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First study of ^{237}Np in Chinese soils: Source, distribution and mobility in comparison with plutonium isotopes

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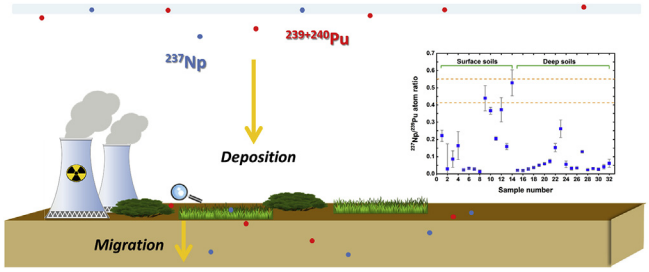
HIGHLIGHTS

- First study of fallout ^{237}Np in soils near two Chinese NPPs was conducted.
- The highest fallout $^{239+240}$Pu concentration in Chinese surface soil was found.
- In the soil core Np showed a "depleted" trend in contrast to Pu over time.
- Apparent dispersion coefficient of Np was higher than Pu in the soil core.
- Vertical distributions of Np and Pu will be more and more even in the future.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the distribution and migration of ^{237}Np and $^{239+240}$Pu in soils in the vicinity (<5 km) of Qinshan and Tianwan Nuclear Power Plants in China were studied, which is the first specific study of global fallout ^{237}Np in Chinese soils. The ^{237}Np and $^{239+240}$Pu concentrations in surface soils showed large spatial inhomogeneity. A remarkable $^{239+240}$Pu concentration (4.783 mBq/g) was observed in a surface soil near Qinshan NPP and stands for the ever reported highest value in the Chinese soils. The inventories of $^{239+240}$Pu in two Qinshan and Tianwan soil cores were estimated to be 128.8 Bq/m^2 and 121.0 Bq/m^2, respectively; while the ^{237}Np inventories were 0.039 Bq/m^2 and 0.035 Bq/m^2 at these sites, respectively. The ^{240}Pu/^{239}Pu atomic ratios in these soils indicated that the global fallout is the main source of Pu in these regions. However, the non-isotopic ^{237}Np/^{239}Pu atomic ratio in environmental soil is not a sensitive indicator for source identification. Furthermore, we conducted pilot study on the migration behaviors of ^{237}Np and $^{239+240}$Pu in soil core at Qinshan site with the Convection-Dispersion Equation (CDE) model. The obtained apparent dispersion coefficients of ^{237}Np (2.82 ± 2.06 cm^2/y) was 5 times higher than that of $^{239+240}$Pu (0.57 ± 0.16 cm^2/y), proving that ^{237}Np has stronger migration ability than Pu isotopes in the Qinshan soil. Finally, we predicted that with the increase of migration time, both ^{237}Np and $^{239+240}$Pu

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concentration in the soil will gradually become more evenly distributed among different soil layers due to the dominant dispersion effects.

1. Introduction

Plutonium (Pu) and neptunium (Np) are anthropogenic radionuclides that have been released into the environment mainly as a result of the global fallout following the atmospheric nuclear weapon tests in the last century. The main Pu isotopes (^{239}Pu and ^{240}Pu) and ^{237}Np have been classified by the IAEA as the most radiotoxic "Group 1" radionuclides (IAEA, 1973). Thus, the presence and behavior of these radionuclides in the environment is of public concern in view of radiation safety and dose assessment (Bunzl et al., 1995a; Muramatsu et al., 2003; Ni et al., 2019a).

The Qinshan nuclear power plant (NPP) and the Tianwan NPP are located in the Zhejiang province and Jiangsu province in China, respectively, both of which are densely populated provinces. In view of environmental radioactivity monitoring, the nuclear power plants are potential sources of radioactive contamination of the environment including Pu isotopes and ^{237}Np. In nuclear reactors, the ^{237}Np is formed by the following pathways (Holm, 1981).

$$^{238}_{92}U(n,2n)^{237}_{92}U \rightarrow ^{237}_{92}U(\beta^-)^{237}_{93}Np \quad (1)$$

$$^{235}_{92}U(n,\gamma)^{236}_{92}U \rightarrow ^{236}_{92}U(n,\gamma)^{237}_{92}U \rightarrow ^{237}_{92}U(\beta^-)^{237}_{93}Np \quad (2)$$

While the ^{239}Pu and ^{240}Pu are present during the operation of reactor not only by the neutron capture of ^{238}U but also due to the direct utilization of MOX fuels that contain Pu in some reactors. Therefore, it is essential to investigate the current presence of Pu isotopes and ^{237}Np in the surrounding environment of these nuclear power plants to establish site-specific baseline database so that any anomalous release and contamination could be correctly screened. Lessons from the FDNPP accident have illustrated the importance of such information on the assessment of the extent of reactor damage and possible environmental impact of the nuclear accident. For example, studies such as capturing the signature of the accidental released Pu, identifying the specific sources of the Pu from the reactors or spent fuel pools and assessing the impact of Pu to the environment have been conducted based on the fruitful knowledge about the pre- and post-accident status on the distribution and characteristics of Pu in the environment (Bu et al., 2014; Ni et al., 2019b; Men et al., 2018; Sakaguchi et al., 2014; Yamamoto et al., 2014; Zheng et al., 2012, 2013). Due to different application purposes and generation procedures, the isotopic ratio ^{240}Pu/^{239}Pu varies, which makes it possible to use this characteristic ratio as a good indicator for source identification to distinguish any newly introduced contaminations. For example, the typical ^{240}Pu/^{239}Pu atomic ratios of the aforementioned global fallout and the Fukushima Daiichi nuclear power plant (FDNPP) accident are 0.180 ± 0.014 and about 0.323–0.330, respectively (Kelley et al., 1999; Zheng et al., 2012). In contrast, the non-isotopic ^{237}Np/^{239}Pu atomic ratio was less discussed in environmental studies although the environmental background of these actinides was both primarily relating to the global fallout. It is informative to investigate the feasibility of using the anthropogenic ^{237}Np/^{239}Pu atomic ratio for source identification in the environmental processes.

Moreover, because the Qinshan NPP is the first nuclear power plant in China that started commercial operation in 1991, the decommissioning of this plant is on the schedule of discussion since it was initially designed to operate for 30 years. Therefore, a comprehensive investigation on the site-specific distribution of Pu isotopes and ^{237}Np in the vicinity of this site is a prerequisite for assessment and prognosis of the radiation conditions before and after the decommissioning. There have been some works referring to the concentration level of Pu and its isotopic composition in the Chinese terrestrial environment (Bu et al., 2015; Dong et al., 2010; Ni et al., 2018; Wu et al., 2010, 2011; Xing et al., 2018; Zheng et al., 2009). However, because the environmental conditions (topography, precipitation, soil type etc.) in China present large diversities among different areas, it is instructive to obtain site-specific studies around the NPPs to gain more accurate and representative information of the distribution characteristic of Pu in specific areas. Besides, the lack of fallout ^{237}Np background baseline in Chinese environment also highlights the need for pioneering studies.

Another issue deserve concern is the migration behaviors of Pu isotopes and ^{237}Np in the soil core since slow migration rates of them can lead to their persistence in the plant-root zones and increase the risks of entering human food chain, while fast migration rates make them more likely to get access to the groundwater (Ni et al., 2018). Since the operation and decommissioning of the nuclear plants are long-term projects, predicting the concentration levels and distribution patterns of radionuclides based on their migration behaviors is useful for future environmental monitoring. For these reasons, it is undoubtedly necessary to investigate the migration behaviors of Pu isotopes and ^{237}Np in the soil core near the NPP.

In this study, the concentration levels of ^{237}Np and Pu isotopes in the surface soils near the Qinshan and Tianwan NPPs were investigated to obtain the site-specific baseline information. Besides, the vertical distribution and migration behavior of these radionuclides in the Qinshan site were studied to provide the first fallout ^{237}Np inventory data in Chinese environment. Based on the modeled migration parameters, we predicted the vertical distribution of Pu and Np at this site in the future centuries.

2. Materials and methods

2.1. Sample collection

The samples were collected around the Qinshan NPP and Tianwan NPP in 2014. Nine surface soil samples and 1 vertical grassland (covered by weeds and shrubs) soil core were collected near the Qinshan NPP. While around the Tianwan NPP 5 surface soils and 1 forest soil core were sampled. The depth intervals of the soil cores were 2 cm for the 0–10 cm soils and 5 cm for the 10–30 cm soils. Each surface sample was made of three sub-sample that collected within approximately 1 m diameter at the corresponding sampling site. The sample information was listed in Table A.1 Sample locations are illustrated in Fig. A.1.

2.2. Determination of ^{237}Np and Pu isotopes

The analysis of ^{237}Np and Pu isotopes in the soil samples was realized by employing the method recently developed by Huang et al. (2019). All the results were given based on dry weight and

the organic matter content of the soil were estimated by loss of ignition under 450 °C. This method utilizes ^{242}Pu as a non-isotopic tracer for simultaneous determination of ^{237}Np and Pu isotopes in soil samples. The final measurement of ^{237}Np and Pu isotopes was conducted with a sector-field (SF) ICP-MS (Element XR, Thermo Fisher Scientific, Bremen, Germany) incorporating a high efficiency sample introduction system (APEX-Q, Elemental Scientific Inc., Omaha, NE, USA) (Zheng, 2015). Details of the analytical procedures were presented in the Appendix. For quality control, deep soils (free from ^{237}Np and Pu isotopes) were spiked with ^{237}Np and ^{239}Pu working solution that has a known amount of these radionuclides. Then the ^{237}Np and ^{239}Pu in the spiked soils were determined to compare with the spiked amount to check the chemical fractionation between Np and Pu (see Table A.2). And a standard reference material NIST 4357 was analyzed for ^{237}Np and Pu isotopes in parallel with our soil samples to check the validity of the method (results were shown in Table A.3).

2.3. Modeling the migration of Pu isotopes and ^{237}Np with Convection-Dispersion Equation (CDE) model

The measured vertical distribution of ^{237}Np and $^{239+240}$Pu in soil profile was fitted with the well-established CDE model. The model equation is based on the convection-dispersion physical processes of the radionuclides in the soil cores and can be written as Eq. (3).

$$\frac{\partial C}{\partial} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - \lambda C \tag{3}$$

Here, C (x,t) is the volumetric concentration (mBq/cm^3) of a radionuclide in the depth x (cm); v (cm/y) is the apparent convection velocity that reflects the convection of the radionuclide with pore water; D (cm^2/y) is the apparent dispersion coefficient which combines both molecular diffusion and hydrodynamic dispersion of the solute into a single constant; and λ (y^{-1}) is the decay constant of the radionuclide.

As has been proved by Bossew and Kirchner (2004), by assuming a pulse-like input J_0 and $C(x,t) = 0$ at the time of $t = 0$ under a half-infinite space-time ($x, t > 0$) boundary condition, the CDE model has an analytical solution as Eq. (4).

$$c(x,t) = J_0 e^{-\lambda t}\left\{\frac{1}{\sqrt{\pi D t}}e^{-(x-vt)^2/4Dt} - \frac{v}{2D}e^{vx/D}erfc\left(\frac{v}{2}\sqrt{\frac{t}{D}} + \frac{x}{2\sqrt{Dt}}\right)\right\} \tag{4}$$

Here, J_0 is the inventories of ^{237}Np or $^{239+240}$Pu (mBq/cm^2) initially deposited in the soil core. The model fitting was realized with the non-linear fitting function of the Origin 8.6 (OriginLab, Northampton, USA). More information about the model application has been introduced in our previous work (Ni et al., 2018).

3. Results and discussion

3.1. Concentration levels of ^{237}Np and $^{239+240}$Pu around Qinshan and Tianwan NPPs

3.1.1. Surface soils

The concentrations of ^{237}Np and Pu isotopes in the surface soils collected around the Qinshan and Tianwan NPPs were listed in Table 1. The ^{237}Np concentration in the soils around Qinshan NPP showed large variation (nearly 100 times) despite the close distances between these sampling locations, ranging from 0.007 mBq/kg to 0.938 mBq/kg. While the ^{237}Np concentrations in the Tianwan surface soils were 0.025–1.277 mBq/kg. The TW-S1 surface soil had the highest ^{237}Np concentration (1.277 mBq/kg) among all the soils in this study. So far, no study aiming at investigating the ^{237}Np distribution in Chinese environment is reported, thus the present data are helpful for the understanding of ^{237}Np level and distribution in Chinese terrestrial environment.

Besides, the $^{239+240}$Pu concentrations in the surface soils near the Qinshan and Tianwan NPPs varied in the ranges of 0.011–4.783 mBq/g and 0.009–0.806 mBq/g, respectively. It is interesting to find that a relatively high $^{239+240}$Pu concentration (4.783 mBq/g) was observed in a surface soil (QS-S7) around Qinshan NPP. This value is significantly higher than those in other nearby (<5 km) surface soils, indicating there is large spatial inhomogeneity of $^{239+240}$Pu concentrations in these surface soils. Studies on the distribution of $^{239+240}$Pu in diverse Chinese terrestrial environment have been continuously conducted by researchers. For example, Xing et al. (2018) reported the $^{239+240}$Pu concentration in surface soils along the eastern coastal areas of China to be from 0.011 to 0.27 mBq/g. Zhang and Hou. (2019) further enlarged the database in these coastal areas by analyzing 71 soil samples, and the determined $^{239+240}$Pu concentrations ranged from 0.002 mBq/g to 0.670 mBq/g. In addition, Bu et al. (2015) systematically investigated the concentration and distribution of $^{239+240}$Pu in the downwind regions of Chinese LopNor nuclear test sites. The $^{239+240}$Pu concentrations in the surface soils in these regions were 0.363–0.927 mBq/g and 0.076–1.988 mBq/g, respectively, even though some of the sampling locations (Jiuquan region) had very high $^{239+240}$Pu inventories (c.a. 400–500 Bq/m^2). Recently, Guo et al. (2019) reviewed the Pu distribution data in Chinese environmental soils from the literature including papers and thesis. They reported the $^{239+240}$Pu concentration in the Chinese surface (≤10 cm) soils were 0.005–1.988 mBq/g (N = 150). Therefore, except the QS-S7 sample, the $^{239+240}$Pu concentration in the surface soils within 5 km of Qinshan and Tianwan NPPs were in the range of the reported concentration levels in the soils in other parts of China. For comparison, the $^{239+240}$Pu concentration (4.783 mBq/g) in QS-S7 sample is the highest value among which ever reported in uncontaminated surface soils in Chinese terrestrial environment and thus further enlarged the database. Interestingly, this value is very close to the highest $^{239+240}$Pu concentration derived from global fallout in Japanese surfaces soils, viz. 4.31 mBq/g in a forest surface soil reported by Muramatsu et al. (2003).

In addition, we analyzed the correlations of $^{239+240}$Pu and ^{237}Np concentrations with the organic matter contents in soils so as to explore possible influence of soil organic matter on the retention of $^{239+240}$Pu and ^{237}Np in soils as in Fig. A.2 a) and b). It is illustrated that after excluding the abnormal QS-S7 sample, the $^{239+240}$Pu concentration in the surface soils positively correlated with the soil organic matter content in both the Qinshan and Tianwan NPP regions. The goodness of fit (R^2) were more than 0.8 for the two sites. These results indicated that the soil organic matters might be effective to retain Pu isotopes in the topsoil. In the study of Zhang and Hou. (2019), they also attributed the higher $^{239+240}$Pu concentration level in the surface soil of 25–40°N than other regions to the relatively more abundant (4–8%) organic matter content in these soils. One possible explanation for this phenomenon is that the soil organic matters especially large molecular weight humic acid can reduce the Pu mobility in soil by forming strong complexes and thus retains it in the surface soils (Bunzl et al., 1995a; Lee and Lee, 2000). Moreover, in the small sampling area, the deposition inventory of Pu was supposed to be relatively even. The higher organic matter content might lead to less weight of surface soil sample per area of land, and consequentially lead to higher concentration of Pu per mass of soil. Similar linear relationships were observed between the ^{237}Np concentration and organic matter content in the surface soils near these two NPP bases (as in Fig. A.2 c) and d)), while the R^2 in this ^{237}Np case were both lower than

Table 1
Results of the ^{237}Np and Pu isotopes in the surface (2 cm) soils around Qinshan and Tianwan NPPs.

Location	Sample ID	OM[a] (%)	^{237}Np concentration (mBq/kg)	$^{239+240}$Pu concentration (mBq/g)	^{237}Np/^{239}Pu atomic ratio	^{240}Pu/^{239}Pu atomic ratio
Qinshan NPP	QS-S1	5.7	0.093 ± 0.012	0.061 ± 0.004	0.221 ± 0.032	0.175 ± 0.027
	QS-S2	7.0	0.007 ± 0.040	0.049 ± 0.013	0.029 ± 0.146	0.191 ± 0.045
	QS-S3	15.8	0.043 ± 0.025	0.076 ± 0.009	0.086 ± 0.048	0.198 ± 0.052
	QS-S4	4.5	0.040 ± 0.020	0.036 ± 0.008	0.164 ± 0.081	0.178 ± 0.081
	QS-S5	31.8	0.257 ± 0.041	1.663 ± 0.049	0.022 ± 0.004	0.171 ± 0.012
	QS-S6	11.0	0.148 ± 0.010	0.677 ± 0.021	0.032 ± 0.003	0.180 ± 0.011
	QS-S7	6.2	0.938 ± 0.130	4.783 ± 0.116	0.028 ± 0.004	0.168 ± 0.009
	QS-S8	5.2	0.010 ± 0.008	0.121 ± 0.007	0.012 ± 0.010	0.165 ± 0.023
	QS-S9	3.4	0.033 ± 0.004	0.011 ± 0.001	0.439 ± 0.073	0.202 ± 0.046
Tianwan NPP	TW-S1	6.3	1.277 ± 0.062	0.510 ± 0.012	0.366 ± 0.021	0.180 ± 0.009
	TW-S2	12.4	1.153 ± 0.053	0.806 ± 0.018	0.205 ± 0.011	0.170 ± 0.008
	TW-S3	2.7	0.025 ± 0.005	0.009 ± 0.001	0.372 ± 0.070	0.183 ± 0.020
	TW-S4	4.5	0.277 ± 0.029	0.250 ± 0.008	0.159 ± 0.017	0.171 ± 0.013
	TW-S5	4.3	0.115 ± 0.015	0.030 ± 0.004	0.529 ± 0.075	0.183 ± 0.021

[a] OM-organic matter content.

those for the $^{239+240}$Pu. Further direct investigation on the association of ^{237}Np and Pu isotopes with soil organic matters (such as fulvic acid and humic acid) is necessary for better verification.

3.1.2. *Vertical distribution of ^{237}Np and Pu isotopes in soil cores*

The vertical distribution of the ^{237}Np and $^{239+240}$Pu concentrations in the Qinshan and Tianwan NPP soil cores were listed in Table A.4 and illustrated in Fig. 1. In the Qinshan soil core, both the ^{237}Np and $^{239+240}$Pu concentration in the soil profile showed a peak in the sub-surface depth. The highest $^{239+240}$Pu concentration in this soil profile is 0.868 mBq/g which presented in the 2–4 cm soil layer; below this depth, the $^{239+240}$Pu in the soil layers decreased monotonically. These vertical distribution characteristics of $^{239+240}$Pu were very similar to those observed in other undisturbed forest, grassland and desert soil cores (Dong et al., 2010; Ni et al., 2018; Xu et al., 2015). In contrast, the ^{237}Np concentrations, within the uncertainties, remained flat in the 0–10 cm depth, while an unconspicuous peak (0.136 mBq/kg) occurred in the 4–6 cm depth. However, in the bottom three layers (15–30 cm), the ^{237}Np concentration seemed increase slightly with increasing depth. For the Tianwan soil core, both the $^{239+240}$Pu and ^{237}Np vertical distribution were more homogeneous compared with the case in the Qinshan soil core. Specifically, the $^{239+240}$Pu concentration in the different soil layers varied in a very narrow range from 0.302 mBq/g to 0.354 mBq/g; while most of the ^{237}Np concentration in this soil profile ranged between 0.051 mBq/kg to 0.122 mBq/kg, except that a peak concentration of 0.276 mBq/kg occurred in the 6–8 cm depth. The reason for the relatively homogeneous distribution of $^{239+240}$Pu and ^{237}Np in the Tianwan soil core was unclear, and we consider a turn-over or disturbance was possible at this site.

The accumulative inventories of ^{237}Np and $^{239+240}$Pu in the Qinshan and Tianwan soil cores can be estimated by Eq. (5).

$$I = \sum_{i=1}^{N} B \times d_i \times C_i \tag{5}$$

where I (Bq/m^2) stands for the accumulative inventory of ^{237}Np or $^{239+240}$Pu; B (g/cm^3) is the soil bulk density; d_i is the depth of each layer and C_i represents the concentration of ^{237}Np or $^{239+240}$Pu in each layer.

According to Eq. (5), the accumulative inventories of ^{237}Np in the Qinshan and Tianwan soil cores were estimated to be 0.039 Bq/m^2 and 0.035 Bq/m^2, respectively. In the 1970 and 1971, the Environmental Measurements Laboratory (EML) of the US Department of Energy (DOE) has collected amounts of soil cores worldwide to study the distribution of global fallout anthropogenic radionuclides. Kelley et al. (1999) measured the ^{237}Np inventories in these

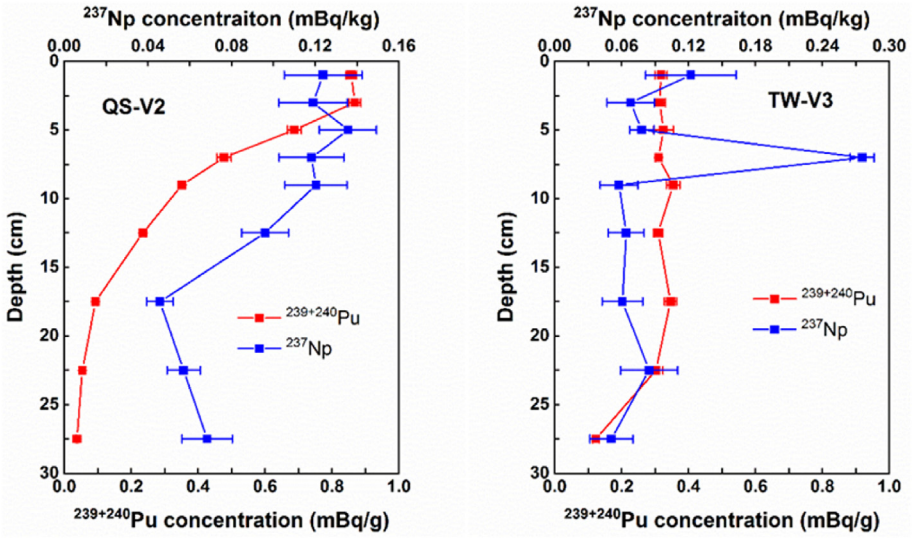

Fig. 1. Vertical distribution of ^{237}Np and $^{239+240}$Pu in Qinshan and Tianwan soil profiles.

soil cores (30 cm depth) by thermal ionization mass spectrometry (TIMS) and using ^{236}Np as yield tracer. For the 12 soil cores in the 30-40°N latitude region, the determined inventories of ^{237}Np ranged from 3.33 Tatoms/m^2 to 31.64 Tatoms/m^2, which corresponded to 0.034 Bq/m^2 to 0.323 Bq/m^2 with an average of 0.205 Bq/m^2 based on $T_{1/2}(^{237}Np) = 2.14 \times 10^6$ y. The ^{237}Np in our Qinshan and Tianwan soil cores were about one tenth of the mean ^{237}Np inventory in the 30-40°N region, and was very close to the lowest value (3.33 Tatoms/m^2, corresponding to 0.034 Bq/m^2) in this latitude band. In addition, Yamamoto et al. (1994) determined the ^{237}Np inventory in paddy field soils collected through 1959–1989 in three Japanese areas (Akita, Niigata and Ishikawa). The ^{237}Np inventories also showed large variation, ranging from 0.038 Bq/m^2 to 0.499 Bq/m^2. Therefore, it was considered that the ^{237}Np inventories in the Qinshan and Tianwan soil cores were close to the lower end of the abovementioned reported inventories in the similar latitude region. These data is the first set of ^{237}Np inventory result in the Chinese terrestrial environment, and facilitates the subsequent enlargement of database in diverse Chinese environments.

For the case of Pu isotopes, the $^{239+240}$Pu in the Qinshan and Tianwan soil cores were estimated to be 128.8 Bq/m^2 and 121.0 Bq/m^2. These inventories were both significantly higher than the reported mean deposition inventory of $^{239+240}$Pu (42 Bq/m^2) in the 30–40°N region (UNSCEAR, 2000). Recently, we have determined the ^{241}Am and $^{239+240}$Pu inventories at another site in the Qinshan NPP (Ni et al., 2018). The $^{239+240}$Pu inventory (139.0 Bq/m^2) was similar to that in our Qinshan soil core (128.8 Bq/m^2) in the present study. These results suggested relatively high deposition density of Pu has occurred in this coastal region and also calls for more detailed investigation of this region in the future.

3.2. Source of ^{237}Np and Pu isotopes in soils

Regarding the sources of ^{237}Np and Pu isotopes presented in these soils, we employed the isotopic ^{240}Pu/^{239}Pu atomic ratio as a characteristic fingerprint for Pu source identification, meanwhile we explored the feasibility to use non-isotopic ^{237}Np/^{239}Pu atomic ratio to identify the source of ^{237}Np. The mean isotopic ^{240}Pu/^{239}Pu atomic ratios in the surface soils around Qinshan and Tianwan NPPs were 0.181 ± 0.012 (0.165–0.202) and 0.178 ± 0.006 (0.170–0.183), respectively. Besides, the mean ^{240}Pu/^{239}Pu atomic ratios in the Qinshan and Tianwan soil cores were also very close to those in the surface soils, being 0.174 ± 0.007 and 0.178 ± 0.008, respectively. The ^{240}Pu/^{239}Pu atomic ratios in these soils were plotted in Fig. A.3. It is clear that the ^{240}Pu/^{239}Pu atomic ratios in these surface and core soils corresponded very well with the characteristic value (0.180 ± 0.014) for the global fallout in the 30-71°N region (Kelley et al., 1999), suggesting that the global fallout is the main source of Pu in the vicinity of Qinshan and Tianwan NPPs.

Compared with the isotopic ^{240}Pu/^{239}Pu atomic ratios, the non-isotopic ^{237}Np/^{239}Pu atomic ratios in the soil sample showed large variations (as in Fig. A.4). In the surface soil around Qinshan NPP, the ^{237}Np/^{239}Pu atomic ratio varied from 0.012 to 0.439 with an average of 0.115 ± 0.134; while in the Tianwan surface soils this ratio ranged between 0.159 and 0.529 and the mean value was 0.326 ± 0.132. The mean ^{237}Np/^{239}Pu atomic ratios in the Qinshan and Tianwan soil cores were 0.078 ± 0.076 and 0.048 ± 0.031, respectively. Kelley et al. (1999) has reported the mean ^{237}Np/^{239}Pu atomic ratio of global fallout in the 30-71°N region was 0.48 ± 0.07 by analysis of soil cores (30 cm) collected worldwide in the 1970 and 1971. The ^{237}Np/^{239}Pu atomic ratios in the 30 cm soil cores in our present study were significantly lower than the mean value in the 30-71°N region soils collected more than 40 years ago reported by Kelley et al. (1999).

However, this does not mean that there must be extraneous contamination apart from the global fallout in the investigated region. In recent studies, Mietelski et al. (2016) reported the first ^{237}Np result along with $^{239+240}$Pu in Poland soils that were collected in 2014. They analyzed the ^{237}Np concentration in five soil columns with a max column depth of 24.5 cm. The ^{237}Np inventories ranged significantly from 10.1 mBq/m^2 to 101 mBq/m^2. They further estimated the ^{237}Np/^{239}Pu atomic ratio in these soil cores was from 0.067 to 0.72, in which some values were also lower than the typical value 0.48 for the global fallout despite that these areas were dominantly influence by the global fallout. The ^{237}Np only produced in the reactor of the NPPs and there did not have any accidents in Qinshan and Tianwan NPPs; besides, both the ^{237}Np inventories and ^{237}Np/^{239}Pu atomic ratios in our study were lower than that in the 1970s' soils (means no observable abnormal Np input); and because the ^{240}Pu/^{239}Pu atomic ratios in the Qinshan and Tianwan region have shown that the global fallout is the dominant source, we reasonably conclude the global fallout is also the dominant source of ^{237}Np in this region.

We also calculated the averaged ^{237}Np/$^{239+240}$Pu activity ratio in the Qinshan and Tianwan soil cores, which resulted to be 0.0005 and 0.0003, respectively. In contrast, Yim et al. (2018) studied the ^{237}Np and $^{239+240}$Pu inventories in 1 m-deep soil cores (collected in 2004 and 2005) in a dead volcanic cracker lake which had received global fallout. They also observed the ^{237}Np/$^{239+240}$Pu activity ratio (1.42×10^{-3}) at that site was lower than other works in the Northern Hemisphere in earlier studies, e.g. 0.0020 in the study of Yamamoto et al. (1994), 0.0032 in the study of Bunzl et al. (1995b) and 0.0031 in the study of Beasley et al. (1998). In summary, both the ^{237}Np/^{239}Pu atomic ratio in our work and the ^{237}Np/$^{239+240}$Pu activity ratios in the recent studies not only had large variations but also were lower than the corresponding ratios of global fallout that was reported decades earlier, and thus showed a "depleted" trend of neptunium compared with plutonium in the soil cores. Therefore, the non-isotopic ^{237}Np/^{239}Pu atomic ratio in soil (especially in single soil layer) is not a sensitive and exclusive indicator for source identification due to the large variation.

The significant variations of the ^{237}Np/^{239}Pu atomic ratio in soil matrix were due to the different environmental behaviors of Np and Pu. In oxidized environment conditions, Np mainly presented in pentavalent state as NpO_2^+, which is relatively soluble in soil pore waters; while for Pu isotopes, it is generally in the tetravalent state and thus became particle-active. And these factors decide the differences in the mobility of Np and Pu (Hursthouse and Baxter, 1991). More specifically, laboratory batch experiments have suggested the migration of Np in loess under artificial rainfall conditions was about 10 times faster than Pu (Li et al., 2004). Moreover, Np in the soil is more available for plant uptake because it has higher soil-to-plant transfer factors (10^{-3} to 10^{-2}) than Pu (10^{-5} to 10^{-4}) (IAEA, 2010). Therefore, there are three possible mechanisms for the low ^{237}Np/^{239}Pu atomic ratios in the soils in this study compared with that (0.48) reported in the 1970s' soils: a) The greater loss of Np from soils by surface runoffs than Pu; b) The more transfer of Np from soil to plants compared with Pu; and c) The migration of Np in the soil is much faster than Pu and some part of ^{237}Np has penetrated to deep soil layers more than 30 cm (meaning those parts were not captured in this study and the obtained ^{237}Np inventories might be the lower limits).

It is difficult to confirm the exact reason for these differences. Among the three possibilities, the loss of Np and Pu and their uptake by plants at this site were impossible to quantify based on the current information (and due to the high organic matter content in these soils, these two pathways for Np are presumably not significant), but trials could be made to quantitatively compare the different downward migration of Np and Pu in the soil core (as

shown in the next section), which would facilitate our understanding of their different environmental mobility.

3.3. Migration of ^{237}Np and Pu isotopes in the Qinshan soil core

The vertical migrations of ^{237}Np and Pu isotopes in the soil were among the most important parts of their environmental behaviors in the soils. It is important to study their downward migration in soils with proper model to acquire quantitative parameters on their migration. Such data are necessary to directly explain the difference in migration behaviors of Np and Pu, and they are also informative for predicting their future distributions in the soils to provide references for long-term monitoring of these radionuclides near the NPP bases.

The CDE model was employed for modeling the downward migration of ^{237}Np and $^{239+240}$Pu in the soil core from the Qinshan sampling site. The Tianwan soil core was not studied because the vertical distributions of ^{237}Np and $^{239+240}$Pu in this soil core were rather homogeneous (Fig. 1) and dissimilar to the distribution characteristics of Pu isotopes in well-preserved soils in the literature. With the CDE model, we calculated the apparent convection velocities (v) and apparent dispersion coefficients (D) for ^{237}Np and $^{239+240}$Pu in the Qinshan soil core, and the results were listed in Table 2. The fitting curve was illustrated in Fig. 2 a).

For $^{239+240}$Pu, the theoretical CDE model fitted perfectly ($R^2 = 0.959$) to the actual vertical distribution of $^{239+240}$Pu in the Qinshan soil core. The apparent convection velocity and apparent dispersion coefficient of $^{239+240}$Pu were calculated to be 0.01 ± 0.02 cm/y and 0.57 ± 0.16 cm^2/y, respectively. These results were very close to the migration parameters (v: 0.03 ± 0.01 cm/y; D: 0.59 ± 0.10 cm^2/y) in a forest soil core which was also collected in the Qinshan region in our recent study (Ni et al., 2018). These results showed that the difference of migration parameters of Pu in forest and grassland types of soils in the Qinshan region was very limited, which was due to the similar soil properties within a small region. Besides, the obtained apparent convection velocity and apparent dispersion coefficient in this soil illustrated that the dispersion process in the Qinshan soil core is prevailing compared to the convection process. This phenomenon is likely to be caused by the acidic soil condition in this region (Ni et al., 2018).

Regarding ^{237}Np in the Qinshan soil core, we conducted pilot study to investigate its migration with the CDE model, which was less studied in the literature partially due to the lack of distribution data. The results of the CDE model fitting for ^{237}Np were listed in Table 2 and the fitting curve was presented in Fig. 2 b). The apparent convection velocity of ^{237}Np was 0.01 ± 0.14 cm/y and the apparent dispersion coefficient of ^{237}Np was 2.82 ± 2.06 cm^2/y in the Qinshan soil core, indicating the migration of ^{237}Np in this soil is also dominated by dispersion process, as that for Pu isotopes. The goodness of fit of the CDE model for ^{237}Np (0.632) was to a mediocre, and was worse than that for $^{239+240}$Pu (0.959). Based on the current fitting results, the apparent dispersion coefficient of ^{237}Np (2.82 ± 2.06 cm^2/y) was about 5 times higher than that for $^{239+240}$Pu (0.57 ± 0.16 cm^2/y), which served as quantitative evidence for the higher mobility of ^{237}Np than Pu isotopes in the soil core and thus could partially explain the large variation of ^{237}Np/^{239}Pu atomic ratios in soil samples. These results also corresponded with that obtained by other field study (Hursthouse and Baxter, 1991) and short-term batch study (Li et al., 2004).

According to the IAEA TRS 472 (2010), the apparent dispersion coefficient of a radionuclide can be calculated by the following Eq. (6).

$$D = \frac{D_{non}}{1 + \frac{\rho}{\varepsilon} K_d} \quad (6)$$

where the D (cm^2/y) represents the apparent dispersion coefficient of a radionuclide showing adsorption to soil particles; D_{non} (cm^2/y) is the dispersion coefficient of a non-sorbing trace substance; ε represents the total porosity of the soil; ρ (g/cm^3) is the bulk density of the soil and K_d (L/kg) stands for the distribution coefficient of the radionuclide. As recommended by the IAEA (2010), the soil-solution distribution coefficient (K_d) of Np (3.5×10^1 L/kg) is generally about one order of magnitude lower than that of Pu (7.4×10^2 L/kg) for various types of soils. Because ^{237}Np has lower K_d than the Pu isotopes, the apparent dispersion coefficient of ^{237}Np is expected to be higher than that of the $^{239+240}$Pu in the same soil core. Therefore, the fitting results of ^{237}Np and $^{239+240}$Pu in the Qinshan soil core with CDE should be reasonable.

By applying these migration parameters, we predicted the future vertical distribution of ^{237}Np and $^{239+240}$Pu in the soil at the Qinshan site. This prediction was based on the assumption that the soil remains undisturbed and there is no significant change on soil characteristics in the simulated timespan. The simulated vertical distributions of $^{239+240}$Pu after 100 y, 200 y and 500 y since the deposition time mark (1963) were presented in Fig. 2 a). With the increasing of migration time, the distribution of $^{239+240}$Pu in the soil core will become more and more even due to the dominant dispersion processes. For example, in the medium term (t = 200 y, namely 2163), although the surface several layers still have slightly higher $^{239+240}$Pu concentration compared with the bottom layers, the $^{239+240}$Pu concentration in the whole soil core will be lower than 0.6 mBq/cm^3. Similar to the case of $^{239+240}$Pu, the simulated future vertical distribution of ^{237}Np in the Qinshan soil core (Fig. 2 b)) also showed a gradually homogeneous trend over time. After 500 y time of migration since 1963, the ^{237}Np concentration in every layer of the 30 cm soil core would be near 0.00005 mBq/cm^3. The whole 30 cm soil core could become almost evenly distributed at that time.

4. Conclusions

In this study, the distribution of ^{237}Np and $^{239+240}$Pu in the surface and core soils in the vicinity of Chinese Qinshan and Tianwan NPPs was investigated, which is the first specific study of global fallout ^{237}Np in Chinese soils. The ^{237}Np concentrations in surface soils around Qinshan and Tianwan NPPs were 0.007–0.938 mBq/kg and 0.025–1.277 mBq/kg, respectively. While the $^{239+240}$Pu concentration in these surface soils were 0.011–4.783 mBq/g and 0.009–0.806 mBq/g, respectively. The inventories of ^{237}Np in the Qinshan and Tianwan soil cores were estimated to be 0.039 Bq/m^2 and 0.035 Bq/m^2, while the $^{239+240}$Pu inventories in these two soil

Table 2
The apparent convection velocity (v) and apparent dispersion coefficient (D) for ^{237}Np and $^{239+240}$Pu in the soil cores in Qinshan region by CDE model.

	Soil type	V (cm/y)	D (cm^2/y)	Goodness of fit (R^2)	Reference
$^{239+240}$Pu	Grassland soil	0.01 ± 0.02	0.57 ± 0.16	0.959	This study
^{237}Np	Grassland soil	0.01 ± 0.14	2.82 ± 2.06	0.632	This study
$^{239+240}$Pu	Forest soil	0.03 ± 0.01	0.59 ± 0.10	0.977	Ni et al. (2018)

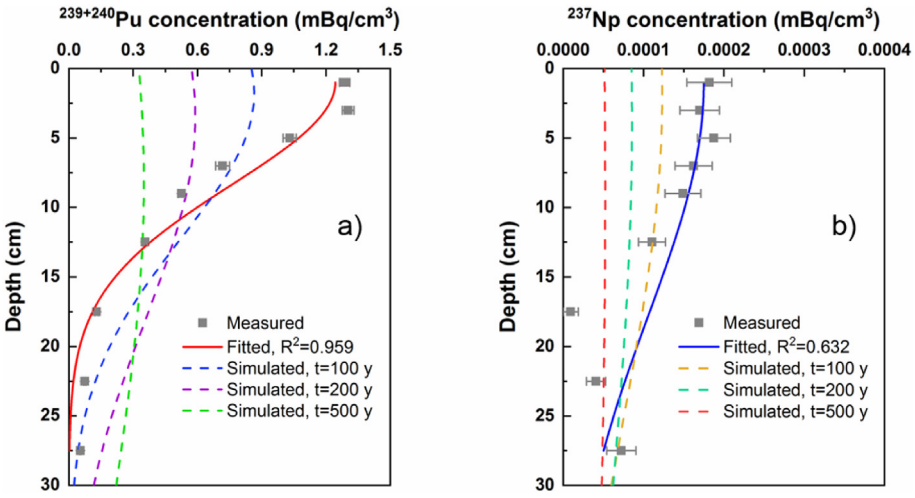

Fig. 2. Fitting and simulation curves for ^{237}Np and $^{239+240}$Pu concentrations in Qinshan soil profile with CDE model.

cores were 128.8 Bq/m^2 and 121.0 Bq/m^2, respectively. The ^{240}Pu/^{239}Pu atomic ratio in these samples illustrated that the global fallout is the main source of Pu in these regions. However, the non-isotopic ^{237}Np/^{239}Pu atomic ratio in environmental soil is not sensitive for source identification. CDE model fitting results suggested the apparent dispersion coefficients of ^{237}Np (2.82 ± 2.06 cm^2/y) was 5 times higher than that of $^{239+240}$Pu (0.57 ± 0.16 cm^2/y), and thus proved that ^{237}Np has stronger migration ability than Pu isotopes in the Qinshan soil core. Based on model simulation we predict that with the increasing of migration time, both the $^{239+240}$Pu and ^{237}Np concentration in the soil core layers will become more evenly distributed.

Declaration of competing interest

None.

CRediT authorship contribution statement

Youyi Ni: Conceptualization, Investigation, Methodology, Writing - original draft, Writing - review & editing. **Qiuju Guo:** Conceptualization, Resources, Writing - review & editing, Funding acquisition. **Zhaoya Huang:** Methodology, Validation, Writing - review & editing. **Jian Zheng:** Conceptualization, Investigation, Methodology, Resources, Writing - review & editing, Funding acquisition. **Sixuan Li:** Resources, Writing - review & editing. **Wenna Huang:** Resources, Writing - review & editing. **Wenting Bu:** Resources, Writing - review & editing.

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Appendix A. Supplementary data

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