.2 cm/y. Compared with literature values in other regions that were calculated by the same compartment model as in Table A.4, the migration velocities of Pu in Chinese soils were somewhat lower than in European forest and grassland soils which varied from 0.24 cm/y to c.a. 0.80 cm/y (Bunzl et al., 1992, 1994; 1995; Guillén et al., 2015; Komosa, 1999; Orzeł and Komosa, 2014).

Furthermore, we calculated the ratio of the mean migration velocity $v_{m(\boldsymbol{Pu})}$ obtained by the compartment model to the apparent convection velocity v_c obtained with the CDE in Table 2 so as to roughly evaluate the effectiveness of the compartment model compared with the well-founded CDE. Interestingly, the values of the ratio $v_{m(\boldsymbol{Pu})}/v_c$ of the GZ and CD cores were close to 1 while those for the QS and GY cores were higher. Because the apparent convection velocity of Pu in the grassland and desert (0.17 cm/y at both CD and GZ sites) was larger than the velocities in the forest soils, it suggested that the effects of convection in the grassland and desert soils were more pronounced than the forest soils. Because the compartment model is not a physically based model, it has been demonstrated to be more applicable to the convection-dominated migration processes (Kirchner, 1998). Thus, it is reasonable to expect smaller differences between $v_{m(\boldsymbol{Pu})}$ and v_c in the convection-dominated grassland and desert soils than in the forest soils. And this discrepancy was the most pronounced for the QS forest soil

which was characterized by the highest apparent dispersion coefficient *D*.

3.3.2. ^{241}Am

So far, field data on the migration of ^{241}Am in actual environments are very limited. In China, no related reports have been presented yet. Since there is no analytical solution for the CDE of ^{241}Am, a compromised approach is to fit the measured ^{241}Am data with the compartment model. It should be pointed out that the compartment model is not a strictly "realistic" model and the returned migration velocities can't be used for prediction purposes since it is not based on the fundamental migration processes (Kirchner, 1998). However, it has been recommended for the purpose of comparing the migration behaviors of radionuclides (Bunzl et al., 1992, 1994, 1995; Kirchner, 1998). The fitting results for ^{241}Am were listed in Table A.3. The migration velocities of ^{241}Am in different soil layers varied slightly. On average, the mean migration velocities of ^{241}Am in the two forest soils were 0.19 cm/y (QS) and 0.29 cm/y (GY), while for the grassland and desert soils they were 0.27 cm/y (CD) and 0.27 cm/y (GZ), respectively. In contrast, the migration velocities of ^{241}Am in these Chinese soils were systematically lower than those in the German grassland and forest soils which have been estimated to be approximately 0.62–0.8 cm/y as in Table A.4 by Bunzl et al. (1992, 1994, 1995). Besides the differences of the environmental conditions and soil characteristics, the deviations during model fittings using the compartment model should be another reason for the slightly lower migration velocities of ^{241}Am in these Chinese soils since the calculated values were not strictly physically based. However, we still need to note that these differences were small and the migration velocities of ^{241}Am in all these mentioned regions were in the same order of magnitude (<1 cm/y).

3.4. Comparative migration behaviors of $^{239+240}Pu$ and ^{241}Am

With the lack of analytical solution for the CDE of ^{241}Am, the compartment model provides a compromised choice to study the migration of Pu and Am under these natural field conditions comparatively (Bunzl et al., 1992, 1994, 1995). As shown in Table A.3, regardless of the soil type, in each layer of the four sampling sites, the migration velocities of $^{239+240}$Pu (v_{Pu}) were close to those of ^{241}Am (v_{Am}). Their relationship could be presented by $v_{Am} = 1.11^{*}v_{Pu}$-0.01 ($R^2 = 0.938$) (Fig. A.2). Since the slope of the curve was very close to 1, it suggested the migration behaviors of $^{239+240}$Pu and ^{241}Am in these soils were rather similar after being introduced into the environment for half a century. In the German grassland soils, the migration velocities of $^{239+240}$Pu were almost identical to the migration velocities of ^{241}Am in the corresponding layers (Bunzl et al., 1994). And the ratios v_{Am}/v_{Pu} were also around 1 in the spruce and pine forests (Bunzl et al., 1992, 1995). Thus, similar migration of $^{239+240}$Pu and ^{241}Am in natural field soils was supposed. Among the parameters quantifying the interaction of radionuclides and soil particles, the distribution coefficient (K_d) was thought to be related to the migration of the radionuclides in the soils because K_d is used to quantify the association of radionuclides with soil particles (IAEA, 2010). The geometric mean K_d values of Pu and Am in soils were similar (7.4×10^2 L/kg and 2.6×10^3 L/kg, respectively), indicating they were both particle-reactive. Therefore soils can retard their migration, leading to very slow and similar migration velocities of Pu and Am. Besides, in this study, the ^{241}Am in the profile was produced from ^{241}Pu. Theoretically, for a bulk of ^{241}Pu, before it decays to ^{241}Am, the ^{241}Pu migrates identically to $^{239+240}$Pu; after it decays to ^{241}Am, the produced ^{241}Am would continue migrates concurrently with $^{239+240}$Pu and their migration behaviors were similar. Consequently, it is reasonable to expect similar vertical profiles of the global fallout derived ^{241}Am and $^{239+240}$Pu in undisturbed soil profiles.

In addition, simulation experiments using field-collected soil columns to study the migration of artificially added Pu and Am tracers have also been reported in China. Li et al. (2004a) conducted controlled field experiments to study the migration of ^{237}Np, ^{238}Pu and ^{241}Am in unsaturated Chinese loess under artificial rainfall conditions for 3 years. The migration velocities of ^{238}Pu and ^{241}Am were estimated to be 0.259 cm/y and 0.184 cm/y, respectively. Li et al. (2004b) have also studied the migration of these radionuclides in Chinese aerated zone loess using two soil columns. In the 665 and 1073 day migration experiments, the average migration velocities of ^{238}Pu and ^{241}Am were identical to each other: both were 0.14 cm/y for the 665-day period and 0.09 cm/y for the 1073-day period. Guo et al. (2003) performed a simulation test for radionuclide migration in aquifer soils with an undisturbed soil column. Similar migration behavior of ^{238}Pu and ^{241}Am was observed after a 527.5-day experiment, as both the ^{238}Pu and ^{241}Am activity concentration peaks moved less than 0.2 cm under an pore water velocity of 6.13 cm/d. These results from short-term (a few years) simulation experiments were compatible to our findings that the migrations of both $^{239+240}$Pu and ^{241}Am in soils were rather slow, and similar to each other. Our results not only have enhanced the database of the quantitative migration of $^{239+240}$Pu and ^{241}Am in Chinese soils, but they have also verified that after downward migrating in actual environments for decades, the migration behaviors of $^{239+240}$Pu and ^{241}Am remained similar to each other. These results are useful for a comprehensive understanding of their long-term fates and behaviors in the environment.

4. Conclusions

In this study, we studied the vertical distribution characteristics and migration behaviors of $^{239+240}$Pu and ^{241}Am in diverse Chinese soils collected in two forests, one grassland and one desert. The mean $^{239+240}$Pu and ^{241}Am activity concentrations in these four cores ranged from 0.28 to 0.69 mBq/g and 0.13–0.37 mBq/g, respectively. Judged from both the characteristic ^{240}Pu/^{239}Pu atom ratio and the ^{241}Am/$^{239+240}$Pu activity ratio, we supposed the Pu isotopes and ^{241}Am in these soils originated from the global fallout.

The apparent convection velocity and apparent dispersion coefficient of Pu in these soils were 0.03–0.17 cm/y and 0.10–0.59 cm^2/y, respectively. A trend was found that higher apparent dispersion coefficients were observed for sites with lower soil pH. Focusing on the migrations of $^{239+240}$Pu and ^{241}Am that have been in the realistic environment for decades, we found our results of field study were comparable to the results of short-term (a few years) simulation experiments in China on two points: the migration behaviors of $^{239+240}$Pu and ^{241}Am were similar and their migration were very slow, being less than 0.3 cm/y in diverse types of Chinese soils.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2018.09.021.

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