J Radioanal Nucl Chem (2015) 303:1513–1518
DOI 10.1007/s10967-014-3530-2

Plutonium isotopes and ^{241}Am in surface sediments off the coast of the Japanese islands before and soon after the Fukushima Dai-ichi nuclear power plant accident

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Received: 23 August 2014 / Published online: 9 September 2014

Abstract The concentrations of $^{239+240}$Pu, ^{241}Pu and ^{241}Am in the sediments at the coast of Japanese islands from 2008 to 2011 varied widely from one sampling site to another and were generally lower in sandy sediments at shallower sites, and higher in clayey sediments at deeper sites. In contrast, there seemed to be no temporal variation in the concentrations during the survey period. The ^{241}Am/$^{239+240}$Pu activity ratio was relatively higher than the global fallout presumably owing to the ingrowth of ^{241}Am from the ancestor, ^{241}Pu originating mainly from the hydrogen bomb explosion tests in the Marshall Islands in the 1950s.

Keywords Pu isotopes · ^{241}Am · Sediment · Fukushima Dai-ichi nuclear power plant accident

Introduction

As a result of the Fukushima Dai-ichi Nuclear Power Plant (FDNPP) accident, a large amount of ^{131}I, ^{134}Cs, ^{137}Cs and other radionuclides have been released into the environment. Especially for the waters, Tsumune et al. [1] estimated the total amount of ^{137}Cs activity directly released into the sea was estimated to be 3.5 ± 0.7 PBq by the end of May 2011. A comprehensive survey project was initiated immediately after the accident to clarify the distribution of highly volatile radionuclides [2, 3]. However, scientific information on the Pu isotopes and ^{241}Am is limited both in the number of samples and on the extent of the survey, if any [4–6] in comparison with that obtained by the intensive surveys on the volatile fission and activation products. Thus, efforts toward actinide elements derived from the accident in the marine environment have not yet been sufficient to evaluate their impacts on a nationwide scale.

We have been engaged in a monitoring survey since 2008 to determine the levels of Pu isotopes and ^{241}Am in the sediments of the coastal sea areas near nuclear power plants all over Japan. This paper represents the results of this nationwide survey, which provides information on the variations of Pu isotopes and ^{241}Am in the sediments during the period from 2008 to 2011. Emphasis was placed on clarifying what was the extent of the impacts of the FDNPP accident on the levels of actinides on a nationwide scale.

Experimental

Bottom sediment samples were collected at 15 sites in the waters off the nuclear power stations (Fig. 1) once a year in May–July from 2008 to 2011 using a box-type sampler, which took sediments from the ocean floor with a conventional method [2, 7]. For the annual monitoring survey, the upper 3 cm layer samples of the sediments in the sampler were taken for analysis that the same as usual [2,

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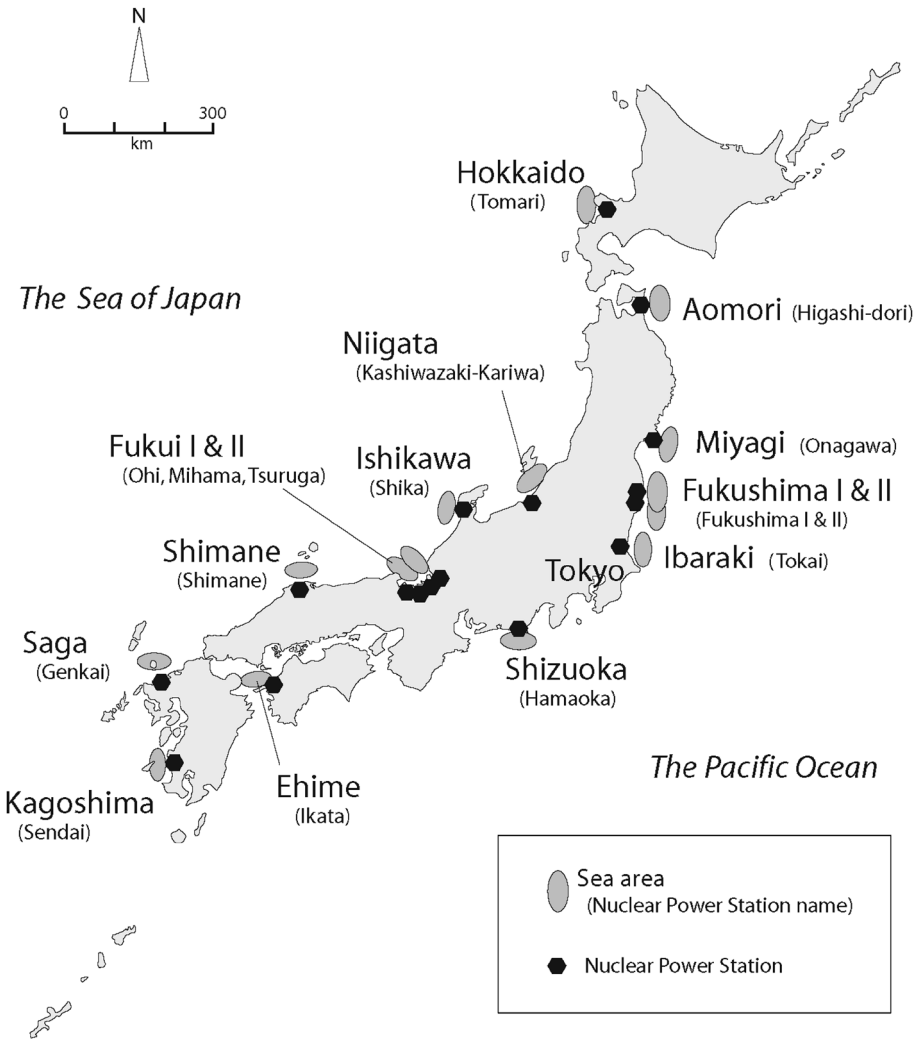

Fig. 1 Sampling sea areas (totally 15 areas) set up off the nuclear power stations in Japan

7]. The sediments were dried at 105 °C, passed through a sieve (<2 mm mesh), and then pulverized again to a homogeneous powder in a tabletop grinder. Particle size distribution of the sediments was observed by a laser diffraction particle size analyzer when necessary.

Plutonium in the sediments were extracted in HNO_3 and several drops of H_2O_2 with a known amount of ^{242}Pu tracer. The Pu in the leachate was separated by co-precipitation with $Fe(OH)_3$. The Pu was further purified by passing through an anion exchange column and then electrodeposited on a stainless steel disk. Alpha spectrometry was used to measure $^{239+240}Pu$ radioactivity on the disk. After measuring $^{239+240}Pu$ radioactivity, the Pu on the disk was leached by immersion in mixture of HF/HNO_3 for a few minutes. The isotopes of Pu were purified by repeating the anion exchange resin procedure. A sector field ICP-MS (ELEMENT 2) was used to measure the $^{240}Pu/^{239}Pu$ atom ratio. Details of the operating conditions have been described elsewhere [7].

Another aliquot of sediments was used to measure ^{241}Pu and ^{241}Am through the same procedure as mentioned above after an addition of a known amount of ^{242}Pu and ^{243}Am tracers. The leachate was concentrated by evaporation. After adding 8 M $HNO_3/NaNO_2$ solution to the condensate, the solution was heated to adjust the Pu valence to the IV state. Pu was then separated from Am by using an anion exchange column. The ^{241}Pu activity was measured by a liquid scintillation counter for 500 min and ^{241}Pu activity was decay-corrected to the sampling date. The Am was further purified using co-precipitation and an anion exchange step. The purified Am was electrodeposited on a stainless steel disk. Alpha spectrometry was used to measure ^{241}Am radioactivity.

Results and discussion

Levels of Pu isotopes and ^{241}Am before the FDNPP accident

Analytical results of the sediments prior to the accident are summarized in Table 1 with information relevant to the

sampling sites. The concentration of $^{239+240}$Pu widely varied from one site to another within the range from 0.37 to 3.5 Bq/kg-dry, which was comparable to those reported previously [6]. Although surveying there only for a short period, the temporal variations of $^{239+240}$Pu concentration at each sampling site were not so great as the spatial variation from the 3 years variation of $^{239+240}$Pu concentration at each site. The ^{240}Pu/^{239}Pu atom ratio ranged from 0.212 to 0.270, which was higher than the global fallout Pu(0.178) as shown in land-source Pu [8] and comparable to the reported values [6, 7, 9]. It was likely that the ^{240}Pu/^{239}Pu atom ratio was nearly constant at each site during the period of the survey, that it remained at a level specific to the site, and that it clearly depended on the depth (or apparent density and particle size distribution); namely there were higher ^{240}Pu/^{239}Pu atom ratios at shallower sites (e.g. Shizuoka, Saga and Kagoshima) and lower ratios at deeper sites (e.g. Hokkaido, Aomori and Niigata), and vice versa for $^{239+240}$Pu concentrations. The depth dependence of the ^{240}Pu/^{239}Pu atom ratio had been also observed in previous survey carried out in the coastal sea off Aomori and Miyagi Prefectures, although what caused the depth dependence and the convergence on a given value still remained unknown [7].

The concentrations of both ^{241}Pu and ^{241}Am widely varied from one sampling site to another within the respective ranges from 0.87 to 3.9 Bq/kg-dry and from 0.22 to 2.1 Bq/kg-dry. The lowest values were observed in sandy (the percentage contribution of coarse, medium and fine sands was larger than 70 % to the total weight of a sediment sample) sediments from the shallower sites in Ishikawa and Saga Prefectures for ^{241}Pu and ^{241}Am, whereas the highest values were observed in clayey (the percentage contribution of silt and clay was larger than 70 %) sediments from the deeper site in Aomori. Generally, the levels of ^{241}Pu and ^{241}Am concentrations were similar to those of the $^{239+240}$Pu concentrations in sediments.

After the FDNPP accident

Analytical results of the sediments collected after the accident are summarized in Table 2. The locations of sampling sites in Table 2 were the same as those in Table 1 except for the site in Shizuoka, which was moved 20 km west of the site before the accident.

The $^{239+240}$Pu concentrations in April–June 2011 after the accident ranged from 0.42 to 3.7 Bq/kg-dry, which was corresponding to the typical background levels shown above. The highest concentration of 3.7 Bq/kg-dry was found in the clayey sediments from Aomori and the lowest of 0.42 Bq/kg-dry in the sandy sediments from Ehime. The ^{240}Pu/^{239}Pu atom ratio was nearly constant (ca. 0.24), ranging from 0.218 to 0.267 with the average value of 0.240 ± 0.014, which comparable to the pre-accident values shown above. The ^{240}Pu/^{239}Pu atom ratio decreased with increasing depth of the site and seemed to converge on the value of 0.22. The Pu found in the sediments of the coastal sea area of the Japanese islands is a mixture of Pu from global fallout deposition and Pu from the nuclear weapons testing conducted at the Pacific Proving Ground (PPG) in the Marshall Islands; the latter has a higher ^{240}Pu/^{239}Pu atom ratio of 0.33–0.36 and this Pu was transported mainly by the Kuroshio Current [6]. It is well known that heavier Pu isotopes become more abundant with increased burn-up of the nuclear fuels, and the ^{240}Pu/^{239}Pu atom ratio can be regarded as a good indicator to identify the source of Pu contamination. The ^{240}Pu/^{239}Pu atom ratio would have been altered if an appreciable amounts of Pu isotopes from the accident were added to pre-existing ones. The ^{240}Pu/^{239}Pu atom ratio found in the sediments in the present study, however, had no significant differences between the pre-accident and the post-accident ones.

The Pu isotope, ^{241}Pu, which had been released from the atmospheric nuclear weapons tests mainly conducted in the 1950s–1960s was detected in some samples having relatively high $^{239+240}$Pu concentration (ca. > 0.7 Bq/kg-dry). The ^{241}Pu concentrations ranging from 0.63 to 3.9 Bq/kg-dry after the accident would correspond to the background level in the sediment samples in the coast of the Japanese islands before the FDNPP accident. The ^{241}Pu/$^{239+240}$Pu activity ratio in the sediments varied among the sites and ranged from 0.75 to 1.2 although the sediment samples were collected in the same time period. Zheng et al. [5, 10] estimated that the ^{241}Pu/$^{239+240}$Pu activity ratio derived from the FDNPP accident was 107.8 on the 15th of March 2011 and that was higher than in the Chernobyl accident (83 on the 1st of May 1986). They also mentioned that the relatively higher ^{241}Pu/$^{239+240}$Pu activity ratio resulted from damage to the Unit 3 reactor which had a mixed oxide fuel containing both enriched U and Pu (about 6 % Pu). By comparing the FDNPP accident and the Chernobyl accident values, it could be concluded that there was no additional ^{241}Pu input to the sediments on the occasion of the accident judging from the ^{241}Pu/$^{239+240}$Pu activity ratio found in the global fallout (1.2 in March 2011) [5, 10].

The ^{241}Am concentration ranged from 0.22 to 2.1 Bq/kg-dry and there were also regional differences as seen in the $^{239+240}$Pu concentration. The ^{241}Am/$^{239+240}$Pu activity ratio was nearly constant (ca. 0.56 ± 0.07) except at Shizuoka. The half-life of ^{241}Am is much longer than its ancestor nuclide ^{241}Pu and therefore its activity increases as time passes, namely the ^{241}Pu/$^{239+240}$Pu activity ratio decreases and as a result, the ^{241}Am/$^{239+240}$Pu activity ratio increases exponentially [5]. In 1976, Krey et al. [8]

Table 1 Summary of $^{239+240}$Pu, ^{241}Pu and ^{241}Am concentration and ^{240}Pu/^{239}Pu atom ratio in the surface sediments (0–3 cm) of the coast of the Japanese islands. (Before the FDNPP accident)

Sampling site	Position of the site[a]		Depth (m)[b]	May–July, 2008				May–July, 2009		May–July, 2010	
	N	E		$^{239+240}$Pu (Bq/kg-dry)	^{240}Pu/^{239}Pu atom ratio	^{241}Pu[c] (Bq/kg-dry)	^{241}Am (Bq/kg-dry)	$^{239+240}$Pu (Bq/kg-dry)	^{240}Pu/^{239}Pu atom ratio	$^{239+240}$Pu (Bq/kg- dry)	^{240}Pu/^{239}Pu atom ratio
Hokkaido	43° 05′	140° 16′	415	2.5 ± 0.1	0.228 ± 0.008	2.1 ± 0.2	1.0 ± 0.05	2.3 ± 0.1	0.227 ± 0.007	2.4 ± 0.1	0.226 ± 0.002
Aomori	41° 13′	141° 40′	665	3.5 ± 0.1	0.222 ± 0.001	3.9 ± 0.2	2.1 ± 0.08	3.3 ± 0.1	0.223 ± 0.003	3.1 ± 0.1	0.223 ± 0.002
Miyagi	38° 25′	141° 45′	161	0.70 ± 0.04	0.236 ± 0.003	0.98 ± 0.21	0.36 ± 0.027	0.68 ± 0.04	0.232 ± 0.007	0.62 ± 0.037	0.235 ± 0.004
Fukushima I	37° 35′	141° 25′	133	0.70 ± 0.04	0.240 ± 0.003	–[d]	0.39 ± 0.023	0.76 ± 0.04	0.239 ± 0.004	0.83 ± 0.044	0.240 ± 0.002
Fukushima II	37° 12′	141° 20′	141	1.0 ± 0.05	0.243 ± 0.009	0.99 ± 0.20	0.56 ± 0.029	0.71 ± 0.04	0.244 ± 0.006	0.68 ± 0.038	0.244 ± 0.002
Ibaraki	36° 25′	140° 51′	119	1.1 ± 0.1	0.248 ± 0.003	1.2 ± 0.2	0.52 ± 0.028	0.93 ± 0.05	0.247 ± 0.003	0.84 ± 0.042	0.249 ± 0.003
Shizuoka	34° 31′	138° 15′	75	0.59 ± 0.03	0.253 ± 0.003	–	0.41 ± 0.024	0.63 ± 0.04	0.261 ± 0.005	0.55 ± 0.032	0.261 ± 0.002
Niigata	37° 50′	138° 35′	498	2.2 ± 0.1	0.212 ± 0.003	2.5 ± 0.2	1.4 ± 0.06	2.2 ± 0.1	0.218 ± 0.004	2.1 ± 0.1	0.219 ± 0.002
Ishikawa	37° 08′	136° 26′	190	0.90 ± 0.04	0.234 ± 0.003	0.87 ± 0.19	0.36 ± 0.021	0.93 ± 0.05	0.233 ± 0.005	0.94 ± 0.045	0.235 ± 0.004
Fukui I	35° 57′	135° 50′	259	2.6 ± 0.1	0.228 ± 0.003	2.9 ± 0.2	1.3 ± 0.06	2.6 ± 0.1	0.228 ± 0.003	2.8 ± 0.1	0.231 ± 0.002
Fukui II	35° 50′	135° 35′	202	2.3 ± 0.1	0.233 ± 0.001	–	0.98 ± 0.044	2.2 ± 0.1	0.238 ± 0.006	2.1 ± 0.1	0.238 ± 0.003
Shimane	35° 41′	133° 04′	82	0.44 ± 0.02	0.255 ± 0.002	ND[e]	0.23 ± 0.017	0.50 ± 0.03	0.248 ± 0.009	0.37 ± 0.023	0.254 ± 0.012
Ehime	33° 38′	132° 17′	60	0.41 ± 0.02	0.251 ± 0.010	–	0.24 ± 0.020	0.49 ± 0.03	0.256 ± 0.004	0.44 ± 0.027	0.255 ± 0.004
Saga	33° 37′	129° 53′	53	0.43 ± 0.03	0.265 ± 0.009	–	0.22 ± 0.018	0.43 ± 0.03	0.263 ± 0.026	0.46 ± 0.027	0.270 ± 0.010
Kagoshima	31° 45′	130° 01′	83	0.70 ± 0.04	0.267 ± 0.003	0.89 ± 0.21	0.35 ± 0.023	0.73 ± 0.04	0.268 ± 0.004	0.71 ± 0.040	0.269 ± 0.004

[a] Presented by the World Geodetic System 84 (WGS85)

[b] Water depth at the site for reference (2008)

[c] The ^{241}Pu radioactivity was decay-corrected to the sampling date

[d] – not determined

[e] *ND* not detected

Table 2 Analytical results of $^{239+240}$Pu, ^{241}Pu and ^{241}Am concentration and ^{240}Pu/^{239}Pu atom ratio in the surface sediments (0–3 cm) of the coast of the Japanese islands. (Immediately after the FDNPP accident)

Sea area	Sampling date	Depth (m)	Apparent density (g/cm^3)	$^{239+240}$Pu (Bq/kg-dry)[a]	^{241}Pu (Bq/kg-dry)[a, b]	^{241}Am (Bq/kg-dry)[a]	^{240}P u/^{239}Pu atom ratio[c]	^{241}Pu/$^{239+240}$Pu activity ratio	^{241}Am/$^{239+240}$Pu activity ratio
Hokkaido	2011. 5.25	411	1.27	2.3 ± 0.09	2.1 ± 0.18	1.1 ± 0.03	0.229 ± 0.003	0.91 ± 0.09	0.48 ± 0.02
Aomori	2011. 5.23	669	1.29	3.7 ± 0.15	3.9 ± 0.19	2.1 ± 0.05	0.222 ± 0.002	1.1 ± 0.1	0.57 ± 0.03
Miyagi	2011. 5.11	165	1.71	0.59 ± 0.032	ND[d]	0.33 ± 0.021	0.234 ± 0.007	–[e]	0.56 ± 0.05
Fukushima I	2011. 6. 2	131	1.82	0.53 ± 0.027	ND	0.33 ± 0.014	0.239 ± 0.002	–	0.62 ± 0.04
Fukushima II	2011. 6. 3	140	1.73	0.83 ± 0.039	ND	0.49 ± 0.018	0.244 ± 0.008	–	0.59 ± 0.04
Ibaraki	2011. 5.10	120	1.69	0.88 ± 0.043	0.66 ± 0.17	0.44 ± 0.02	0.249 ± 0.009	0.75 ± 0.20	0.50 ± 0.03
Shizuoka*	2011. 5. 9	579	1.51	1.7 ± 0.07	1.8 ± 0.18	1.8 ± 0.06	0.248 ± 0.004	1.1 ± 0.1	1.1 ± 0.1
Niigata	2011. 5.22	496	1.13	1.9 ± 0.08	2.2 ± 0.19	1.4 ± 0.04	0.218 ± 0.002	1.2 ± 0.1	0.74 ± 0.04
Ishikawa	2011. 5.15	190	1.55	0.85 ± 0.04	0.75 ± 0.17	0.43 ± 0.016	0.233 ± 0.002	0.88 ± 0.20	0.51 ± 0.03
Fukui I	2011. 5.19	259	1.21	2.7 ± 0.11	2.6 ± 0.19	1.7 ± 0.05	0.227 ± 0.002	0.96 ± 0.08	0.63 ± 0.03
Fukui II	2011. 5.18	202	1.27	2.2 ± 0.08	2.2 ± 0.19	1.1 ± 0.03	0.235 ± 0.002	1.0 ± 0.1	0.50 ± 0.02
Shimane	2011. 5.12	80	1.73	0.52 ± 0.028	ND	0.26 ± 0.014	0.248 ± 0.007	–	0.50 ± 0.04
Ehime	2011. 4.30	62	1.61	0.42 ± 0.024	ND	0.26 ± 0.015	0.253 ± 0.003	–	0.62 ± 0.05
Saga	2011. 5. 3	55	1.65	0.43 ± 0.025	ND	0.22 ± 0.011	0.267 ± 0.006	–	0.51 ± 0.04
Kagoshima	2011. 5. 2	86	1.60	0.76 ± 0.039	0.63 ± 0.18	0.42 ± 0.027	0.263 ± 0.005	0.83 ± 0.24	0.55 ± 0.05

* The site (34°31′ N, 137°59′ E) is different from the site which located about 20 km north of the site in Table 1

[a] The error shows counting error

[b] Decay-corrected to the sampling date

[c] The error shows one standard deviation for three times acquisition replicates

[d] *ND* not detected

[e] – not determined

estimated that the $^{241}Am/^{239+240}Pu$ activity ratio will increase and reach a peak value of 0.42 in the year 2037. In 1990, Yamamoto et al. [11] concluded that the $^{241}Am/^{239+240}Pu$ activity ratio of global fallout had increases and will reach a maximum value of 0.41 in the year 2030. By using the FDNPP-derived $^{241}Pu/^{239+240}Pu$ activity ratio of 107.8, Zheng et al. [5, 10] estimated that the $^{241}Am/^{239+240}Pu$ activity ratio would increase quickly, surpass the value of 1 in the year 2018, and reach the maximum value of 3.18 in 2081 followed by a gradual decrease. As can be seen in Table 2 the $^{241}Am/^{239+240}Pu$ activity ratio (ca. 0.62 ± 0.04 and 0.59 ± 0.04) in the sediments off Fukushima Prefecture was higher than expected value for the global fallout that was expected to reach the maximum value of 0.36 in 2042 [5, 11, 12], and the PPG (27 in 1952–1954 [10, 13]), presumably resulting from the composition of Pu isotopes of different origins. It is difficult to quantify the contribution of each origin to the isotopic composition of Pu based on the concentrations of Pu isotopes even if it is taken into account that the ingrowth of ^{241}Am as a result of the decay of ^{241}Pu from the PPG could raise the $^{241}Am/^{239+240}Pu$ activity ratio.

Conclusions

A radioactivity monitoring survey particularly for actinides in sediments in the coastal seas around the Japanese islands has been done since 2008. The concentrations of $^{239+240}Pu$, ^{241}Pu and ^{241}Am were in the surface sediments were within the range of 0.42–3.7, 0.63–3.9 and 0.22–2.1 Bq/kg-dry, respectively, soon after the FDNPP accident, which corresponded to the background levels. The highest concentration was found in clayey sediments at deeper sites, while the lowest concentration was in sandy sediments at shallower sites. The $^{240}Pu/^{239}Pu$ atom ratios ranged from 0.212 to 0.267 and were relatively higher than the global fallout Pu(0.178). The $^{241}Pu/^{239+240}Pu$ and $^{241}Am/^{239+240}Pu$ activity ratios were nearly identical among the sites around the Japanese islands. In addition, there were significant differences neither in the concentrations of Pu isotopes and ^{241}Am nor in the activity ratios, $^{241}Pu/^{239+240}Pu$ and $^{241}Am/^{239+240}Pu$ between the situations before and soon after the Fukushima accident.

Acknowledgments We sincerely thank our colleagues at the Marine Ecology Research Institute for their help with sampling and for logistical support for the survey. We also acknowledge the crews of the R/Vs and technicians who assisted greatly with onboard fieldwork. This research was conducted under contract with the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

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