Super weapons grade $^{239+240}Pu$ as a contaminant of concern in sediment, soil, water and vegetation: Acid Canyon and Los Alamos Canyon, New Mexico

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Fundamental question to be addressed: *Where is LANL-attributed Pu present in off-site areas near the laboratory?*

- **Using the Nuclear Watch New Mexico interactive map as a guideline, we investigate concentrations of $^{239+240}$Pu *via* ground-truthing of LANL IntellusNM's results**
- **We provide New Mexicans with an unambiguous, direct look at the relative contributions of plutonium from LANL vs. from "fallout", using Pu isotopes as provenance tools**

Study areas
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Hotels
Things to do
Museums
Transit
Pharmacies
ATMs
N Mesa Rd
San Ildefonso Rd
Canyon Rd
Canyon Inn - Downtown Los Alamos
Top rated
Subway
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Smith's Marketplace
E Jemez Rd
Holiday Inn Express & Suites Los Alamos Entra...
Los Alamos Project Main Gate
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SAN ILDEFONSO OFF-RESERVATION TRUST LAND
Salaiz Landscaping
Anderson Overlook
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Background

- **During the 1940's, LANL discarded aqueous acidic wastes containing dissolved Pu at the top of Acid Canyon from a location near the present-day Los Alamos Aquatic Center; since then, LANL has conducted multiple remedial efforts in attempts to remove contaminated sediments.**
- **Under monsoon storm flow conditions, Pu-laden water and sediment flow through Acid Canyon and into Los Alamos Canyon and ultimately, the Rio Grande.**
- **On July 2 and July 17, 2024, water was flowing in Acid Canyon but no flow was observed in lower Los Alamos Canyon. The Acid Canyon water was sampled, along with floodplain sediments, soil above the floodplain in Acid Canyon, and vegetation growing in Acid Canyon and lower Los Alamos Canyon.**
- **Samples were collected by the author with assistance from Jay Coghlan, Scott Kovac, and Sophie Stroud.**
- **The samples were prepared and analyzed by mass spectrometry at Northern Arizona University to determine $^{239+240}$Pu activities (in pCi/gram or pCi/Liter) along with the ^{240}Pu/^{239}Pu atom ratios. The former is a measure of "how much" contamination is present, and the latter is a fingerprint of "where from" (i.e., is Pu originating from LANL vs. 1950's-1960's weapons-test stratospheric fallout).**

Samples collected

- **One liter samples of water from Acid Canyon were collected on July 2 and July 17, 2024 under conditions when recent rains had produced flow in the arroyo. Four samples were collected on July 2 and three samples were collected on July 17 in PET bottles. Samples were not filtered or preserved, and the entire sample (water + solids) was analyzed. Four water samples were analyzed destructively, and three samples have been archived.**

- **Sediments from the floodplains (arroyos) of Acid Canyon and lower Los Alamos Canyon were collected on both dates.**

- **Soils were also collected on July 17, from areas of Acid Canyon situated well above the floodplain, in positions unaffected by water flow and sediments in the arroyo.**

- **Vegetation was collected from the floodplain areas of both canyons on July 17. Vegetation consisted of aquatic grasses in Acid Canyon, in areas observed to be wet from recent flow. Vegetation was collected from lower Los Alamos Canyon from a sandbar within the arroyo channel, having established vegetation and some degree of soil horizon development.**

Analytical work – water samples

- The spike isotope ^{242}Pu (28 picograms) was added to the samples to determine quantities of ^{239}Pu and ^{240}Pu present. The spike is prepared from NIST 4334i (Pu-242 solution), and is handled in a restricted-access lab at Northern Arizona University, under a State of Arizona radioactive materials license.
- The entire one liter sample was analyzed; 1 g $NaHSO_4$ and 5 mL 16 M HNO_3 were added; the samples were evaporated to dryness and then re-dissolved with 50 mL of 4 M HNO_3. The un-dissolved material was filtered and is archived for potential future study. The filtered sample was treated with 0.1 g $FeSO_4*7H_2O$ and 1 g $NaNO_2$, heated to complete conversion to Pu(IV), and Pu was purified using EIChrom TEVA resin.
- A 2 mL Pu fraction was analyzed by inductively coupled plasma mass spectrometry using a Thermo X2 quadrupole ICPMS and a high-efficiency APEX HF fluoropolymer sample introduction system.
- A blank water sample and a negative Pu control sample were prepared/analyzed to validate the Pu activity and isotopic results.

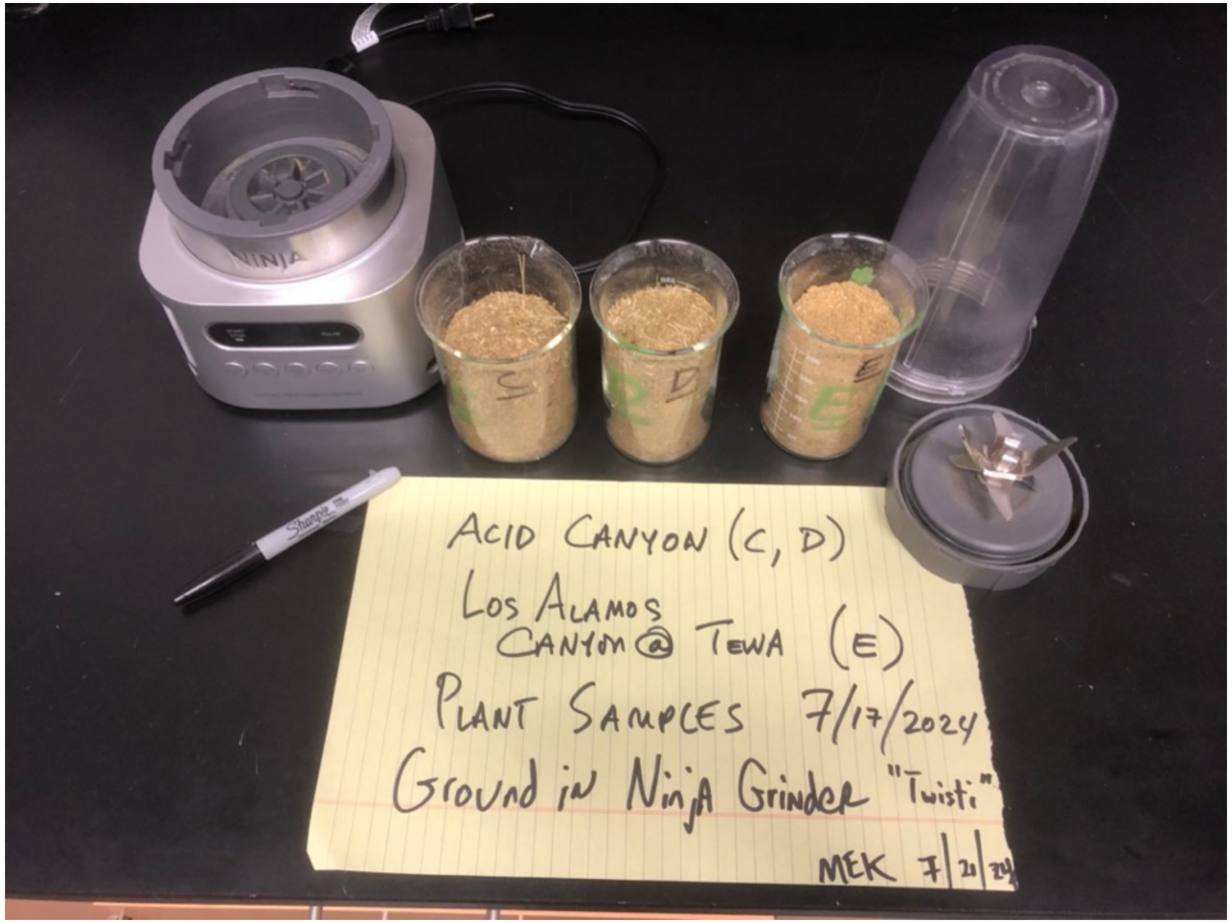
Analytical work – soil/sediment samples

- **The spike isotope ^{242}Pu was added as described for the water samples after weighing and dry-ashing a 5 gram analytical aliquot.**
- **The bulk soil and sediment samples were oven dried and sieved with a 200 mesh (75 micron) brass sieve; the < 75 micron (i.e., "-200 mesh") fraction has been analyzed herein. Sub-samples were dry-ashed at 450º C, spiked with ^{242}Pu, and leached with 10 mL of 16 M HNO_3. An additional 15 mL H_2O is added; the sample is mixed and further leached; the settled solution is filtered, and the oxidation state adjustment/Pu purification was performed in the same manner as conducted for the water samples.**
- **A 2 mL Pu fraction was analyzed by inductively coupled plasma mass spectrometry using a Thermo X2 quadrupole ICPMS and a high-efficiency APEX HF fluoropolymer sample introduction system.**
- **Controls of soils and sediments were prepared/analyzed to validate the Pu activity and isotopic results.**

Analytical work – vegetation samples

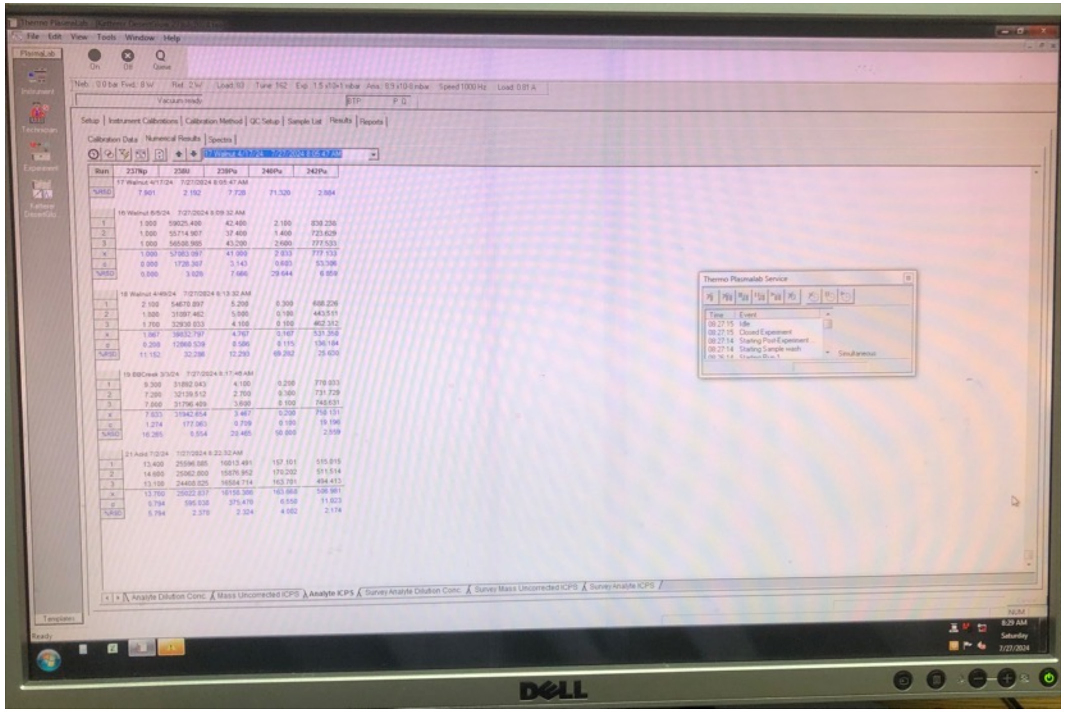
- The spike isotope ^{242}Pu was added as described for the water samples after weighing and dry-ashing an analytical aliquot of milled vegetation.
- The vegetation was oven-dried and milled with a 750 mL blender jar equipped with stainless steel chopping blades. Analytical aliquots were weighed, ashed at 450° C, and the post-ash mass was recorded. The ^{242}Pu spike was added after ashing.
- Two to five gram quantities of plant ash were leached with 50 mL of 4 M HNO_3. The settled solution was filtered, and the oxidation state adjustment/Pu purification was performed in the same manner as conducted for the water and soil/sediment samples.
- A 2 mL Pu fraction was analyzed by inductively coupled plasma mass spectrometry using a Thermo X2 quadrupole ICPMS and a high-efficiency APEX HF fluoropolymer sample introduction system.

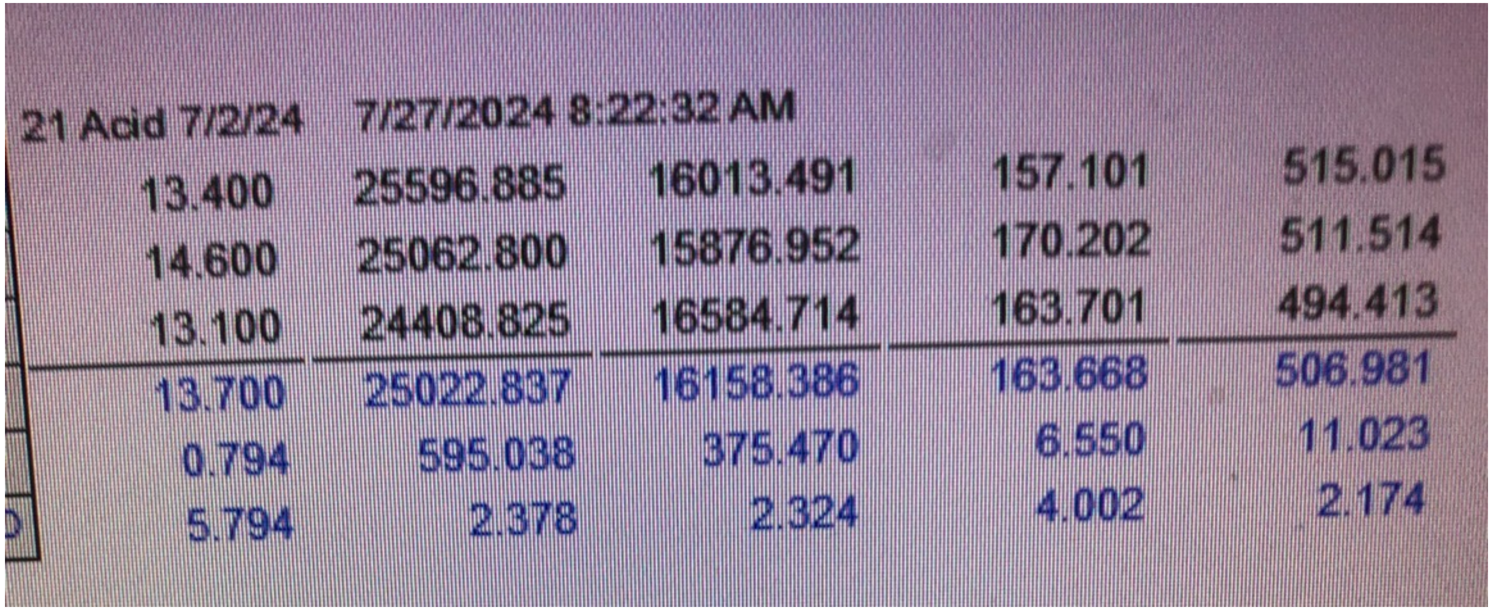
Vegetation from Acid Canyon (left, middle) and lower Los Alamos Canyon (right), shown after milling with the depicted apparatus.



Water samples were evaporated in two liter polypropylene jars in a convection oven at at 80-90^{o} C. The evaporated one liter water samples are shown prior to re-dissolution of the residue with 50 mL of 4 M HNO_3 (aq).

Photos of solid phase extraction columns with EIChrom TEVA resin for purification of Pu from aqueous HNO_3 solutions. The sample is mixed with 100 or 150 mg resin beads, equilibrated by agitation, and the resin is collected in 23 mL lab-fabricated polyethylene columns. After rinsing the columns to de-contaminate U and Th, Pu is eluted with 0.05 M aqueous ammonium oxalate.





^{239}Pu and ^{240}Pu are detected at very high ion count rates in Acid Canyon water sample 07022024-01. The detection thresholds are ~ 2 counts per second at mass 239 and 1 cps at mass 240; both isotopes are present (third and fourth columns in the lower image).

The ion count rates shown in the scan (left to right) are: ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, and ^{242}Pu (spike).

The ratios of the ^{240}Pu vs. ^{239}Pu signals indicate an ^{240}Pu/^{239}Pu atom ratio of ~ 0.01.

The instrumentation used at NAU for the measurements is the same make/model as was used by LANL researchers in the following study: https://link.springer.com/article/10.1007/s10967-015-4402-0

A. Acid Canyon water samples collected July 2 and July 17, 2024

Sample ID	Description	Findings
07022024-01	Acid Canyon, 1 liter water from stream flow on July 2, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	$^{239+240}$Pu activity = 78 ± 3 pCi/L ^{240}Pu/^{239}Pu atom ratio = 0.0102 ± 0.0005
07022024-04	Acid Canyon, 1 liter water from stream flow on July 2, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	$^{239+240}$Pu activity = 70 ± 1 pCi/L ^{240}Pu/^{239}Pu atom ratio = 0.0106 ± 0.0005
07022024-08	Acid Canyon, 1 liter water from stream flow on July 2, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	Sample is archived
07172024-03	Acid Canyon, 1 liter water from stream flow on July 17, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	Sample is archived
07172024-04	Acid Canyon, 1 liter water from stream flow on July 17, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	$^{239+240}$Pu activity = 51 ± 1 pCi/L ^{240}Pu/^{239}Pu atom ratio = 0.0105 ± 0.0001
07172024-08	Acid Canyon, 1 liter water from stream flow on July 17, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	$^{239+240}$Pu activity = 86 ± 1 pCi/L ^{240}Pu/^{239}Pu atom ratio = 0.0137 ± 0.0002
07172024-11	Acid Canyon, 1 liter water from stream flow on July 17, 2024 Unpreserved, unfiltered, obtained with PET plastic bottle immersed	Sample is archived

B. Acid Canyon and Los Alamos Canyon sediment samples collected July 2, 2024

Sample ID	Description	Findings
07022024-02	Acid Canyon, sediments collected on July 2, 2024 Eddy area near discarded refrigerator -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 27.8 $\pm$ 0.7 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0109 $\pm$ 0.0003
07022024-03	Acid Canyon, sediments collected on July 2, 2024 Fines in front of discarded refrigerator -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 78 $\pm$ 1 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0115 $\pm$ 0.0001
07022024-05	Acid Canyon, sediments collected on July 2, 2024 At location of water sample 07022024-04 -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 29.1 $\pm$ 0.4 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0107 $\pm$ 0.0001
07022024-06	Acid Canyon, sediments collected on July 2, 2024 Top of canyon near apparent location of former outfall -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 2.28 $\pm$ 0.02 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0217 $\pm$ 0.0004
07022024-07	Acid Canyon, sediments collected on July 2, 2024 Surface sediments inside concrete chamber -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 0.43 $\pm$ 0.03 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.024 $\pm$ 0.002
07022024-09	Acid Canyon, sediments collected on July 2, 2024 Surface sediments at LANL's water sampler -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 35 $\pm$ 1 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0127 $\pm$ 0.0004
07022024-10	Los Alamos Canyon sediments collected on July 2, 2024 Surface sediments at NM Hwy 502 Totavi gas station -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 0.036 $\pm$ 0.001 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.038 $\pm$ 0.002

C. Acid Canyon and Los Alamos Canyon sediment samples collected July 17, 2024

Sample ID	Description	Findings
07172024-01	Acid Canyon, soil collected on July 17, 2024 0 - 10 cm depth composite, well out of floodplain -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 0.105 $\pm$ 0.002 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.049 $\pm$ 0.004
07172024-02	Acid Canyon, soil collected on July 17, 2024 0-5 cm depth composite, well out of floodplain, atop rocks -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 0.287 $\pm$ 0.002 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.038 $\pm$ 0.002
07172024-09	Acid Canyon, sediment collected on July 17, 2024 Near LANL water sampler -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 30.8 $\pm$ 0.3 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0120 $\pm$ 0.0002
07172024-10	Acid Canyon, sediment collected on July 17, 2024 Near LANL water sampler -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 29 $\pm$ 1 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.0124 $\pm$ 0.0003
07172024-13	Los Alamos Canyon sediments collected on July 17, 2024 0 - 10 cm, NM 502 Totavi station, atop sandbar with sage -200 mesh (< 75 micron) sieved fraction analyzed	$^{239+240}Pu$ activity = 0.274 $\pm$ 0.002 pCi/g $^{240}Pu/^{239}Pu$ atom ratio = 0.016 $\pm$ 0.001

D. Acid Canyon and Los Alamos Canyon vegetation samples collected July 17, 2024

Sample ID	Description	Findings
07172024-06	Acid Canyon vegetation collected on July 17, 2024 Near LANL water sampler, tall aquatic grasses Not washed, milled/ashed	$^{239+240}$Pu activity = 5.74 $\pm$ 0.04 pCi/g (ash basis) $^{239+240}$Pu activity = 0.616 $\pm$ 0.004 pCi/g (dry mass basis) ^{240}Pu/^{239}Pu atom ratio = 0.0138 $\pm$ 0.0002
07172024-07	Acid Canyon vegetation collected on July 17, 2024 Near LANL water sampler, tall aquatic grasses Not washed, milled/ashed	$^{239+240}$Pu activity = 1.86 $\pm$ 0.01 pCi/g (ash basis) $^{239+240}$Pu activity = 0.215 $\pm$ 0.001 pCi/g (dry mass basis) ^{240}Pu/^{239}Pu atom ratio = 0.0135 $\pm$ 0.0009
07172024-12	Los Alamos Canyon vegetation collected on July 17, 2024 In arroyo at NM 502 Totavi station, several species Not washed, milled/ashed	$^{239+240}$Pu activity = 0.30 $\pm$ 0.01 pCi/g (ash basis) $^{239+240}$Pu activity = 0.023 $\pm$ 0.001 pCi/g (dry mass basis) ^{240}Pu/^{239}Pu atom ratio = 0.013 $\pm$ 0.001

Principal findings – soil and sediment activities

- Extremely elevated environmental activities of ^{239}Pu and ^{240}Pu are found in Acid Canyon sediments; $^{239+240}Pu$ activities in arroyo sediments are hundreds to thousands of times higher than can plausibly be attributed to atomic weapons testing fallout.
- Acid Canyon arroyo sediments exhibited a considerable range of $^{239+240}Pu$ activities (min = 0.43, max = 78, geometric mean = 14, avg = 29, sd = 24 pCi/g), reflecting the results of two very brief grab sampling visits in a complex, dynamic geomorphological setting.
- Soils from non-floodplain areas of Acid Canyon exhibited lower activities of $^{239+240}Pu$, indicating past LANL Pu air emissions and/or weapons-test fallout rather than the documented aqueous discharges into the arroyo.

Principal findings – water activities

- **Extremely elevated environmental activities of $^{239+240}Pu$ are found in Acid Canyon water under the conditions present in July 2024 (avg = 71, sd = 15, min = 51, max = 86 pCi/L).**
- **The $^{239+240}Pu$ activities in all four water samples exceed USEPA's relevant gross alpha standard of 50 pCi/L, and draw attention to an egregious water contamination problem mandating prompt USEPA and/or State intervention.**
- **New Mexico lacks an enforceable primary drinking water standard for $^{239+240}Pu$, but has a recommended (guidance) level of 1.5 pCi/L, applicable exclusively to Rio Grande waters. Colorado has an enforceable water quality standard of 0.15 pCi/L $^{239+240}Pu$, with which DOE is obligated to comply and self-monitor under terms of the Rocky Flats Legacy Management Agreement.**
- **The activities found in Acid Canyon are, quite obviously, elevated in an extreme sense in comparison to either the Colorado or New Mexico $^{239+240}Pu$ water standards.**
- **The activities of $^{239+240}Pu$ found in waters of Acid Canyon, in publicly accessible areas, warrant immediate postings and efforts by State/local agencies to warn people and their pets away from contacting Acid Canyon water.**

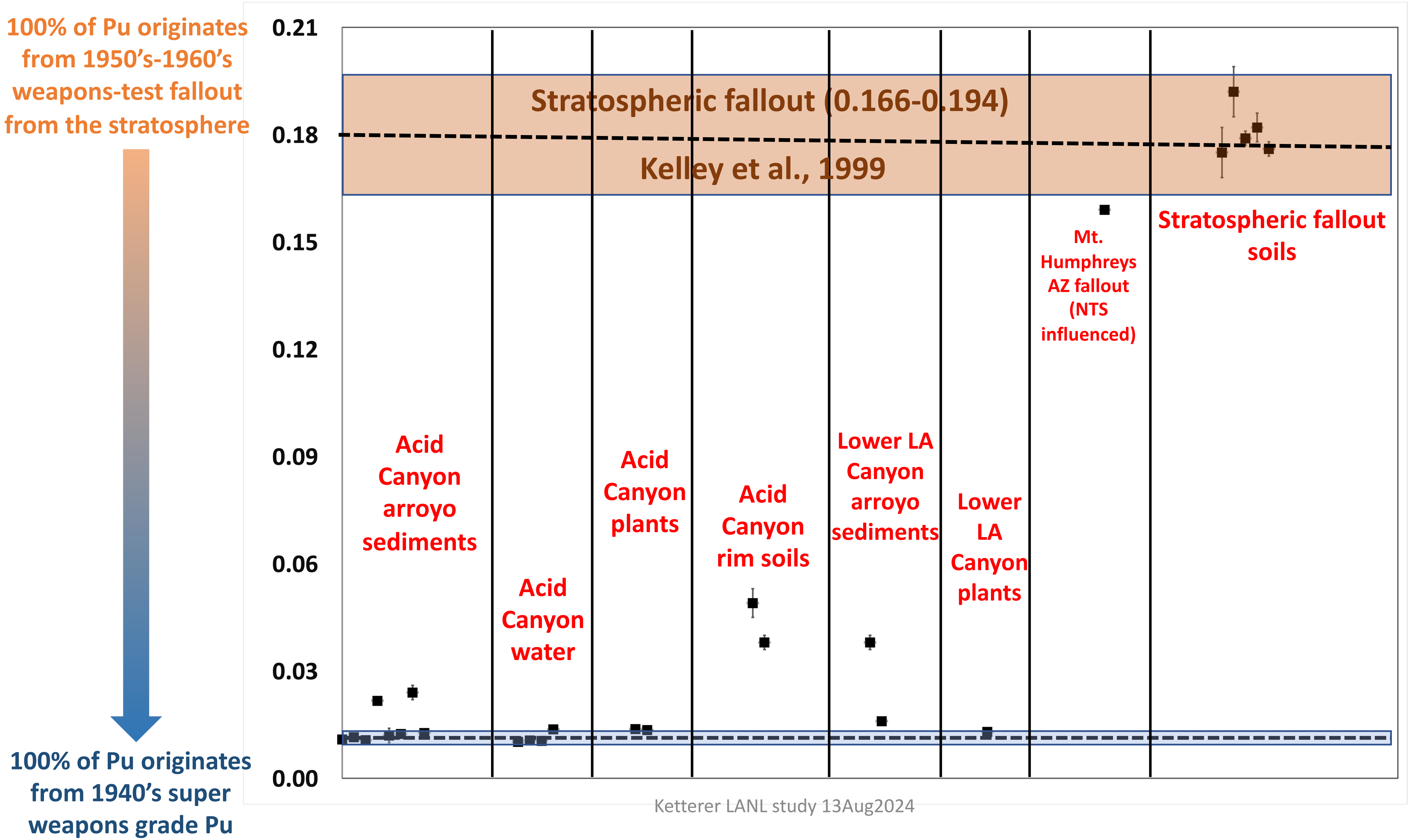
Principal findings – vegetation

- The $^{239+240}Pu$ activity results for tall grasses growing in the contaminated (arroyo) portions of Acid Canyon reflect significant plant uptake of Pu from the sediments and/or contaminated water into the freshly growing/recent plant material. The top, green shoot portions of vegetation were cut to specifically avoid introducing any contaminated sediment present on the lower stems, hence reflecting actual uptake of Pu into the vegetation, rather than superficial/exterior contamination with adhering Pu-contaminated sediments.
- The average $^{239+240}Pu$ activity in the dry Acid Canyon arroyo vegetation of 0.42 pCi/g vs. the geometric mean $^{239+240}Pu$ of 14 pCi/g in sediments, indicate that the soil-to-plant transfer factor is on the order of 0.01 to 0.05.
- Significant plant uptake of $^{239+240}Pu$ was also noted in a composite of several species growing in lower Los Alamos Canyon near the Totavi Philips 66 station along NM Highway 502. Soil/sediment (07172024-12) and vegetation (07172024-13) were collected from a shallow, regularly flooding terrace in the arroyo with some developed vegetation and soil horizons; the respective $^{239+240}Pu$ activities indicate a soil-to-plant transfer factor on the order of ~ 0.08.

Principal findings – $^{240}Pu/^{239}Pu$ provenance

- **The $^{240}Pu/^{239}Pu$ ratios of the Acid Canyon water, sediment, and vegetation samples all are consistent with Manhattan Project "super weapons grade" Pu. Most of the samples exhibit $^{240}Pu/^{239}Pu$ of < 0.02, and reflect some of the earliest produced Pu, where efforts were made to produce material of very low ^{240}Pu content. The repeated, consistent pattern of $^{240}Pu/^{239}Pu$ in the range 0.010 – 0.015, observed in the highly contaminated Acid Canyon sediments, water and vegetation, indicates that the Pu in Acid Canyon is some of the oldest known Pu contamination in the ambient environment – a portion of which likely pre-dates the Trinity Test itself.**
- **The consistent $^{240}Pu/^{239}Pu$ agreement between contaminated sediments, water, and vegetation in Acid Canyon shows that the contaminated sediments have a large inventory of Pu that is both mobile in the hydrosphere, and amenable to uptake in vegetation growing in the arroyo.**
- **It cannot be concluded that Pu is relatively "immobile" geochemically in this specific environment. Determining the physical/chemical form of the Pu present in the water warrants further work and is beyond the scope of this study.**
- **The $^{240}Pu/^{239}Pu$ atom ratios in soils from the discharge-unaffected canyon rim above the arroyo reflect different sources of Pu besides the Acid Canyon aqueous wastes, indicative of atmospheric deposition from early operations at neighboring lab buildings, and are not explainable as "weapons-test" fallout ($^{240}Pu/^{239}Pu = 0.18$, refer to: https://www.sciencedirect.com/science/article/abs/pii/S0265931X97000337).**

$^{240}Pu/^{239}Pu$ provenance in Acid Canyon and lower Los Alamos Canyon, July 2024



Additional inferences

- **Contaminated water episodically flows in Acid Canyon, and without doubt, at times significant dissolved/suspended/colloidal Pu is migrating downstream with contaminated water and suspended sediment. The arroyo sediment is extremely heterogeneous; a geometric mean value of -200 mesh material is used as a reasonable proxy for "how contaminated" a given location is.**
- **Vegetation is an apparent proxy for migration of Pu in areas farther afield of Los Alamos. When used in conjunction with $^{240}Pu/^{239}Pu$ provenance methods, as shown herein, it is expected that LANL Pu will be detectable in many areas of the affected canyons draining the Pajarito Plateau, and will be evident downstream in the Rio Grande itself.**
- **LANL should refrain from identifying any Pu found near the laboratory as "background" or "fallout" without showing $^{240}Pu/^{239}Pu$ isotopic evidence thereof.**
- **The activity concentrations of $^{239+240}Pu$ in Acid Canyon sediments and plant matter, along with the canyon's close proximity to residential areas of Los Alamos, represents an alarming potential situation of Pu releases into the air, should a wildfire engulf the canyon. It is an easily anticipated occurrence e.g., from a lightning strike or even an EV fire in one of the surrounding neighborhoods on a windy day. The concerned public and residents are urged to discuss this topic with the responsible local fire protection agencies.**