Characterization of Plutonium Activities in Soil – 15429

Raymond L. Kidman, Matthew Knop, and Dorothy C. Sloop
Navarro, Las Vegas, Nevada 89030

ABSTRACT

Plutonium (Pu) contamination in soils at the Nevada National Security Site (NNSS) is characterized using Am-241 activity results from gamma spectroscopy (gamma Am-241) analysis. This is done by inferring the Pu activities using Pu to Am-241 ratios developed from Pu and Am-241 results from alpha spectroscopy isotopic analyses (isotopic Pu and isotopic Am-241).

Although the isotopic Pu and Am-241 methods can accurately measure isotopic activities within the sampled material, the amount of soil analyzed is small (typically 1 gram [g] of soil). If there is heterogeneity of particle distribution within the contaminated release site soil, isotopic methods may provide results that are not representative of the contaminated site. The degree of potential heterogeneity needs to be considered before using isotopic analyses to characterize a Pu-contaminated site. Results from various Pu-contaminated sites at the NNSS are presented that demonstrate significant heterogeneity.

A larger sample size (~1,600 g) within a Marinelli container is used for the gamma spectroscopy analysis. This greatly reduces the impact of heterogeneously distributed discrete particles and provides results that are more representative of true contaminant activities at the release site. However, this method cannot provide Pu activities and has the potential to provide less accurate results due to the haphazard location of contaminant particles within the Marinelli container at the time of measurement. The distance of particles from the detector would result in some differential self-absorption of the emissions from radioactive particles. As the magnitude of this problem was not previously understood, a study was conducted to evaluate the variability in Am-241 results due to self-absorption from particle position. Results from this study are shown that demonstrate that this effect provides minimal variability in replicate Am-241 measurements.

The method used at the NNSS to characterize Pu activities in soil takes advantage of the accuracy of the alpha spectroscopy isotopic analyses to establish Pu to Am-241 ratios and the more representative gamma spectroscopy results for Am-241 to provide a reliable characterization of Pu activities at contaminant release sites.

INTRODUCTION

The heterogeneity of plutonium (a major contaminant at nuclear safety experiment sites) in soil samples has been observed in several studies [1, 2]. Different aliquots of the same sample submitted for analysis give results differing by many orders of magnitude depending on the number of particles present and their size distribution in each aliquot [2].

The variability in analytical results decreased with an increase in amount of sample analyzed [1]. These results are supported by results from NNSS soil samples as presented in the following sections.

Accurate characterization of Pu at release sites requires collecting samples that are characteristic of the site [3, 4, 5]. To maximize the potential for samples to represent site contamination under conditions of heterogeneity, sample plots (with an area of 100 square meters) are used at the NNSS to provide a larger sample that integrates plutonium concentrations over the defined area [6]. At least four composite samples are collected from each established sample plot, and each composite sample comprises nine aliquots taken from unbiased locations within each plot. The entire volume of the composited material collected is submitted to the laboratory for analysis.

Accurate characterization of Pu at release sites also requires that analytical results adequately represent the activities contained within the collected soil sample. Isotopic Pu analyses are commonly used to characterize Pu within contaminated soil samples and typically use a small amount of soil (typically, 1 g of soil). Estimating Pu contamination from soil samples is problematic due to the particle nature of Pu (where particles may be non-uniformly distributed within soil samples) and the relatively small aliquots used for isotopic Pu analyses (that may or may not capture the discrete Pu particles). The presence or absence of an individual Pu particle in a small isotopic Pu soil sample can significantly influence the resulting analytical result for Pu isotope concentrations. A larger sample volume increases the likelihood that Pu analytical results would be representative of the sampled location (i.e., reduce the influence of an individual particle on sample concentration). However, it is not practical for the analytical laboratory to digest a large volume of soil.

Isotopic analyses can accurately measure isotopic activities within the sampled material. In the isotopic analyses, a suitable isotopic tracer is added to the soil sample which is then dissolved by acid digestion. The isotope is separated from the sample using chemical (primarily ion exchange) procedures. The isolated isotope is micro-precipitated and the precipitate collected on a 25-milimeter filter. An alpha spectrum of the sample is obtained using an ion-implanted silicon detector mounted in a vacuum chamber. Appropriate electronics and software are utilized to provide the data needed to determine the sample activity.

Another method of characterizing Pu activities in soil is the characterization of Am-241 activities by gamma spectroscopy and inferring Pu activities using an isotopic Pu to gamma Am-241 ratio. This ratio is theoretically a constant value for all soil samples collected from a specific release source at any specific time regardless of the activity based on the ratio of these isotopes in the contaminant source and the effect of radioactive ingrowth and decay since the release. The larger sample size (~1,600 g) within a Marinelli container for the gamma spectroscopy analysis greatly reduces the impact of heterogeneously distributed discrete particles and provides a result that is more representative of release site conditions.

The degree of potential variability associated with both the heterogeneous distribution of soil contaminants and measurement errors associated with the analytical methods needs to be considered before selecting a methodology for characterizing Pu in soil. The method used to describe potential variability in this study is the coefficient of variation (CV). This is an estimate of the amount of variability in the population based on the distribution of sample results relative to the average sample value. Because it is standardized to the average, the CV is unitless, and it can be used instead of the standard deviation (SD) to compare the spread of datasets that have different units or different means. For datasets that have sufficient data to calculate an SD, the CV was calculated as the SD divided by the mean. For datasets that compare duplicate samples, the CV is estimated using the percent difference. This was calculated as the absolute difference between the two duplicates divided by the mean.

The following three sections provide approaches for assessing the variability due to the spatial heterogeneity of Pu, the effect of heterogeneity on gamma spectroscopy results, and Pu-239/240 to Am-241 ratios.

PLUTONIUM DUPLICATE VARIABILITY

The degree of heterogeneity associated with discrete radioactive particles in contaminated soil can be estimated from differences of the combined Pu-239 + Pu-240 (Pu-239/40) activities observed in isotopic analyses from aliquots taken from the same soil sample (i.e., duplicates). Figure 1 shows 177 pairs of duplicate Pu-239/40 results from soil samples collected at various locations within the NNSS.

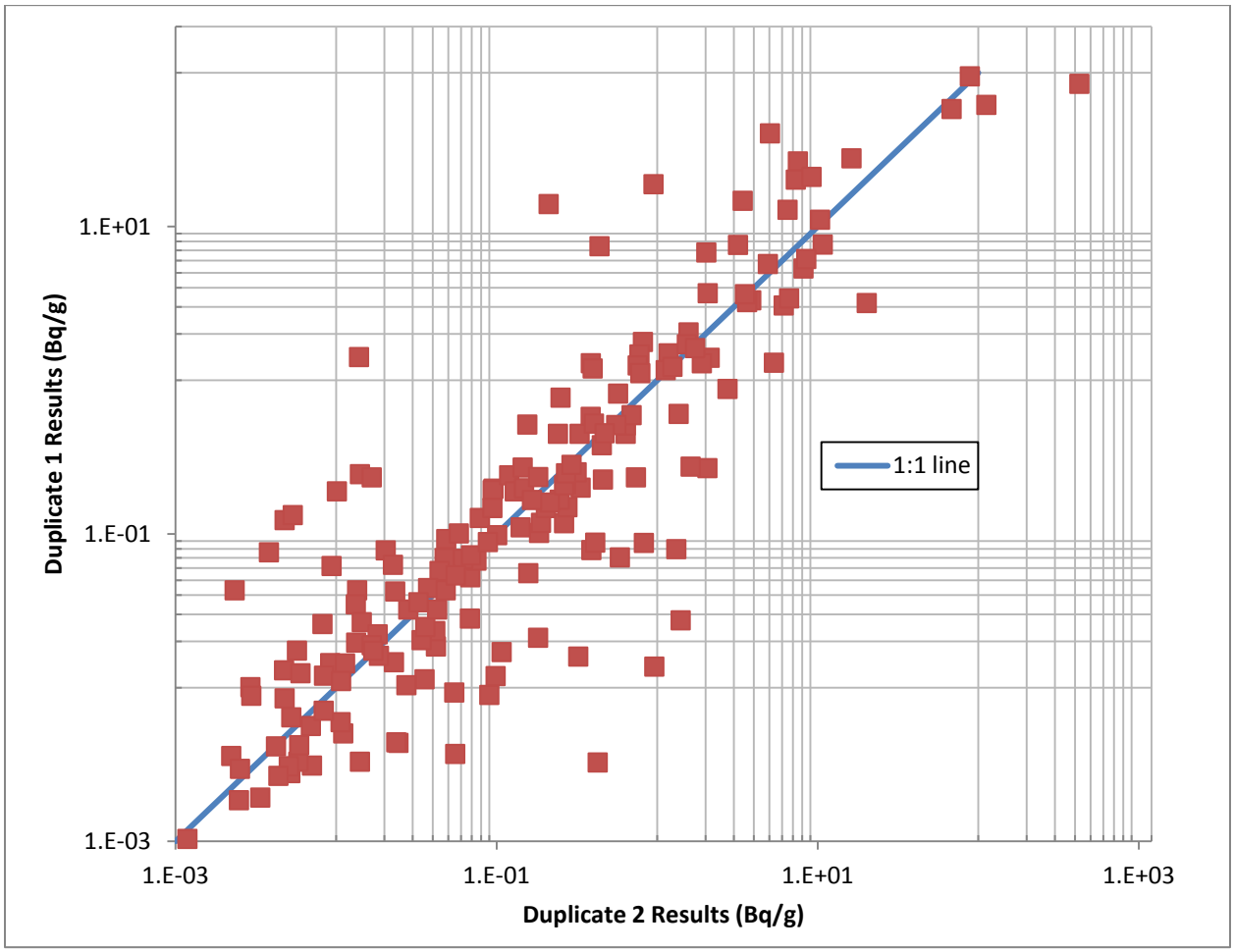

Fig. 1. Isotopic Pu-239/40 duplicate sample comparison.

In almost 1/3 of 177 duplicate Pu-239/40 analyses from NNSS soil samples, the difference between results was greater than their corresponding average activity (i.e., resulted in a CV of greater than 100%) (Figure 2). The average CV of all 177 duplicates was 70%. Of particular interest in Figure 2 is that the variability appears to be consistent throughout the range of activities (i.e., the variability is independent of total activity).

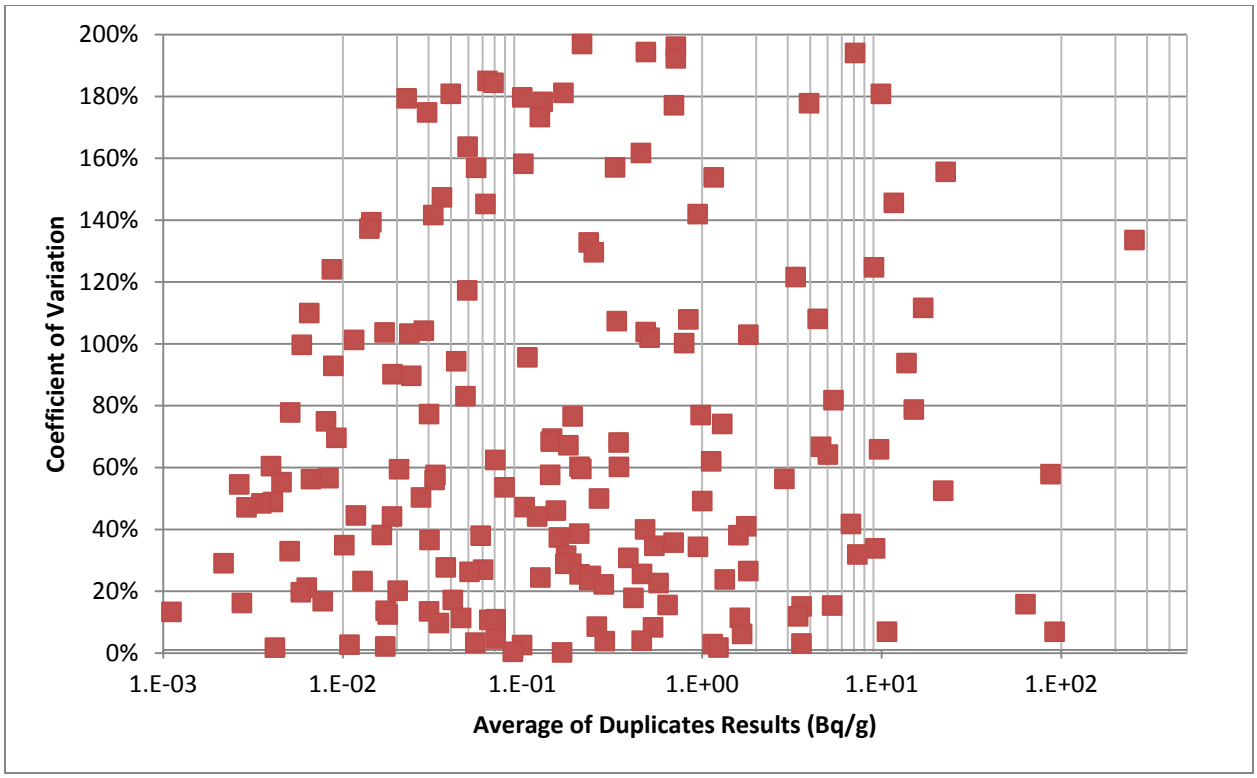

Fig. 2. Coefficient of variation with Pu-239/240 activity.

This demonstrates that the variabilities associated with isotopic Pu-239/40 analytical results are not dependent upon the amount of Pu-239/40 in the sample. The significant differences in duplicate analytical results identify the presence of heterogeneously distributed discrete particles in soil samples collected from the NNSS.

AMERICIUM DUPLICATE VARIABILITY

The presence of significant heterogeneity of discrete radioactive particles can also be evaluated by examining the differences between the isotopic alpha spectroscopy Am-241 (isotopic Am-241) and the gamma Am-241 results. Figure 3 shows the correlation of 812 pairs of isotopic and gamma Am-241 results from soil samples collected at various locations within the NNSS.

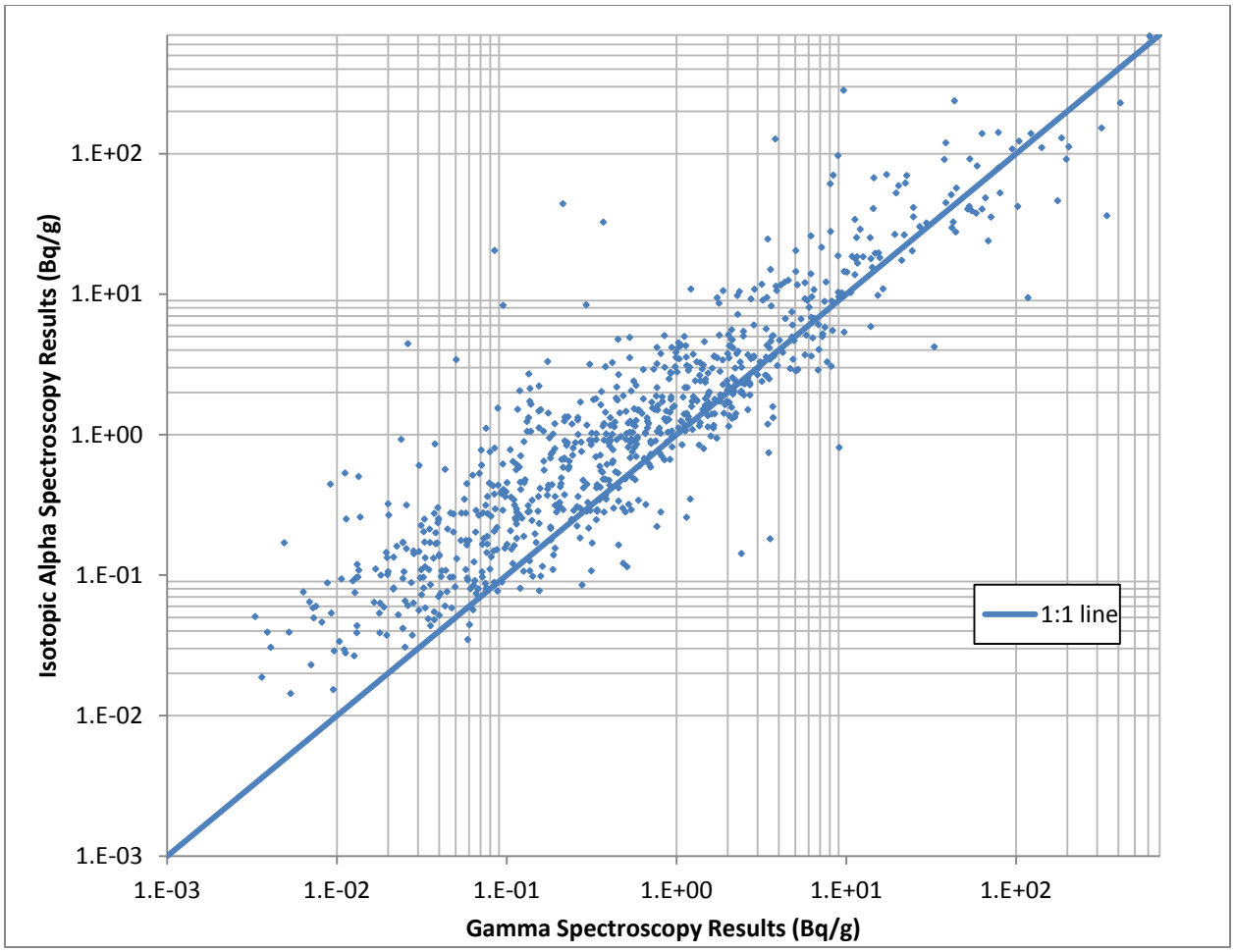

Fig. 3. Isotopic Am-241 to gamma Am-241 comparison.

The results should be similar if the contaminants are distributed homogeneously through the sample material. Differences between the results from these two analytical methods provide an indication of the spatial heterogeneity of Am-241 distribution within the sampled material. As the Am-241 and Pu isotopes are co-located, the Am-241 heterogeneity is assumed to be equal to the Pu heterogeneity. The apparent bias (especially for lower activity samples) in the results is not well understood but is believed to be related to differences in particle activity versus total activity (e.g., fewer particles of higher activity relative to the total activity). An additional study is currently in progress in an attempt to better understand this apparent bias.

As shown in Figure 4, the CV was greater than 100% in over 1/3 of the duplicate analyses from NNSS soil samples. The average CV of all 812 duplicates was 77%. As with the CV plot from the isotopic Pu-239/240 duplicate analyses, the variability appears to be consistent throughout the range of activities (i.e., the variability is independent of total activity).

This demonstrates that the isotopic and gamma Am-241 analytical results are not dependent upon the amount of Am-241 in the sample. The significant differences in the analytical results identify the presence of heterogeneously distributed discrete particles in soil samples collected from the NNSS.

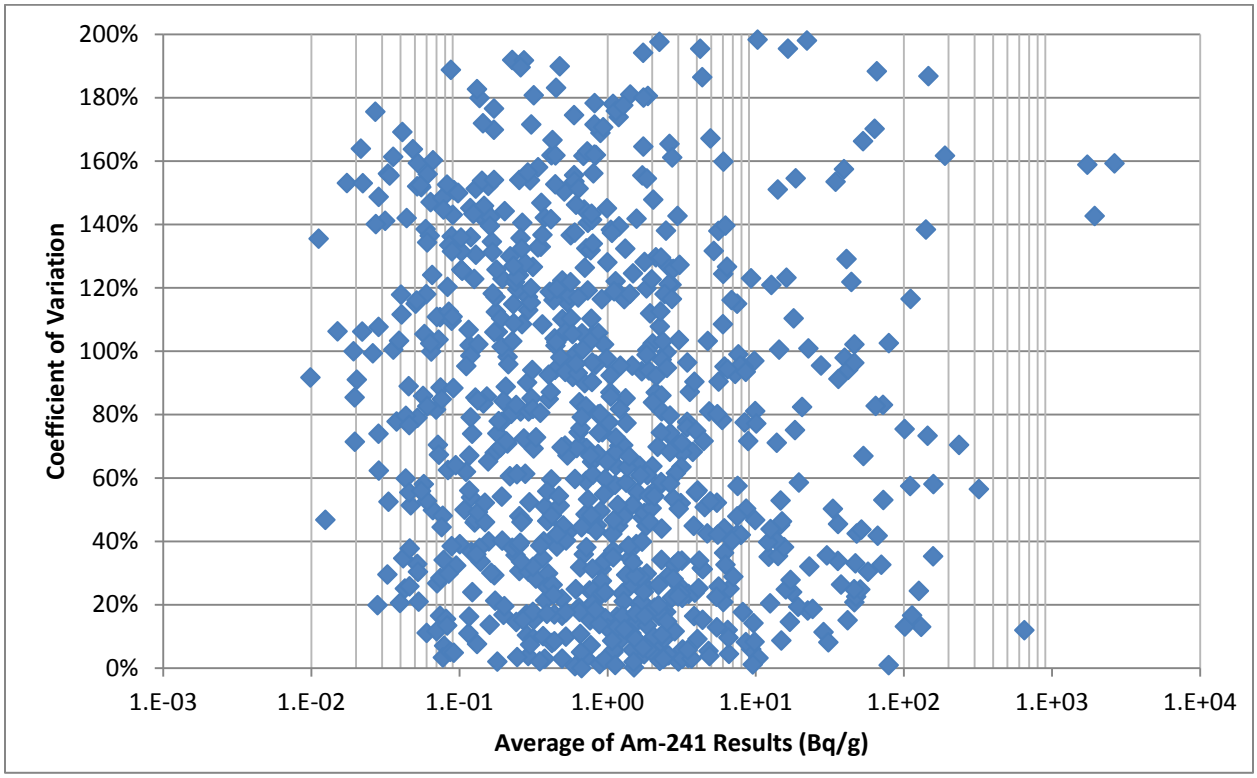

Fig. 4. Coefficient of variation with Am-241 activity.

GAMMA AM-241 REPLICATE VARIABILITY

The gamma Am-241 analysis provides a more representative estimate of site contamination activities as it reduces the effect of discrete contaminant particles through the use of a much larger sample volume (i.e., the gamma analysis uses 1,000 cubic centimeters [cm^3], while the isotopic analysis uses approximately 0.6 cm^3). However, the gamma spectroscopy method cannot produce Pu activities. The ability of this method to produce consistent results (i.e., method variability) was investigated due to the potential for differential self-absorption of the gamma emissions of radioactive particles based on their physical position within the Marinelli container. The variability of gamma Am-241 results caused by self-absorption within the container was examined by conducting 10 replicate gamma spectroscopy measurements on each of four soil samples from within the contaminant plume of a single nuclear test at the NNSS. The Marinelli containers were emptied, and the soil was mixed between each measurement to create different particle distributions within the Marinelli containers. The effect of these different distributions on gamma Am-241 results is shown in Table I in units of bequerels per gram (Bq/g). For the purpose of comparison, Table II presents these results as normalized values (i.e., multiples of the average activity).

TABLE I, Gamma spectroscopy replicate results (Bq/g)

Sample No.	A602		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.01	0.34	14.5
Replicate 2	1.03	0.32	12.0
Replicate 3	1.06	0.32	13.6
Replicate 4	0.99	0.33	12.7
Replicate 5	1.01	0.33	14.2
Replicate 6	1.08	0.32	12.9
Replicate 7	1.05	0.31	12.4
Replicate 8	1.07	0.32	12.2
Replicate 9	1.03	0.33	14.0
Replicate 10	1.02	0.30	12.3
Average	1.04	0.32	13.1
SD	0.03	0.01	0.9
sample size	10	10	10
degrees of freedom	9	9	9
t statistic	2.3	1.8	1.8
95%LCL	1.0	0.3	12.6
95%UCL	1.1	0.3	13.6

Sample No.	A605		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.09	2.06	108.1
Replicate 2	1.07	1.94	101.9
Replicate 3	1.06	1.95	99.3
Replicate 4	1.15	1.96	104.4
Replicate 5	1.10	1.93	102.2
Replicate 6	1.11	1.85	101.9
Replicate 7	1.09	1.97	103.0
Replicate 8	1.10	1.93	100.7
Replicate 9	1.10	1.94	100.7
Replicate 10	1.08	1.98	102.2
Average	1.10	1.95	102.4
SD	0.02	0.05	2.4
sample size	10	10	10
degrees of freedom	9	9	9
t statistic	1.8	1.8	1.8
95%LCL	1.1	1.9	101.0
95%UCL	1.1	2.0	103.9

Sample No.	A658		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.08	0.03	2.9
Replicate 2	1.05	0.03	4.0
Replicate 3	1.01	0.03	3.1
Replicate 4	1.00	0.03	3.9
Replicate 5	1.01	0.03	3.9
Replicate 6	1.04	0.03	4.0
Replicate 7	1.04	0.03	3.7
Replicate 8	1.04	0.03	3.7
Replicate 9	1.04	0.03	3.0
Replicate 10	1.07	0.03	3.4
Average	1.04	0.03	3.6
SD	0.03	0.00	0.4
sample size	10	10	10
degrees of freedom	9	9	9
t statistic	2.3	1.8	1.8
95%LCL	1.0	0.0	3.3
95%UCL	1.1	0.0	3.8

Sample No.	A662		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.09	0.05	3.9
Replicate 2	1.08	0.03	2.8
Replicate 3	1.14	0.03	2.9
Replicate 4	1.11	0.03	3.2
Replicate 5	1.12	0.03	2.8
Replicate 6	1.04	0.03	2.9
Replicate 7	1.03	0.03	2.7
Replicate 8	1.06	0.03	2.9
Replicate 9	0.99	0.03	2.8
Replicate 10	1.13	0.03	2.8
Average	1.08	0.03	3.0
SD	0.05	0.01	0.3
sample size	10	10	10
degrees of freedom	9	9	9
t statistic	1.8	1.8	1.8
95%LCL	1.1	0.0	2.8
95%UCL	1.1	0.0	3.2

LCL = Lower confidence limit

UCL = Upper confidence limit

TABLE II, Normalized (multiples of average)
gamma spectroscopy replicate results with variability

Sample No.	A602		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	0.97	1.05	1.11
Replicate 2	0.99	0.99	0.92
Replicate 3	1.02	1.00	1.04
Replicate 4	0.96	1.01	0.97
Replicate 5	0.98	1.04	1.09
Replicate 6	1.04	0.99	0.98
Replicate 7	1.02	0.98	0.95
Replicate 8	1.04	0.99	0.93
Replicate 9	1.00	1.01	1.07
Replicate 10	0.98	0.95	0.94
CV	2.8%	2.9%	7.0%
Unexplained		0.1%	4.2%

Sample No.	A605		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.00	1.06	1.06
Replicate 2	0.98	0.99	0.99
Replicate 3	0.97	1.00	0.97
Replicate 4	1.05	1.01	1.02
Replicate 5	1.00	0.99	1.00
Replicate 6	1.02	0.95	0.99
Replicate 7	1.00	1.01	1.01
Replicate 8	1.00	0.99	0.98
Replicate 9	1.01	0.99	0.98
Replicate 10	0.98	1.01	1.00
CV	2.2%	2.7%	2.4%
Unexplained		0.5%	0.2%

Sample No.	A658		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.04	1.09	0.80
Replicate 2	1.01	1.10	1.13
Replicate 3	0.97	1.01	0.89
Replicate 4	0.96	1.02	1.08
Replicate 5	0.97	1.01	1.08
Replicate 6	1.00	0.93	1.13
Replicate 7	1.00	0.95	1.04
Replicate 8	1.01	0.99	1.04
Replicate 9	1.01	0.95	0.85
Replicate 10	1.03	0.95	0.96
CV	2.5%	6.0%	11.9%
Unexplained		3.5%	9.3%

Sample No.	A662		
Isotope	**K-40**	**Cs-137**	**Am-241**
Replicate 1	1.01	1.55	1.30
Replicate 2	1.00	0.95	0.96
Replicate 3	1.06	0.92	0.97
Replicate 4	1.03	0.91	1.08
Replicate 5	1.04	0.91	0.94
Replicate 6	0.97	0.98	0.96
Replicate 7	0.95	0.88	0.90
Replicate 8	0.98	1.00	0.98
Replicate 9	0.92	0.94	0.96
Replicate 10	1.04	0.96	0.95
CV	4.5%	19.7%	11.5%
Unexplained		15.2%	6.9%

Also shown in Table I and Table II are gamma K-40 and Cs-137 results. The K-40 was included to estimate the variability that is associated with the measurement technique. This is based on the assumption that the K-40 is homogeneously distributed through the sample. Therefore, the variability of the K-40 is only attributable to the variability of the measurement system. This variability (when normalized to the average) can be subtracted from the total variabilities for Cs-137 and Am-241 results resulting in net unexplained variabilities. These net unexplained variabilities are believed to be associated with particle distributions and self-absorption within the Marinelli containers. The unexplained variabilities for each of the four samples are shown in Table II.

Some influence of the particle problem is also evident in the gamma Cs-137 results for samples A658 and A662 (a major contaminant associated with weapons testing). These two samples contained very low activities of Cs-137 (0.03 becquerels per gram [Bq/g]). As shown in Figure 5, the variabilities of both Cs-137 and Am-241 in replicate gamma spectroscopy results are dependent upon the magnitude of each radionuclide activity in the sample. This demonstrates that the variability associated with particle distributions on gamma spectroscopy results decreases with higher concentrations of Cs-137 and Am-241.

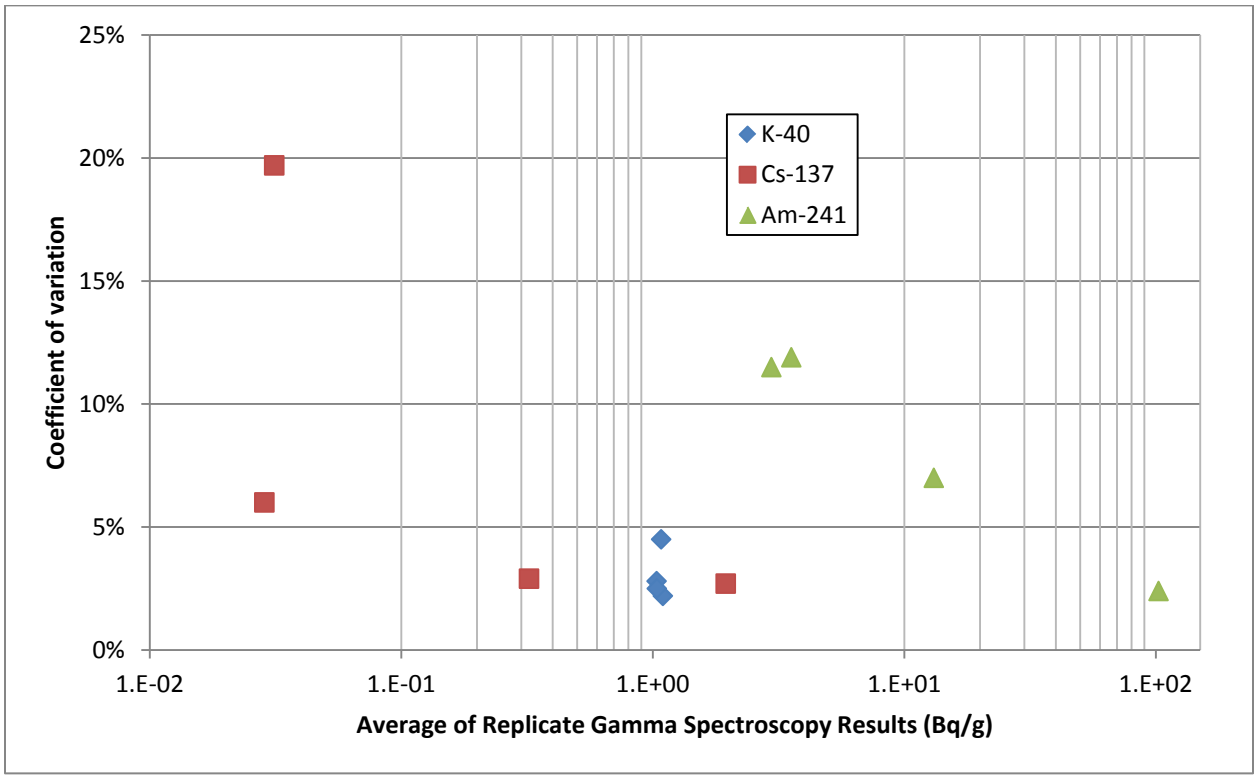

Fig. 5. Coefficient of variation by isotope activity.

These results show that the variability between gamma spectroscopy replicates is much smaller than the variability observed in the isotopic Pu duplicate results (Figure 1) or the isotopic Am-241 to gamma Am-241 results (Figure 3). For comparison purposes, each of these estimated variabilities is shown in Table III.

TABLE III, Variability associated with heterogeneity by analytical method

Method	Coefficient of Variation
Isotopic Pu duplicates	70%
Isotopic Am / Gamma Am	77%
Gamma Am Replicates	8%

PU-239/40 TO AM-241 RATIO VARIABILITY

To improve the estimate of Pu-239/40 concentrations, the NNSS infers the concentrations of these isotopes in each sample using Am-241 as a surrogate. This is done by measuring the Am-241 concentration in a 1,600-g soil sample using the gamma spectroscopy analytical method. The Pu-239/40 to Am-241 ratios are established from isotopic analyses (average ratios from the isotopic analysis of the 1-g soil samples). As previously explained, the Pu-239/40 to Am-241 ratio in contaminated soil from a specific release is expected to be the same throughout the contaminant plume.

The method used at the NNSS to characterize Pu-239/40 activities in soil takes advantage of the accuracy of the alpha spectroscopy isotopic analyses to establish Pu-239/40 to Am-241 ratios and the more representative Am-241 gamma spectroscopy results to provide a more reliable characterization of Pu activities at release sites.

To establish Pu/Am-241 ratios, the results from each release site are plotted to show the comparison of isotopic Am-241 and isotopic Pu results. Figure 6 shows data from an example site. If there is more than one source of radioactive contamination, the data may not show a linear trend or may show multiple linear trends. When this condition is observed, the data locations are examined with respect to the conceptual site model to determine whether there is a spatial distinction between the sources. If so, the conceptual site model is reevaluated and revised as appropriate to explain the observed results. The data shown in Figure 6 were evaluated, and it was determined that the data could be attributed to two different releases. The conceptual site model was modified to include two separate sources of contamination. The data from each source were plotted separately as shown in Figures 7 and 8. The isotopic Pu-239/40 and isotopic Am-241 data in these figures show very strong correlations (both coefficients of determination [R^2s] are greater than 0.98). Poor R^2 values, such as the one shown in Figure 6, may also indicate the presence of multiple release sources. If correlations are poor, inferring Pu isotopic activities from gamma spectroscopy Am-241 results should not be used. However, when the contamination is from a distinct source—even if the source is a mixture of releases—the comparison of isotopic Am-241 and isotopic Pu values should result in very strong correlations such as those shown in Figures 7 and 8. Strong correlations can also exist when the contaminant plume is a well-mixed composite from several releases. Figure 9 shows an isotopic Am-241 and isotopic Pu correlation from a location at the NNSS where the contaminant plume is a combination of seven different nuclear tests. The highly linear trends shown in these figures demonstrate the accuracy of the isotopic analyses.

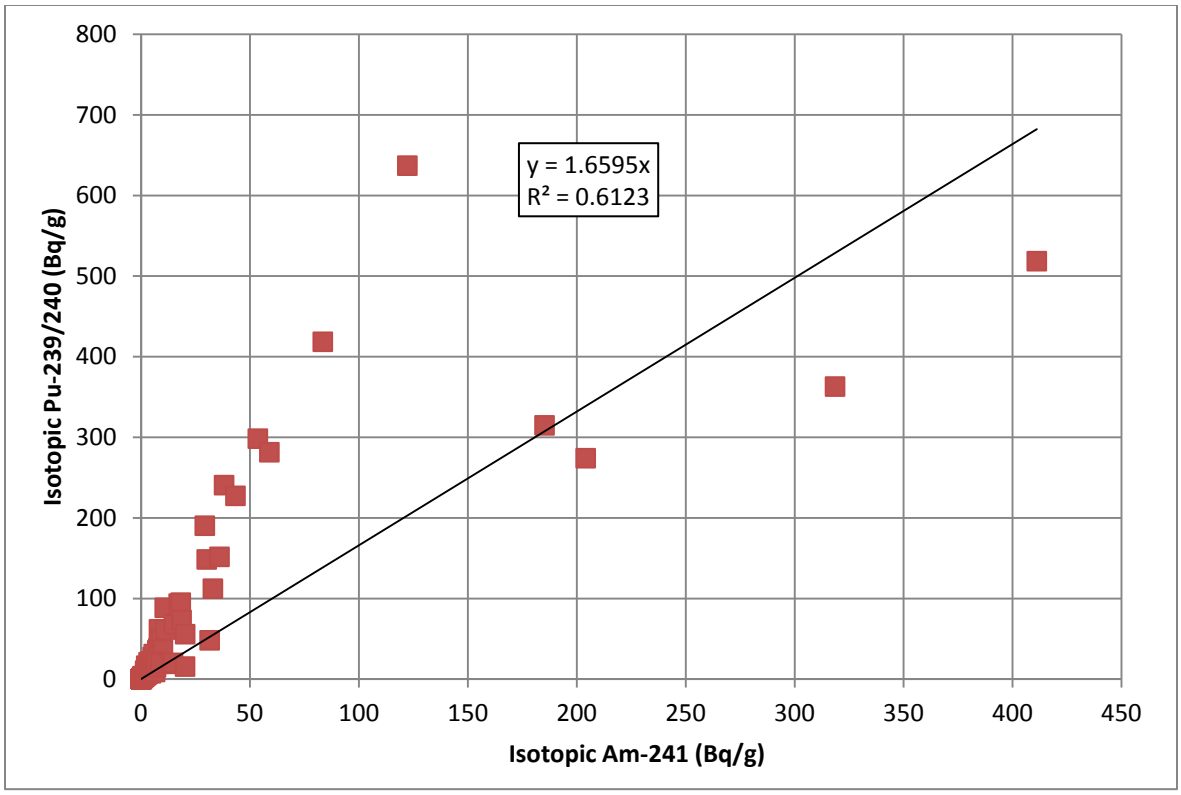

Fig. 6. Isotopic Am-241 to isotopic Pu-239/240 comparison.

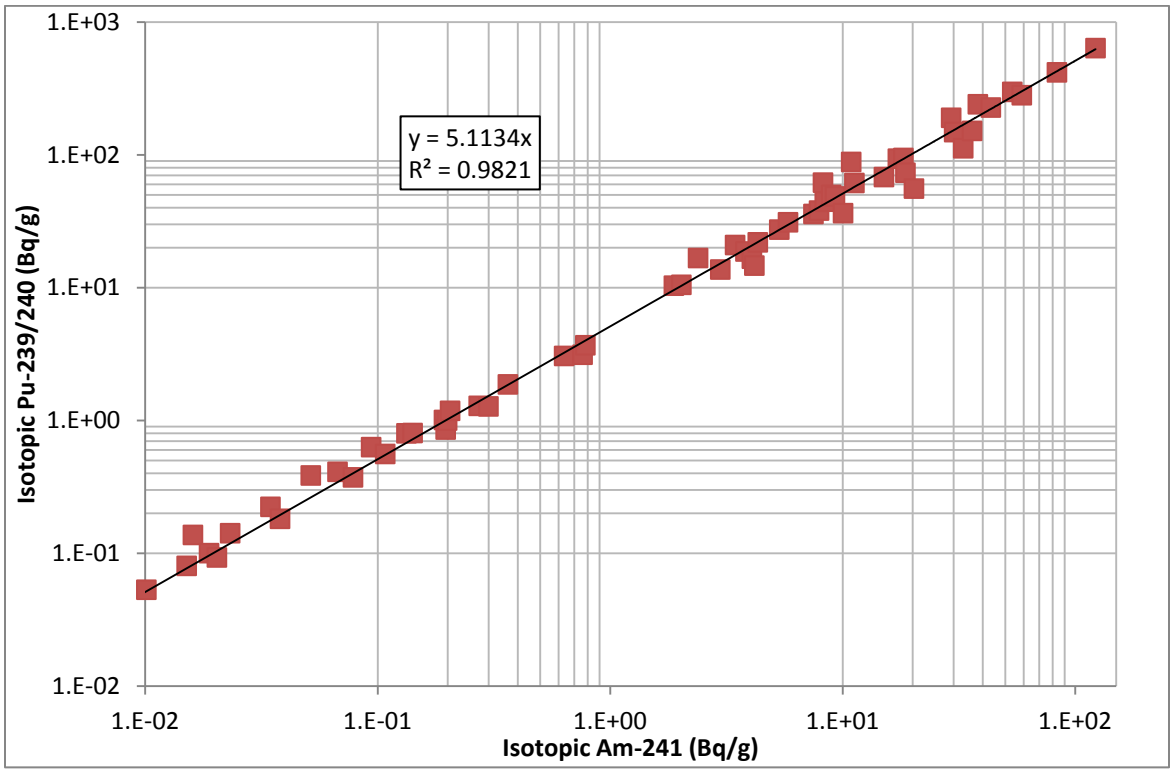

Fig. 7. Isotopic Am-241 to isotopic Pu-239/240 ratio.

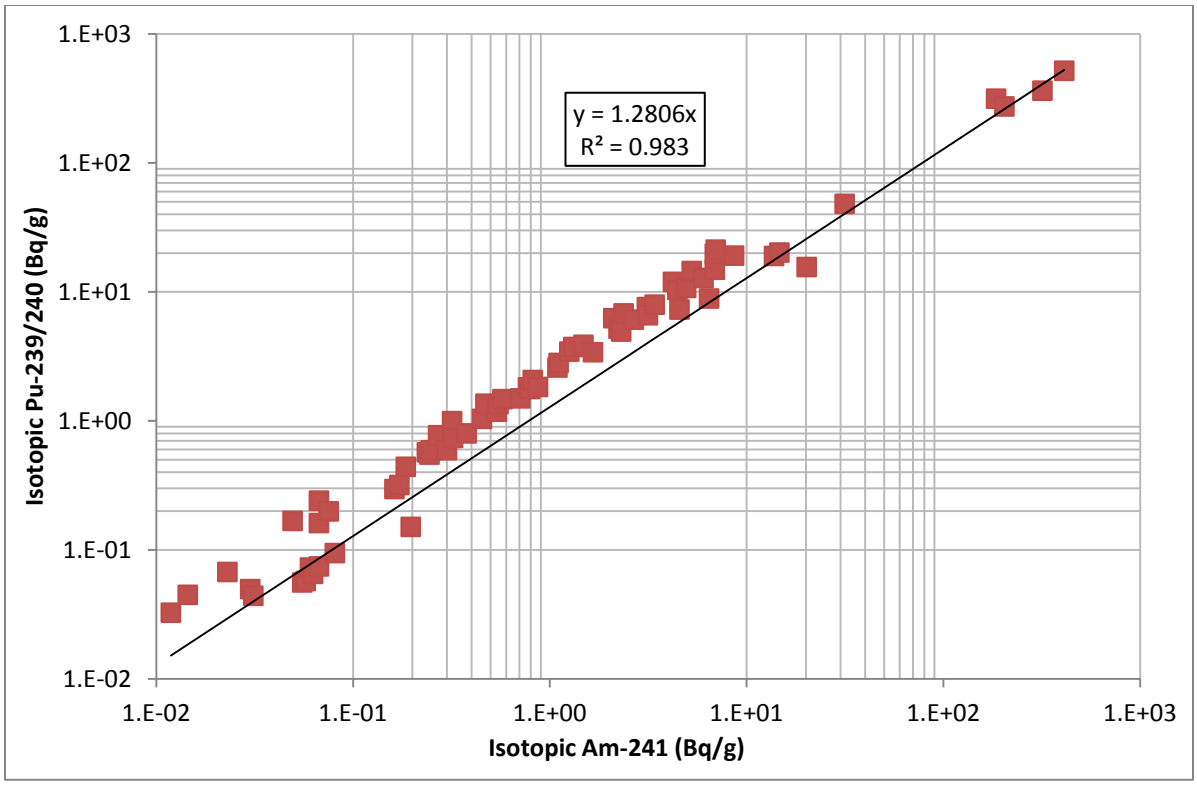

Fig. 8. Isotopic Am-241 to isotopic Pu-239/240 ratio.

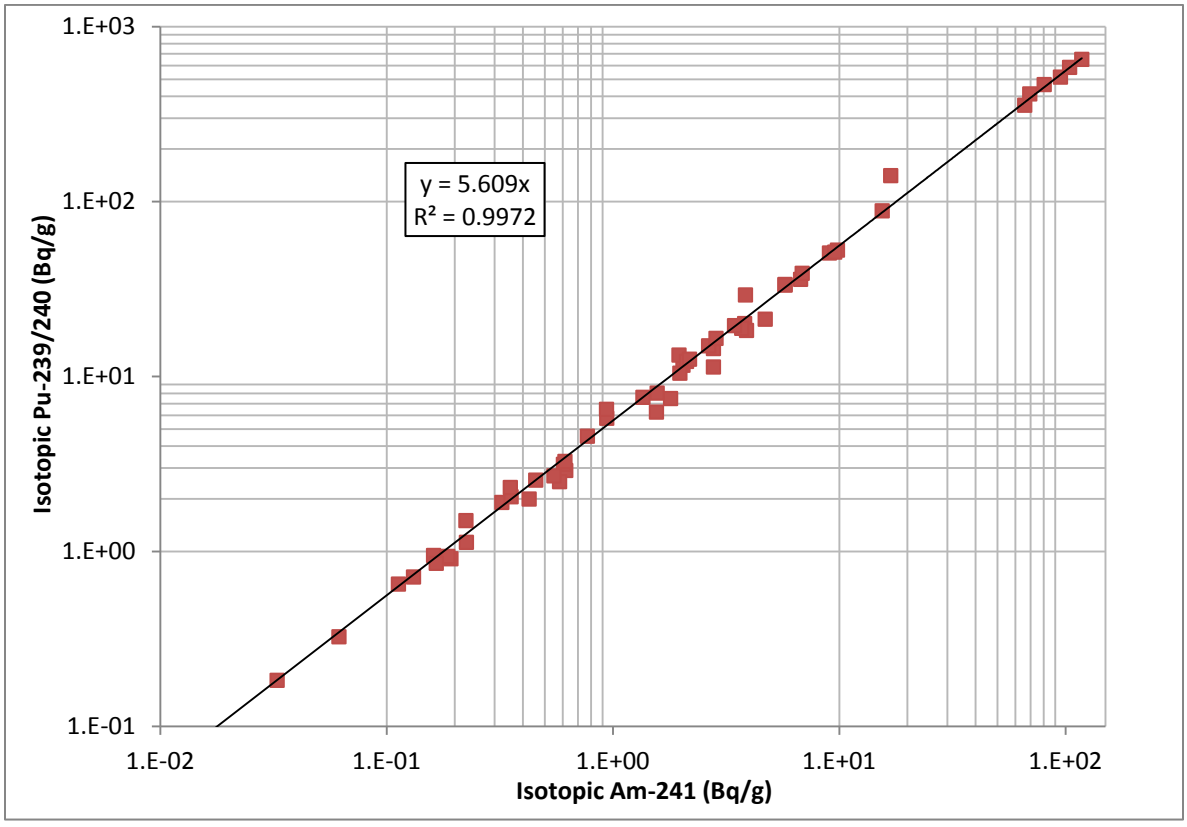

Fig. 9. Isotopic Am-241 to isotopic Pu-239/240 ratio.

CONCLUSIONS

Isotopic analyses results are very accurate in defining the activities of specific isotopes in the digested material, but they may not be representative of isotope activities in soil at a contaminated location when significant heterogeneity in the distribution of soil contaminants is present. However, the isotopic Pu-239/40 to Am-241 to Pu ratios can be determined with confidence using isotopic analyses. Am-241 activities that are representative of site contamination can be determined with high confidence using gamma spectroscopy analyses. Multiplying the gamma Am-241 result from each sample by the Pu-239/40 to Am-241 ratio will result in higher confidence in the characterization of Pu-239/40 contamination at the release site.

REFERENCES

1. Sill, C.W. (1971). "The Particle Problem as Related to Sample Inhomogeneity." In *Proceedings of the Environmental Plutonium Symposium*, LA-4756, Los Alamos National Laboratory, Los Alamos, NM.

2. Berhhardt, D.E. (1976). "Evaluation of Sample Collection and Analysis Techniques for Environmental Plutonium," ORP/LV-76-5, Office of Radiation Programs, LVF, USEPA, Las Vegas, NV, April 1976.

3. Kidman, L., P. Matthews, and K. Cabble. (2011). "Determining Corrective Action Boundaries at Nevada Test Site Aerially-Dispersed Radiological Release Sites – 11155," WM2011 Conference, Phoenix, AZ, February 27–March 3, 2011.

4. Kidman, R.L., H. Anagnostopoulos, P. Matthews, R. Boehlecke, and K. Cabble. (2010). "Methods to Determine Corrective Action Boundaries at Aerially-Dispersed Radiological Release Sites – 10334," WM2010 Conference, Phoenix, AZ, March 7–11, 2010.

5. Anagnostopoulos, H.W., R.L. Kidman, P.K. Matthews, J. Jones, J. MacDougall. (2009). "An Approach for Estimating the Total Effective Dose at Atmospheric Nuclear Weapons Test Sites –9235," WM2009 Conference, Phoenix, AZ, March 1–5, 2009.

6. Kidman, R.L., H. Anagnostopoulos, P. Matthews, J. Jones, R. Boehlecke, and J. MacDougall. (2009). "Determining Corrective Action Boundaries at Atmospheric Nuclear Release Sites," WM2009 Conference, Phoenix, AZ, March 1–5, 2009.