



NORTHERN ARIZONA UNIVERSITY

August 7, 2018

Plan for Independent Evaluation of Findings Sampling and Analysis Plan, Rocky Mountain Greenway Trail Crossings, prepared for Jefferson County et al., by Engineering Analytics, Inc.

Summary: This independent evaluation is to be conducted on behalf of interested local citizens, represented by Mr. Randal Stafford. The evaluation study will analyze splits of soils collected by Engineering Analytics, Inc. (EA) from the highway crossings access points to the Rocky Flats National Wildlife Refuge at two locations: Indiana Street, and Highway 128, as defined in EA's Sampling and Analysis Plan (June 2018, Rev 1.0). The splits of EA's primary samples will be analyzed by Michael E. Ketterer (Professor Emeritus of Chemistry and Biochemistry). Dr. Ketterer will also be present in-person to observe the sampling conducted by EA. Plutonium activities, expressed as $^{239+240}\text{Pu}$, will be measured by inductively coupled plasma mass spectrometry using procedures published in the peer-reviewed scientific literature. The atom ratio $^{240}\text{Pu}/^{239}\text{Pu}$ will also be measured in the samples in the same analysis, in order to distinguish between weapons-grade Rocky Flats plutonium ($^{240}\text{Pu}/^{239}\text{Pu} \sim 0.05 - 0.06$) and background "global fallout" having a $^{240}\text{Pu}/^{239}\text{Pu}$ of ~ 0.18 . Results will be reported to Mr. Stafford and will be disseminated to the interested public. The Principal Investigator's qualifications to successfully conduct this work are outlined in the attached *curriculum vita*.

Methods: The Principal Investigator, Michael E. Ketterer, will obtain splits of the 25 soil samples that are anticipated to be collected by EA from the two soil access points. Transfer of custody will take place in person between Michael E. Ketterer and representatives of EA, coincident with observing the sample collection. Samples will be maintained under Michael E. Ketterer's custody/control in all subsequent phases of the preparation and analysis.

Each sample will be homogenized and a split of ~ 25 -30 grams will be hand-milled with a porcelain mortar/pestle. Representative aliquots of $(2.0 \pm 0.1 \text{ g})$ of each milled soil will be taken for analysis. Samples will be dry-ashed at 450°C , and subsequently spiked with $\sim 0.003 \text{ Bq}$ of a ^{242}Pu yield tracer, and then fused with sodium pyrosulfate (Ketterer and Szechenyi, 2008). This treatment dissolves "global fallout" Pu as well as plutonium present in refractory, high-fired PuO_2 particles. After fusion, the pyrosulfate flux is dissolved in 6 M aqueous nitric acid; the solutions from the samples are treated with ferrous sulfate and sodium nitrite adjustment to adjust plutonium to the Pu(IV) oxidation state. The plutonium is subsequently separated and purified using Eichrom TEVA resin; a fraction containing the recovered Pu in 1.0 -1.5 mL of 0.015 M ammonium oxalate is obtained. The Pu fractions are analyzed by inductively coupled plasma mass spectrometry; a Thermo X2 quadrupole ICPMS equipped with an APEX HF high-efficiency sample introduction system will be used. Anticipated detection limits for a 2 gram sample are $\sim 0.1 \text{ Bq/kg } ^{239+240}\text{Pu}$ ($\sim 0.003 \text{ pCi/g}$). It is expected atom ratio fingerprinting of the origin of Pu will be possible for 2 gram aliquots of samples containing $> 1 \text{ Bq/kg } ^{239+240}\text{Pu}$.

Based upon a batch of 25 anticipated soil samples, quality control measures to be included with the unknown samples will consist of the following:

- * Five duplicate preparations from randomly selected soils from the unknown group (n=25; 20% duplicate frequency);
- * Five preparations of a negative control “blank” consisting of Pu-devoid pre-bomb soil/sediment or pulverized rock;
- * Five selected samples of positive controls, consisting of soils known to contain elevated activities and Pu originating from Rocky Flats;
- * Five selected samples, containing “global fallout” plutonium at background levels from Front Range locations
- * Five samples of reference material of known $^{239+240}\text{Pu}$ activity, will be analyzed; these will be produced by blending 0.05 – 0.10 g aliquots of IAEA 384 (Fangataufu sediment, 107 Bq/kg $^{239+240}\text{Pu}$) with ~ 1.9 grams of pulverized Pu-devoid pre-bomb soil/sediment/rock.

All steps commencing with the addition of the ^{242}Pu yield tracer will be conducted at the Department of Chemistry and Biochemistry, Northern Arizona University. The laboratory has a Radioactive Materials License with the State of Arizona for specific use of ^{242}Pu in the analysis of environmental samples, and is overseen by the NAU Radiation Safety Officer (James Biddle).

Interpretations: Comparisons will be presented between the $^{239+240}\text{Pu}$ activities and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios encountered in the trail crossings soils vs. Front Range control locations. Additional comparisons will be made between the $^{239+240}\text{Pu}$ activities reported from EA’s study vs. the present work.

Reference Cited: Ketterer, M.E.; Szechenyi, S.C., “Review: Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences”, *Spectrochimica Acta B* **2008**, 63, 719-737.

Respectfully Submitted:



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Education: B.S., Chemistry, University of Notre Dame (1980)
Ph.D., Analytical Chemistry, University of Colorado, Boulder CO (1985)

Professional Positions:

2018-present Professor Emeritus, Chemistry and Biochemistry, Northern Arizona University
2016-2018 Professor of Chemistry, Metropolitan State University of Denver
2013-2015 Professor and Chair, Chemistry, Metropolitan State University of Denver
2005-2013 Professor, Chemistry and Biochemistry, Northern Arizona University
2001-2005 Associate Professor, Chemistry and Biochemistry, Northern Arizona University
1998-2001 Assistant Professor, Chemistry and Biochemistry, Northern Arizona University
1993-1998 Assistant Professor, Chemistry, John Carroll University, Cleveland Ohio
1987-1993 Chemist, US EPA, National Enforcement Investigations Center
1985-1987 Research Chemist, Gates Corp., Denver, CO

Experience and interests: isotopic studies of lead and long-lived actinides in the environment; inductively coupled plasma mass spectrometry; measurement of uranium and plutonium in environmental samples; forensic geosciences and case studies of contamination; distinguishing and apportioning actinides sources using ICPMS data; using Pu as a tracer of recent Earth surface processes (soil erosion, sedimentation)

Key Publications:

Ketterer, M.E.; Szechenyi, S.C., "Review: Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences", *Spectrochimica Acta B* **2008**, 63, 719-737

Ketterer, M.E., Hafer, K.M., Link, C.L., Kolwaite, D. Wilson, J., Mietelski, J.W., "Resolving global vs. local/regional Pu sources in the environment using sector ICPMS", *Journal of Analytical Atomic Spectrometry* **2004**, 19, 241-245

Ketterer, M.E., Hafer, K.M., Jones, V.J., Appleby, P.G., "Rapid dating of recent sediments in Loch Ness: inductively coupled plasma mass spectrometric measurements of global fallout plutonium", *The Science of the Total Environment* **2004**, 322, 221-229

Ketterer, M.E., Hafer, K.M., Mietelski, J.W., "Resolving Chernobyl vs. global fallout contributions in soils from Poland using plutonium atom ratios measured by ICPMS", *Journal of Environmental Radioactivity* **2004**, 73, 183-201

Ketterer, M.E.; Hafer, K.M.; Link, C.L.; Royden, C.S.; Hartsock, W.J., "Anthropogenic ^{236}U at Rocky Flats, Ashtabula River Harbor, and Mersey Estuary: Three case studies by sector ICPMS", *Journal of Environmental Radioactivity* **2003**, 67, 191-206

Ketterer, M.E.; Lowry, J.H.; Simon, J. Jr.; Humphries, K.; Novotnak, M.P., "Lead isotopic and chalcophile element compositions in the environment near a zinc smelting – secondary zinc recovery facility, Palmerton, Pennsylvania, USA", *Applied Geochemistry* **2001**, 16, 207- 229

Ketterer, M.E.; Wetzel, W.C.; Layman, R.R.; Matisoff, G.; Bonniwell, E.C., "Isotopic studies of sources of uranium in sediments of the Ashtabula River, Ohio, USA", *Environmental Science and Technology* **2000**, 34, 966-972

Courses Taught: Analytical Chemistry and Lab; Instrumental Analysis and Lab; General Chemistry I, II and Labs; Principles of Chemistry (non-majors); Environmental Chemistry (majors and non-majors); Chemometrics; Topics in Mass Spectrometry; professional short courses in environmental forensics; isotope analysis and fingerprinting at conferences and workshops

Key Grant Support:

A Pilot Study of Plutonochronology: Rapid Dating of Recent Sediments and Soils using Pu Activities and $^{240}\text{Pu}/^{239}\text{Pu}$ Determined by ICPMS, 09/01/2001-04/30/2003, \$48,963, Ketterer, PI, NSF-EAR012593

Acquisition of a High-Resolution ICPMS for Research in Chemistry and Earth Sciences, 10/01/2001-09/30/2004, \$407,620, Ketterer, PI, NSF CHE-0116804

Examples of Consulting Projects:

The ASARCO El Paso Smelter: A Source of Local Contamination of Soils in El Paso, Ciudad Juarez and Anapra, prepared for Sierra Club (2006)

Sources of Uranium in Soils near the Starmet Site, Concord, Massachusetts, prepared for Citizens Research and Environmental Watch (*pro bono*, 2008)

Sources of Uranium near the Nuclear Fuel Services Erwin TN Site (*pro bono*, 2011)

Review of "Geochemical Findings from the Core Sampling Investigation at the Tuba City Open Dump" by Dr. William J. Walker, and related documents relevant to the origin of uranium in the groundwater in the vicinity of the Tuba City Open Dump, prepared for Toeroek Associates Inc., on behalf of US EPA Region 9 (2012)

Reading, Pennsylvania Exide Source Footprint Study, prepared for the Reading Eagle Company (*pro bono*, 2017)