Fate of Plutonium at a Former Nuclear Testing Site in Australia

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Originally published:

August 2016

Environmental Science & Technology 50(2016)17, 9098-9104

DOI: https://doi.org/10.1021/acs.est.6b01864

The fate of plutonium released from nuclear weapons tests

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ABSTRACT

A series of the British nuclear tests conducted on mainland Australia between 1953 and 1963 dispersed long-lived radioactivity and nuclear weapons debris, the legacy of which is a long-lasting source of radioactive contamination to the surrounding biosphere. A reliable assessment of the environmental impact of these types of radioactive contaminants and their implications for human health requires an understanding of their physical/chemical characteristics on the molecular scale. However, mainly due to the technical difficulties associated with the chemical diversity of environmental samples, these contaminants have never been characterized adequately. In this study, we identify the chemical form of plutonium (Pu), one of the most problematic radionuclides dispersed, in the local soils collected from one of the former weapons test sites, Maralinga. We herein reveal the first direct spectroscopic evidence that the Pu legacy exists as particulates of fine Pu oxyhydroxide compounds, a very concentrated and low-soluble form of Pu, which will serve as ongoing radioactive sources far into the future. We also verify that the Pu in the particles originated in the so-called "*Minor trials*" that involved the dispersal of weapon components by highly explosive chemicals, not in the nuclear explosion tests called "*Major trials*". The obtained results help us to understand the chemical transformation of the original Pu materials dispersed in the semi-arid environment more than fifty years ago. These findings further highlight the importance of the comprehensive physical/chemical characterization of Pu contaminants for reliable environmental- and radiotoxicological assessment, which is significantly influenced by the original physical/chemical form of the contaminant.

INTRODUCTION

From 1953 to 1963, the British nuclear weapons testing programme conducted twelve nuclear detonation tests ("*Major trials*") and more than five hundred non-nuclear explosion tests ("*Minor trials*") in the Great Victoria Desert, South Australia (Fig. 1-(a)).[1-2] These tests caused radioactive contamination with nuclear weapons debris in the test sites and their surroundings. After completion of official remediation operations in 2002, radionuclides including plutonium (Pu) remain in activity concentrations that represent extensive environmental contamination with deposition plumes extending for tens of kilometers outside the clean-up area.[3] A reliable assessment of the environmental fate of the remaining radioactive contamination and its potential implication for human health requires detailed knowledge of their chemistry in the relevant environment; little of which is understood, mainly due to technical difficulties associated with the analysis of environmental samples with low activity concentrations and complex matrices.[4] Here we report on a unique analytical approach combining radiochemical analysis with synchrotron-based X-ray fluorescence microscopy (XFM) to comprehensively characterize the Pu contaminants resulting from the nuclear weapons tests in Maralinga, Australia (Fig. 1-(a)).

Figure 1

EXPERIMENTAL

Isolation of Pu-containing particle. An initial screening of the soil samples to search for the remaining Pu contaminants was performed by measuring ^{241}Am activity in the soils with gamma spectrometry. The presence of ^{241}Am is largely the result of in-growth following neutron-capture

and beta decay reactions from the parent ^{239}Pu. As a result, the activity concentrations of ^{241}Am are proportional to those of ^{239}Pu (^{239}Pu/^{241}Am ratios of 3.4 mean, 0.5 standard deviation) as measured in the soils of the NW plume. This ratio can vary from plume to plume depending on the composition of the original tested material.[3, 5] Among the collected fifty soil samples, one soil sample containing the highest ^{241}Am activity concentration of 1.3 kBq/kg was selected for further treatment to isolate Pu contaminants. The selected soil sample was then passed through a 125 μm sieve to remove large sand particles and debris. Ten grams of the sieved sample was then dispersed in 30 ml of lithium heteropolytungstate (LST) heavy liquid (D = 2.9 g/ml) for density separation. The sample was centrifuged for 5 minutes at 2,000 rpm and the bottom sediments containing heavy particles were collected. The centrifugation-sediment collection process was repeated to ensure that the supernatant did not contain heavy particles. The resultant sediments and supernatant were analysed by gamma spectrometry, which confirmed that the collected sediments (0.32 g) held at least one particle showing high ^{241}Am activity. The collected sediments were further dropped onto the top of a new LST solution to allow the sediments to stratify only with gentle agitation. Four subsamples were obtained from this stratification process, only the third densest of which contained almost all of the original ^{241}Am activity. This subsample containing ^{241}Am was further split within small droplets of aqueous solution, measured by gamma spectrometry, and repeated until a single particle (approximately 150-200 μm in diameter) was identified as a Pu-rich particle. The isolated particle was found to be highly friable, and, when placed between thin glass slides, easily fragmented into smaller pieces (Fig. S1 in SI). All fragments exhibited ^{241}Am activity approximately proportional to their respective masses, and thus indicated the presence of Pu in similar per mass activity concentrations, consistent with their origin from a single particle. The isolation process of the Pu particle

involved only physical sieving and use of LST solution and deionised water. As the Pu particle was in a stable chemical form when collected, contact with LST solution (*i.e.*, Li^+ and polytungstate anions) and deionised water would not cause any further change in the chemical composition of the particle. Additionally, the employed LST solution was almost saturated (D = 2.9 g/ml, where 2.95 g/ml is the maximum density at 298 K). Hence, the dissolution of other co-existing minerals/soils during the LST density separation process and subsequent sorption of the dissolved mineral/soil components on the particle surface is very unlikely. Therefore, the isolated particle should reflect the current chemical form of Pu at the Taranaki test site.

X-ray fluorescence microscopy and X-ray absorption spectroscopy. Fragmented pieces of the isolated particle (five pieces in total) were mounted on a Kapton tape and covered with Ultralene X-ray fluorescence film (4 μm in thickness) for transport to the Australian Synchrotron. Figure S3 in the SI shows optical microscope images of the fragments employed for XFM experiments. XFM measurements were performed at the XFM beamline[6] of the Australian Synchrotron under ring operating conditions of 3 GeV and 200 mA with top-up mode. Scanning X-ray fluorescence (XRF) mapping[7] and X-ray absorption near edge structure (XANES) mapping in fluorescence mode[8] at the Pu L_{III}-edge (18.057 keV) were carried out under ambient conditions with a Kirkpatrick-Baez (KB) mirror pair and the Maia detector.[9] XANES mapping produces a XANES spectrum from the X-ray fluorescence signal at selected pixels in a stack of images collected as a function of incident beam energy. For XANES mapping measurements, X-ray absorption spectra of Zr foil was acquired simultaneously in transmission mode for energy calibration (at the Zr K-edge, defined as 17999.35 eV at the 1st inflection point) upstream of the KB mirrors. The acquired data were treated and analysed with the software GeoPIXE (Version 6.6)[10] and WinXAS (Version 3.2).[11] The acquired X-ray fluorescence data were deconvoluted based on the

106 Dynamic Analysis matrix transform method[12] to obtain elemental concentration maps as a
107 function of incident beam energy. Pu L_{III}-edge X-ray absorption spectra were produced based on
108 the total counts of the observed Pu L fluorescence lines (Fig. S4 in SI) on a selected region
109 covering the whole area of each sample fragment. The data treatment for the extended X-ray
110 absorption fine structure (EXAFS) region was performed with the software WinXAS[11] according
111 to the standard procedure.[13] Theoretical phase and amplitude for EXAFS theoretical fitting were
112 calculated by a program code FEFF8.20[14] based on the crystal structures of metallic Pu and
113 PuO_2.[15]

114

115 **RESULTS AND DISCUSSION**

116 **History of plutonium legacy at the Taranaki test site, Maralinga.** Soil samples were collected
117 in September 2010 at a distance of 2.0 km from the former firing pad of the Taranaki site, one of
118 the test sites at Maralinga (Figs. 1-(b) and -(c)). At the Taranaki site, in addition to one "*Major*
119 *trial*" in 1957, twelve "*Minor trials*" were conducted between 1960 and 1963.[2] These tests
120 dispersed more than 22 kg of Pu, resulting in four contaminated plumes radiating from the test
121 site.[2] The sampling point is situated within the northwest (NW) plume (Fig. 1-(c)), where the
122 main radioactive contamination was caused by the Minor trial "*Vixen B2* – Round 5" undertaken
123 in May 1961.[2, 16] The "*Vixen B*" trials involved the burning and detonation of nuclear weapon
124 components with high-explosives to ascertain the potential for accidents to trigger nuclear
125 explosions.[2] A "limited number of fissions" during testing were reported,[2] suggesting that the
126 original Pu materials employed for the trials was presumably metallic Pu with fissile ^{239,241}Pu

isotopes. Hence, the Pu in the soils gathered at the Taranaki site could have originated from nuclear detonation, limited nuclear fission, or non-nuclear high-explosive dispersal events.

Identification of plutonium legacy. The collected soil samples were first analyzed by gamma spectrometry and autoradiography to find Pu debris in the soil mixture. After a repetitive process including sample fractionation, gamma spectrometry and autoradiography, a single particle with approximately 40 Bq-^{241}Am, a major daughter nuclide of ^{239}Pu, was successfully isolated. The gamma-ray spectrum of this particle indicated the absence of fission products (FPs) (Fig. S2 in SI), suggesting that the Pu in the isolated particle did not undergo fission reactions and, hence, it is likely to originate in "*Minor trials*", not from "*Major trials*".

Because of the physical/chemical complexity and diversity, the chemical analysis of environmental samples is always a challenging task.[4] Synchrotron-based XFM is an emerging and powerful tool to comprehensively characterize not only environmental samples[17] but also biological and geological samples,[18] providing the information on elemental distribution, oxidation states and local structural arrangement of the target atoms in a non-destructive manner. Shown in the upper-left of Fig. 2 is an optical microscope image of one fragment of the isolated Pu particle. The X-ray fluorescence spectrum of this fragment was found to be primarily composed of Ca K-, Fe K-, Pb L-, U L- and Pu L-lines (Fig. S4 in SI), suggesting the dominant presence of these elements in the fragment. No major FPs of Pu isotopes (e.g., noble metals or lanthanides) were detected, being consistent with the results of gamma spectrometry (Fig. S2 in SI). The XFM images of the fragment (Fig. 2) further reveal that Pb and Pu are more concentrated inside the fragment, while Ca, Fe and U are distributed mainly on the outer surface of the fragment. These elemental distributions, together with the XFM results for other fragments

from the same Pu particle (Figs. S5-S10 in SI), point to the fact that the isolated Pu particle forms the "*core-shell*" structure composed of the Pu+Pb core surrounded by the external shell containing Ca, Fe and U (Fig. S12 in SI).

Figure 2

The chemical state of Pu in the fragment was further investigated by X-ray absorption spectroscopy. The spectral shape of the fragment in the X-ray absorption near-edge structure (XANES) region is not consistent with that for Pu-metal,[19] the original Pu compound dispersed at the site, but rather similar to those for oxide compounds, such as PuO_2 (inset of Fig. 3).[19] The XANES absorption edge and peak positions of the fragment, both of which are indicative of the oxidation states and chemical compositions,[20] are comparable with those of Pu(IV) compounds, such as PuO_2,[19] or oxyhydroxides[21] (Fig. 3). The extended X-ray absorption fine structure (EXAFS) spectrum further indicates the presence of Pu□O and Pu□Pu arrangements around the Pu atoms in the fragment, which is consistent with the structure of oxide or oxyhydroxide compounds (Fig. S15 and Table S1 in SI). This also excludes the possible presence of intermetallic Pu compounds in the fragment, such as Pu□Pb compounds.

Figure 3

Transformation of original plutonium materials. In the "*Vixen B*" trials, the explosions were reportedly triggered by a high-explosive chemical, such as TNT,[2] which can generate temperatures over 3,000 ºC.[22] The initial Pu component (i.e., metallic Pu) was, therefore, subject to a high temperature environment during explosion, which prompted the instant oxidation to PuO_2, the highest oxidation state and most stable form of Pu oxide compounds.[23] Other lower Pu oxides, such as Pu_2O_3, are unstable and eventually transformed into PuO_2.[24] The metallic Pu is also known to be self-ignitable in the air at temperatures exceeding 500 ºC, resulting in the formation of PuO_2.[25] Based on these facts, it is reasonable to posit that the initial Pu component was transformed into PuO_2 immediately after the explosion and blasted over the test site as fine particles, as illustrated in Fig. 4. Subsequently, the scattered PuO_2 particles underwent local weathering including the interaction with moisture from ambient humidity over more than fifty years before sampling. PuO_2 is susceptible to moisture even under atmospheric conditions and eventually transformed into PuO_{2+x},[24] which can be more accurately described as $PuO_{2+x-y}(OH)_{2y}{\cdot}zH_2O$.[21] The chemical interaction of these Pu compounds with local minerals and soils could potentially occur via, for instance, the dissolution of Pu into water. However, both PuO_2 and $PuO_{2+x-y}(OH)_{2y}{\cdot}zH_2O$ are expected to be sparingly soluble[26] in the local climate conditions at Maralinga,[2] suggesting that the chemical form of Pu would be unlikely to be affected by prolonged exposure to the local minerals and soil environment. Hence, $PuO_{2+x-y}(OH)_{2y}{\cdot}zH_2O$ is likely to be the final form of Pu in the particulate debris remaining at the Taranaki site. This oxyhydroxide form of Pu shows a characteristic high-energy shift in the XANES peak position as compared with PuO_2,[19, 21] which is consistent with our XANES data in Figs. 2 and S13 in SI. The Pu oxyhydroxides could be poorly structured due to the partial oxidation of Pu(IV) to higher oxidation states.[21, 27] This could account for the EXAFS results indicating lower coordination

numbers for Pu□O and Pu□Pu shells in the fragments as compared with those in PuO_2 (Table S1 in SI).

Figure 4

As shown in Fig. 2, the distribution of Pb coincides with that of Pu. This suggests that Pb is an intrinsic component of the particle core and not derived from natural accumulation after the explosion. The gamma-ray spectrum of the fragments confirmed the absence of radioactive Pb isotopes, indicating that the Pb probably originates either in Pb-metal/alloy tampers[1] which surrounded the explosive core of the device, or in the shielding/construction materials of the firing devices[2] blasted with the Pu fuel component. The Ca, Fe and U forming the outer layer of the Pu particle are likely to originate in the evaporation of moisture containing dissolved constituents from local soils, which are reported to be rich in these elements,[28] on the surface of the core particle.

Implication for radioecology. The low solubility of the Pu(IV) oxyhydroxide/oxide particles characterized in this study would reduce Pu mobility in abiotic media. However, it does not prevent its absorption into living organisms. In the mammals inhabiting the studied site, the Pu was absorbed across biological membranes into muscle, liver and bone, at significant activity concentrations.[29] As the Pu particles at the site were friable, any fragmentation will increase potential for uptake by inhalation and lodgement of sub-μm Pu particles deep in the lung. Clearance of such particles from the organism can be slow, leading to persistent and highly

concentrated internal Pu sources.[30] This scenario can explain the elevated Pu activity concentrations observed in some mammals at the Taranaki test site,[29] which could also potentially occur in case of human uptake. However, the current guidance on radiation safety and protection[31] is based largely on the uptake of dissolved Pu forms which behave differently from that of particulates during exposure and uptake. In those cases where particles have been considered, lung deposition and clearance have been a major concern, with sparse information on the physical/chemical characteristics of Pu contaminants, due in large part to the difficulty of evaluating the *in-vivo* behavior of complex Pu particulates.

This study provides spectroscopic evidence that the Pu legacy in the particles obtained at the Taranaki test site originates from unfissioned Pu fuel components, which is a unique source of Pu contamination as compared not only with those found at most other nuclear test sites, but also with worldwide fallout, reactor accidents or waste disposal. For instance, the first nuclear test near Alamogordo, New Mexico, left glassy residues containing fissioned Pu components,[32] known as "*Trinitite*", while the Pu legacy from underground nuclear tests at the Nevada Test Sites (NTS) was associated with mobile colloids facilitating the groundwater transport of fissioned Pu nuclides.[33] Other non-test-related releases of Pu into the environment include non-refractory particulates of Pu oxides from non-nuclear accidents.[34] These different forms of Pu contaminants would behave differently in the environment, resulting in different pathways of their potential introduction to the human body. With a strong advantage of using synchrotron-based X-ray microscopy/spectroscopy for the comprehensive characterization of particulate contaminants, this study highlights the importance of identifying the physical/chemical characteristics of each Pu contaminant for the reliable assessment of their environmental fate and potential implication for humans.

FIGURES

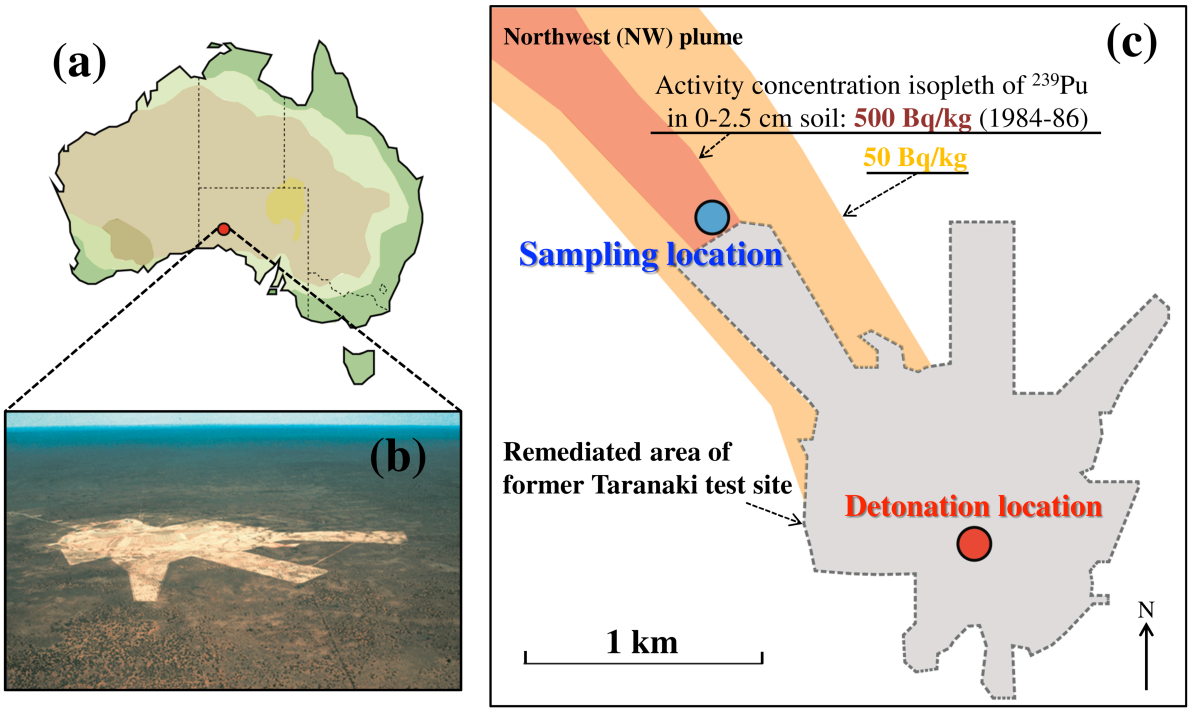

Figure 1. Geographical location of Maralinga (red circle) on an Australian map (a), and an aerial photo (b)* and a local map (c) of the Taranaki test site at Maralinga. *Reprinted with permission from the Department of Communications, Information Technology and the Arts, the Commonwealth of Australia (2002).

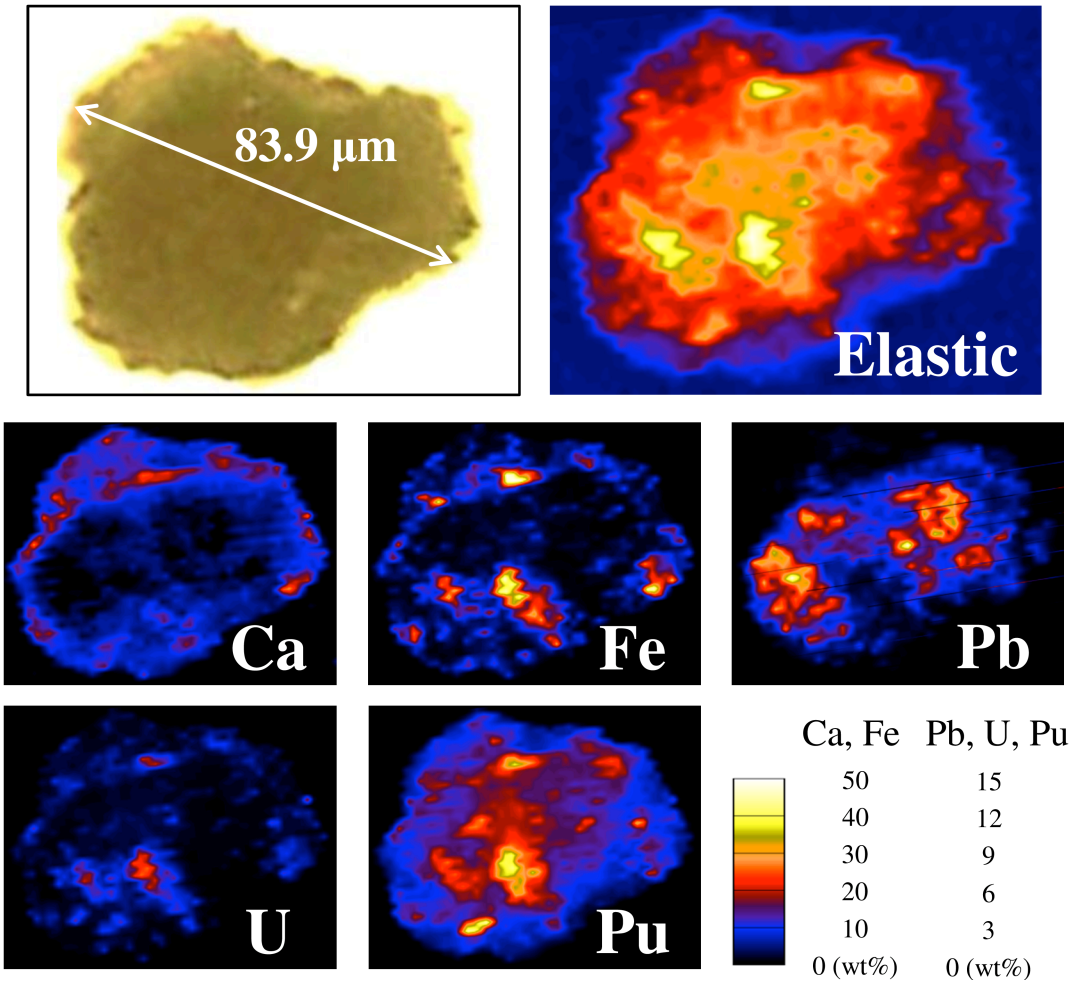

Figure 2. Optical microscope- (top left) and X-ray fluorescence microscope (XFM) images of a fragment of the isolated Pu particle deposited at the Taranaki test site.

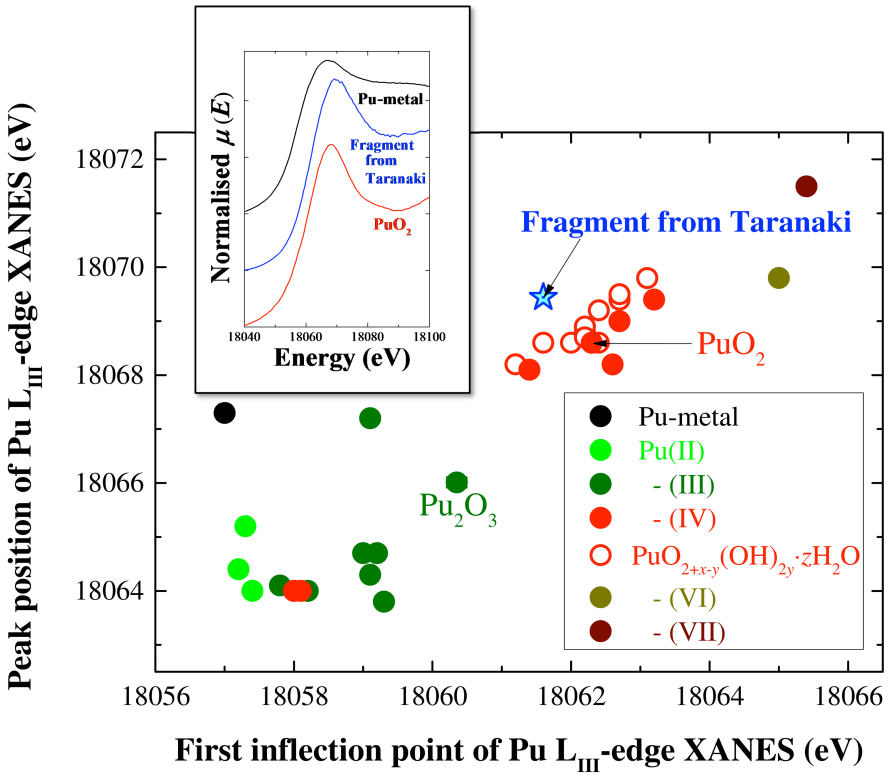

Figure 3. (Upper inset) Pu L_{III}-edge XANES spectra for the fragment of the isolated Pu particle shown in Fig. 2 (blue) and reference compounds of metallic Pu ($Pu_{0.965}Ga_{0.035}$, black)[19] and PuO_2 (red).[21] (Main figure) A plot of XANES first inflection points versus their peak positions at Pu L_{III}-edge for a series of Pu compounds with different oxidation states. The energy of the data was calibrated according to the first inflection point of Zr foil (defined as 17999.35 eV).

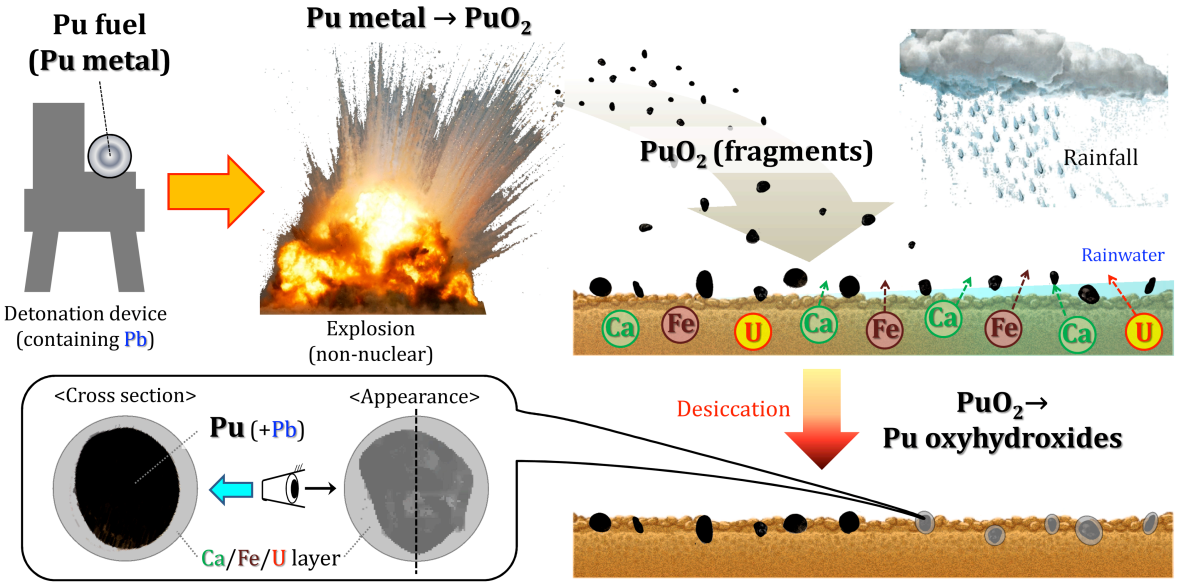

Figure 4. A scenario explaining the possible chemical transformation of Pu weapon components released in the semi-arid environment by non-nuclear detonation events.

ASSOCIATED CONTENT

Supporting Information. Gamma spectrum, X-ray fluorescence spectra, X-ray fluorescence microscopic images and X-ray absorption spectra of the isolated Pu particle, additional descriptions of experimental details and interpretation of experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

XFM measurements were performed at the XFM beamline of the Australian Synchrotron, Victoria, Australia, funded under proposal number 6551. Part of this study was carried out under the IAEA Coordinated Research Project "Environmental Behaviour and Potential Biological Impact of Radioactive Particles" (K41013). We also greatly acknowledge Steven D. Conradson

306 (Los Alamos National Laboratory) and Philippe M. Martin (CEA-Cadarache) for providing XAS
307 data of reference Pu compounds.

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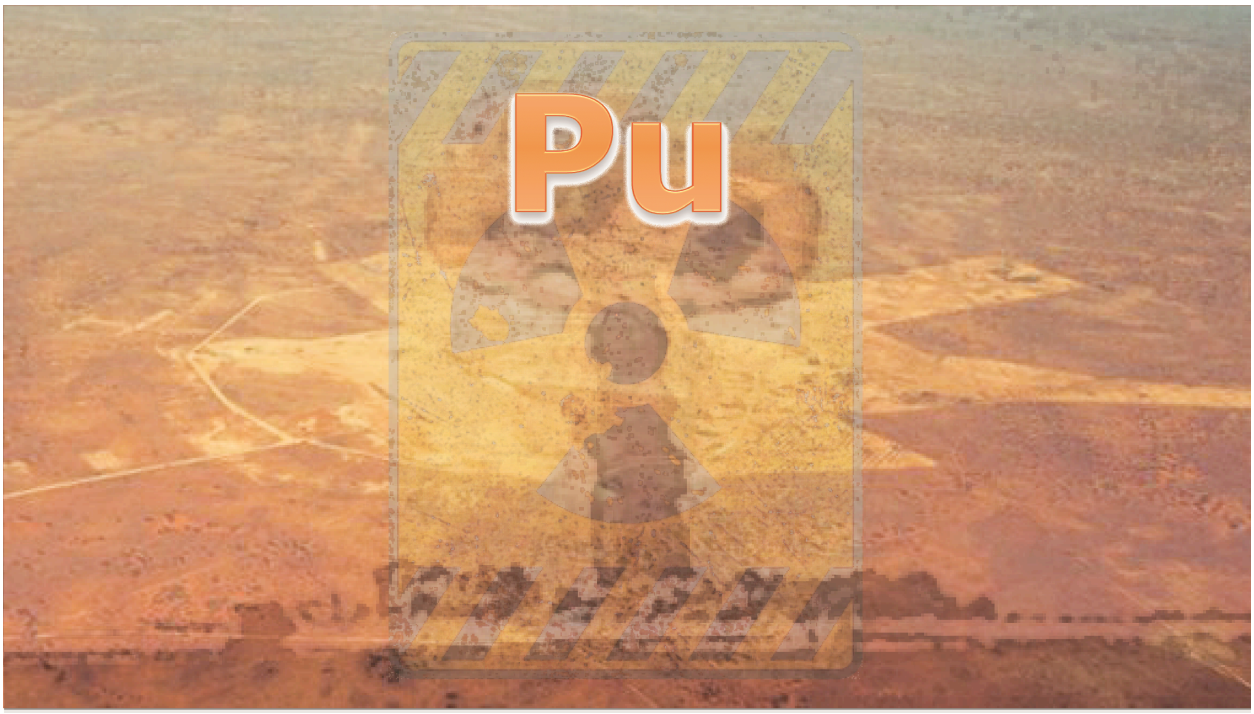
421 **Table of Contents Graphic and Synopsis**



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423 The plutonium legacy from a former nuclear weapons test in Australia was characterized as a
424 particulate form of Pu(IV) oxyhydroxides, which would be a potential source of long-term
425 internal radiation if lodged within an organism.

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