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Concentration and characterization of plutonium in soils of Hubei in central China

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ABSTRACT

To study the Pu concentration and isotope ratio distributions present in China, the $^{239+240}$Pu total activities and ^{240}Pu/^{239}Pu atom ratios in core soil samples from Hubei Province in central China were investigated using Accelerator Mass Spectrometry (AMS). The activities ranged from 0.019 to 0.502 mBq g^{-1} and the $^{239+240}$Pu inventories of 45 and ~55 Bq m^{-2} agree well with that expected from global fallout. The ^{240}Pu/^{239}Pu atom ratios in the soil ranged from 0.172 to 0.220. The ratios are similar to typical global fallout values. Hence, any close-in fallout contribution from the Chinese nuclear weapons tests, mainly conducted in the 1970s, must have either been negligible or had a similar ^{240}Pu/^{239}Pu ratio to that of global fallout. The top 10 cm layer of the soil contributes ~90% of the total inventory and the maximum concentrations appeared in the 2–4 cm or 4–6 cm layers. It is suggested that climatic conditions and organic content are the two main factors that affect the vertical migration of plutonium in soil.

1. Introduction

The testing of nuclear weapons in the atmosphere, which took place between 1945 and 1980, involved unrestrained releases of radioactive materials directly to the environment and caused the largest collective dose thus far from man-made sources of radiation. Plutonium, used or produced in the nuclear weapons, was distributed globally as a result of the tests. There have also been releases of Pu to the environment from nuclear reprocessing facilities, and from satellite and reactor accidents. In total, over 500 atmospheric nuclear tests were carried out around the world since 1945 (UNSCEAR, 2000), and it is estimated that between 3 and 6 tonnes of Pu isotopes have subsequently entered the environment (Harley, 1980).

The isotopic signature of the various sources of the Pu depends on the production process. Therefore, it offers a reliable method for distinguishing weapons-grade Pu from global fallout. Compared with the global fallout ratio (^{240}Pu/^{239}Pu = 0.18, Buesseler, 1997), weapons-grade Pu is characterized by a low ^{240}Pu isotope content, with ^{240}Pu/^{239}Pu atom ratios typically ≤0.05 (Harley, 1980; Cooper et al., 2000).

China's nuclear tests were conducted much later than those of the US and the former USSR. Following the end of the Nuclear Test Moratorium in 1963, China began tests at Lop Nor, Xingjian Province. During the period 1964 to 1996, 45 tests took place, including 22 atmospheric tests. Test debris was distributed over the local surface and was also injected into the stratosphere.

In the past 40 years data on the Pu distribution across many countries has been collected and published. However, data on the regional distribution of Pu in Chinese soil is scarce and, when available, limited: Zhu et al. (2002) used the ^{137}Cs concentration and the global fallout $^{239+240}$Pu/^{137}Cs ratio (0.02) to estimate the $^{239+240}$Pu concentration; Plutonium in the areas surrounding Lake Bosten were reported by Lin et al. (1992), using alpha spectrometry (which does not readily provide a ^{240}Pu/^{239}Pu atom ratio); Sediment cores from the East China Sea, which was proposed to be influenced by the Pacific Proving Ground (PPG) source Pu, are presented by Wang and Yamada (2005); and cores from Hongfeng Lake, in Southwest China, which appear to contain global fallout and hence can be used as a monitor, have been reported by Zheng et al. (2008). Recently, Zheng et al. (2009) studied the concentration and the characterization of Pu in loess from Gansu Province, Northwest China. To our knowledge no systematic study has been published in the literature on the distribution of Pu isotopes, especially in central China.

The work reported here forms part of a larger project investigating the Pu distribution across much of mainland China. This paper presents the fallout Pu concentrations in soil samples

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collected from Hubei Province, in central China. As such, they provide baseline results which can be used to assess samples collected from areas closer to the Chinese nuclear test site.

2. Materials and methods

2.1. Sample collection

The locations of the sampling sites are shown in Fig. 1. Hubei Province, located in the Middle-Lower Yangtze plains, has a typical subtropical humid monsoon climate. The annual precipitation ranges from 800 to 1000 mm and annual mean temperature is 15–17 °C. Hubei Province is well suited to study and characterize the Pu distribution in Chinese soils as significant parts of it remain undeveloped, and hence largely undisturbed from a sampling viewpoint. Furthermore, the area is relatively central to China, and Pu levels and distributions are therefore perhaps more representative of the average for much of the Chinese terrestrial environment.

As part of the larger project, soil core samples, up to a depth of 25 cm, were collected in September 2007 from a rainforest of Gulongzhong (GLZ) National Park in Xiangfan City, and from woodland in DaKou (DK) National Park in Jinmen City. The sites are about 2500 km southeast of the Lop Nor nuclear test area. The soil core samples mainly consisted of humus and a yellow/brown soil. The major mineral components of this yellow/brown soil are typically basalt, gneiss and granite. The sampling sites appeared to be undisturbed.

2.2. Chemical procedures and measurement

Chemical separation of Pu was based on the method described by Everett et al. (2008). Briefly, approximately 4 g of each sample was accurately weighted and 4 pg of ^{242}Pu from a standard solution added as a tracer. The sample was then calcined at 450 °C for 8 h to remove organic materials. The sample was then leached with 8 M HNO_3, and the Pu was separated out using an anion-exchange column. Iron nitrate was then added and the samples ashed at 800 °C to convert the matrix to Fe_2O_3 suitable for AMS measurement. The Fe_2O_3 samples were then mixed with Ag powder, pressed into Al holders and mounted in a sample wheel for AMS measurement. All sample preparation was carried out in a HEPA-filtered analytical laboratory in the Department of Nuclear Physics at the Australian National University.

AMS measurements were carried out using the 14UD tandem accelerator at the Australian National University. Detailed descriptions of the analytical technique have been published in Fifield (2008). PuO^- ions were accelerated to ~4 MeV and then dissociated in a differentially pumped gas stripper. The Pu ions exit the stripper in a distribution of positively charged states, which are then subjected to a further stage of acceleration. After acceleration Pu^{5+} ions, of energy ~24 MeV, were selected by the energy analysing magnet and directed into the detector, which is a propane-filled ionisation chamber. Transmission from the ion source to the detector was ~3%. The isotopes ^{242}Pu, ^{240}Pu and ^{239}Pu were counted in a slow cycling sequence for measurement periods of 1, 3 and 2 min, respectively. At least 2 cycles of the sequence were made for each sample.

The high sensitivity of AMS enabled measurement of ^{239}Pu and ^{240}Pu in all samples. The absolute detection limit was based on the blank samples, and for a 4 g soil sample was ~0.02 μBq ^{239}Pu g^{-1} and ~0.08 μBq ^{240}Pu g^{-1}. Activities of $^{239+240}$Pu were calculated from the measured ^{239}Pu/^{242}Pu and ^{240}Pu/^{242}Pu atom ratios and the known amount of ^{242}Pu tracer added to each sample.

3. Results and discussion

3.1. $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu atom ratio

The results for the $^{239+240}$Pu activities and ^{240}Pu/^{239}Pu atom ratios from the two sites are summarized in Table 1. The $^{239+240}$Pu surface activity at site DK was 0.36 mBq g^{-1} (0–2 cm layer) and reached a maximum at 2–4 cm with an activity of 0.42 mBq g^{-1}. Below this the concentration decreases nearly exponentially with increasing depth. At the GLZ site the top (0–2 cm layer) activity is similar, at 0.38 mBq g^{-1}, the maximum activity, however, appeared in the 4–6 cm layer (0.51 mBq g^{-1}).

In contrast to the variations in the $^{239+240}$Pu activities, the ^{240}Pu/^{239}Pu atom ratios are relatively constant from the top (0–2 cm) layer to the deepest layer (25 cm) at both sites, and ranged from 0.17 to 0.21 with a weighted mean of 0.186 ± 0.008 at site DK, and 0.186–0.219 with a weighted mean of 0.198 ± 0.006 at site GLZ. The atom ratio results below 10 cm at DK and GLZ have been omitted from the above averages owing to the much lower level of plutonium in these samples. It is suggested that the main source of Pu in the soil of Hubei Province is global fallout as the results compare well with the global fallout ^{240}Pu/^{239}Pu atom ratio of 0.18 Considering that the sampling sites are more than 2500 km from the Lop Nor nuclear test area, the deposition of close-in fallout Pu derived from the small-scale Chinese tests should be negligible.

3.2. Inventory and depth distribution of $^{239+240}$Pu

The total inventory of $^{239+240}$Pu is 44.9 Bq m^{-2} for the core soil (0–25 cm) from site DK. The activity depth profile at the site shows little Pu below 25 cm. This agrees well with the integrated atmospheric fallout of 42 Bq m^{-2} for 30–40°N (UNSCEAR, 2000). The total inventory of $^{239+240}$Pu at GLZ is higher and exceeds 54.6 Bq m^{-2}. Zheng et al. (2009) analysed core soil samples from Gansu Province and gave a calculated $^{239+240}$Pu inventory of

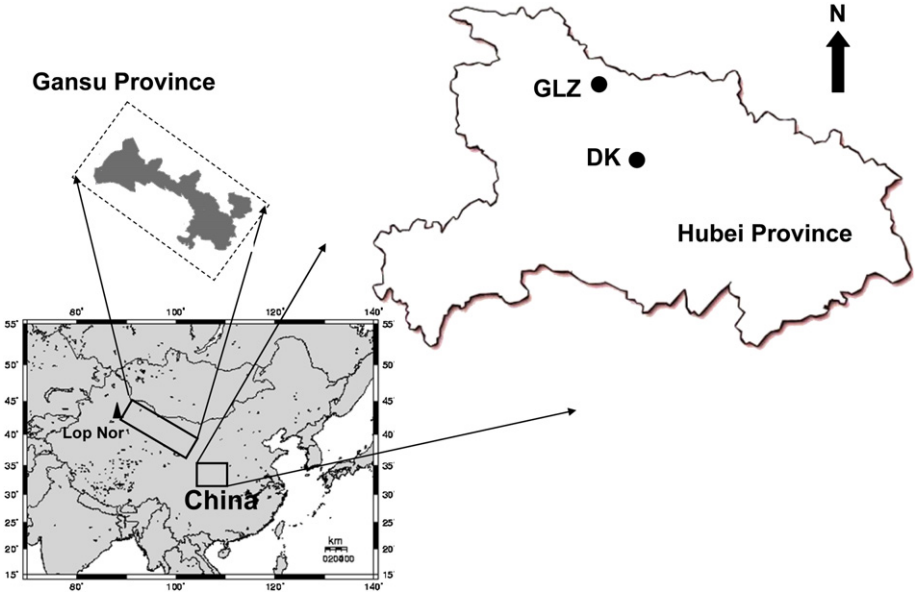

Fig. 1. Map showing the soil sampling sites in Hubei Province, central China.

Table 1
The $^{239+240}$Pu and ^{240}Pu/^{239}Pu atom ratio in core soil samples (0-25 cm) collected from DK (a) and GLZ (b), Hubei Province. Error bars correspond to one standard deviation and comprise contributions from counting statistics and reproducibility of the AMS system (~5%), with the contributions added in quadrature.

Depth (cm)	(a)		(b)	
	$^{239+240}$Pu (mBq.g^{-1})	^{240}Pu/^{239}Pu (atom ratio)	$^{239+240}$Pu (mBq.g^{-1})	^{240}Pu/^{239}Pu (atom ratio)
0-2	0.358±0.021	0.172±0.020	0.380±0.016	0.208±0.014
2-4	0.418±0.019	0.170±0.013	0.410±0.017	0.220±0.014
4-6	0.296±0.014	0.211±0.017	0.502±0.020	0.191±0.012
6-8	0.191±0.011	0.195±0.023	0.432±0.017	0.195±0.012
8-10	0.095±0.007	0.210±0.028	0.409±0.016	0.186±0.011
10-15	0.035±0.003	0.135±0.027	n.a.	n.a.
15-20	0.019±0.003	0.273±0.080	n.a.	n.a.
20-25	0.008±0.002	0.101±0.069	0.005±0.001	0.561±0.216

* n.a.: Not analyzed

32.4 Bq m^{-2} (0–23 cm). Compared with the annual precipitation at DK (~1000 mm y^{-1}), rainfall at Gansu is quite low at 235–328 mm y^{-1}. The inventory at Gansu Province would therefore be expected to be lower, as a result of relatively lower wet deposition.

The vertical profiles are plotted in Fig. 2. As can be seen from Fig. 2(a), the contribution from the first 10 cm layer to total inventory is more than 95% (53% from the first 6 cm). The vertical profiles are similar to those observed in Japan by Mahara and Miyahara (1984) and in Korea by Lee et al. (1996), which are in the same latitudinal band at 30–40°N. These authors found that the Pu accumulated in the first 10 cm layer was more than 85% of the total, which is similar to, but lower than our results.

Lee et al. (1996) obtained two types of depth profile for their Korean soils: in some undisturbed soils the concentration of Pu decreased nearly exponentially with increasing depth, while in other soils the maximum $^{239+240}$Pu concentration was not found on the surface, but rather at 2–4 cm depth. Similarly, the DK profile shows a maximum $^{239+240}$Pu concentration at 2–4 cm, with the concentration decreasing exponentially below this depth. This can be explained by downward percolation through the soil with rainwater and/or by the loss of fine particle fractions that absorb relatively higher amounts of these nuclides and/or by dilution of the upper layer(s) with humic material deposited in the post atmospheric testing era. It is noteworthy that the organic matter distributions for soil from site DK are very similar to those recorded by Lee et al. (1996) for soil from Jungsun, South Korea. Plutonium is known to form complexes with humic substances (Lee et al., 1997), and at both sites the organic matter content for the 0–2 cm depth increment is 11%. Similarly, in the 2–20 cm region the average organic matter content is ~7% at both sites. Furthermore, annual precipitation at the two sites is also similar at ~1000 mm y^{-1} (DK) and 1090–1360 mm y^{-1} (Jungsun). The two sites show similar $^{239+240}$Pu depth profiles and, from a general point of view, are consistent with the Pu distribution and its mobility being determined mostly by the climatic conditions and/or by the proportion of organic matter present in the soil.

However, it should be noted that the Korean soil core profile was reported in 1990s. More than 10 years have now passed and there should be continuous downward migration of Pu. The profile of the DK soil core is similar to the Korean core and shows no obvious additional downward migration of Pu. This could be explained as follows: by considering soil of similar organic matter content, Mahara and Miyahara (1984) estimated the migration rate of Pu in soil in the Nishiyama area, Nagasaki, Japan. These authors found a migration rate of 1.25 mm y^{-1} over 36 years. Annual precipitation in Japan (~1750 mm y^{-1}) however, is more than that at site DK (~1000 mm y^{-1}) which would imply that migration is more likely to be faster. Therefore, the migration rate at site DK is most likely less than 1.25 mm y^{-1} and hence any additional migration over the last 10 years at site DK is probably ≤1 cm. This could only be observed in a more detailed experiment (by reducing the size of the sampling increments for example).

The profile of the GLZ site shown in Fig. 2(b), however, shows the maximum in the concentration to be at 4–6 cm, which indicates the downward migration of Pu is faster than that at site DK. Considering the similar precipitation of the sites the difference could be related to different organic matter contents. The organic matter content of samples at site GLZ was 13.8% for the 0–2 cm

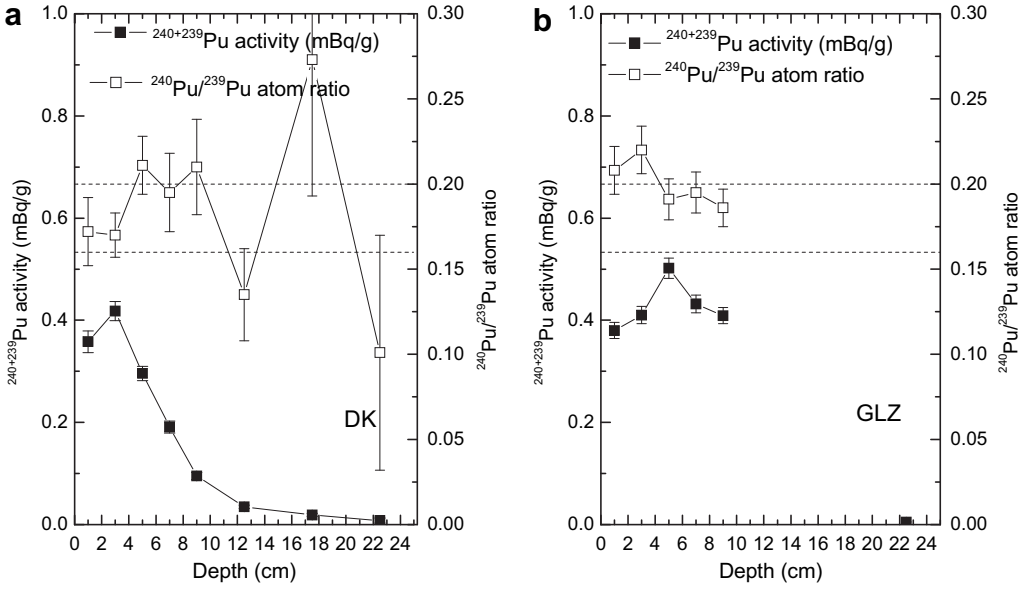

Fig. 2. Vertical profile of $^{239+240}$Pu activity and ^{240}Pu/^{239}Pu ratio in the core soil collected from DK and GLZ, Hubei Province. The dashed lines indicated the ^{240}Pu/^{239}Pu atom ratio range of global fallout (0.18 ± 0.02, Harley, 1980; Kelley et al., 1999; Buesseler, 1997).

layer, an average 4% from 2 to 10 cm and 1.7% for the bottom 20–25 cm layer. This is about half that of the DK profile (except 0–2 cm). In principle, $^{239+240}$Pu binds more strongly with organic material (Lee et al., 1997), which would imply the downward migration rate at site GLZ should be higher. Further study is needed to verify the downward migration mechanics, and the distribution of Pu amongst the various particle size fractions as a function of depth could provide useful information in this regard.

4. Conclusion

The $^{239+240}$Pu activity of the core samples from Hubei Province ranged from 0.019 to 0.502 mBq g^{-1} and the inventories of $^{239+240}$Pu were 44.9 Bq m^{-2} and ~55 Bq m^{-2} which are close to that expected from global fallout (42 Bq m^{-2}). The ^{240}Pu/^{239}Pu ratios are also similar to that of the typical global fallout Pu. The contribution of first 10 cm layer to the total inventory was ~90%, and the maximum in the Pu concentration appeared in the 2–4 cm or 4–6 cm layers. The effects of precipitation and organic content on the vertical migration of Pu have been studied but need further investigation.

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