Comparison of Activity Determination of Radium 226 in FUSRAP Soil using Various Energy Lines - 12299

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ABSTRACT

Gamma spectroscopy is used at the Formerly Utilized Sites Remedial Action Program (FUSRAP) Maywood Superfund Site as the primary radioanalytical tool for quantization of activities of the radionuclides of concern in site soil. When selecting energy lines in gamma spectroscopy, a number of factors are considered including assumptions concerning secondary equilibrium, interferences, and the strength of the lines. The case of the Maywood radionuclide of concern radium-226 (Ra-226) is considered in this paper. At the FUSRAP Maywood Superfund Site, one of the daughters produced from radioactive decay of Ra-226, lead-214 (Pb-214), is used to quantitate Ra-226. Another Ra-226 daughter, bismuth-214 (Bi-214), also may be used to quantitate Ra-226. In this paper, a comparison of Ra-226 to Pb-214 activities and Ra-226 to Bi-214 activities, obtained using gamma spectrometry for a large number of soil samples, was performed. The Pb-214, Bi-214, and Ra-226 activities were quantitated using the 352 kilo electron volt (keV), 609 keV, and 186 keV lines, respectively. The comparisons were made after correcting the Ra-226 activities by a factor of 0.571 [1] and both ignoring and accounting for the contribution of a U-235 interfering line to the Ra-226 line. For the Pb-214 and Bi-214 activities, a mean in-growth factor was employed. The gamma spectrometer was calibrated for efficiency and energy using a mixed gamma standard and an energy range of 59 keV to 1830 keV. The authors expect other sites with Ra-226 contamination in soil may benefit from the discussions and points in this paper.

INTRODUCTION

There were several options considered for measurement of Ra-226 in soil using gamma spectroscopy.

1. The Ra-226 may be quantitated directly by measuring the intensity of the 186 keV energy line.

2. Pb-214, a radioactive decay daughter of Ra-226, may be measured after a 21 day in-growth period.

3. Bi-214, another radioactive decay daughter of Ra-226, may be measured after a 21 day in-growth period.

For the second and third options, the 21 day in-growth represents approximately six half-lives of the Ra-226 daughter, radon-222 (Rn-222). Secondary equilibrium for this must be established before it is established for Pb-214 and Bi-214, which have shorter half-lives.

If it is determined that measurement of Pb-214 or Bi-214 is more favorable than direct Ra-226 measurement, then development of an in-growth curve may be established to expedite determination of the Ra-226 activity. The in-growth curve allows the analyst to use the ratio of the final activity (when secondary equilibrium has been established) of Pb-214 or Bi-214, each of which equals the Ra-226 activity, to the activity of Pb-214 or Bi-214 on day X, a day between 0 and 21 days. Please note that the energy values provided in this paper were taken from the Evaluated Nuclear Structure Data File (ENSDF) provided by the National Nuclear Data Center at the Brookhaven National Laboratory [2]If other energy reference libraries are used, energy values may vary by as much as ± 0.5 keV.

This paper discusses the advantages and disadvantages of each option as considered for the FUSRAP Maywood Superfund Site. It also examines the activity ratios of Ra-226:Pb-214 and Ra-226:Bi-214 in an attempt to identify potential biases in the measurements.

METHOD

Due to the timely decision-making demands of the construction aspects for remediation of radiologically contaminated properties, waiting 21 days for in-growth of Ra-226 daughters to occur was not considered to be a good option. Therefore, either development of a 21-day in-growth curve followed by measurement of either Pb-214 or Bi-214, or direct measurement of Ra-226, was preferred. In order to choose one of these options, the advantages and disadvantages of each were considered.

In the case of direct measurement of Ra-226, an advantage was that one is measuring the actual analyte of interest. The analyst would not have to be concerned about possible disruption of secondary equilibrium due to loss of any Ra-226 daughters, in particular Rn-222. The major disadvantages of direct measurement considered were:

- The yield of the 186.21 keV line is only 3.6% and all other Ra-226 gamma ray lines are insignificant (<0.005%).
- The 186.21 keV line is subject to potentially significant interference from U-235, which has an energy line at 185.71 keV, which is within 0.5 keV of the Ra-226 line.

This is particularly important if the Ra-226 is present due to the decay of naturally occurring radioactive material (NORM) since Ra-226 is a daughter of U-238 and U-234. If this is the case, Giles [1] has shown that for every seven gamma rays counted by the gamma spectrometer, four are due to the Ra-226 and three are due to the U-235. Therefore, by multiplying the overall signal by 4/7 or 0.571, one obtains the contribution from Ra-226.

The correction described in disadvantage 2 assumed that the U-238 and Ra-226 are in secular equilibrium in the environment. In a dynamic environment, even this theoretical contribution from U-235 may vary depending upon the difference in the solubilities of uranium and radium salts. For this reason, and the low yield of the 186.21 line, commercial laboratories typically do not measure Ra-226 in soil directly using gamma spectroscopy.

In the case of the measurement of Pb-214 or Bi-214, a mean ratio between the activity after 21 day in-growth and the activity at time zero was first developed. A volume of sample was prepared (dried, ground, and homogenized), then distributed into several sample containers. The containers were sealed to be air tight to prevent escape of radon gas since Rn-222 is in the Ra-226 decay chain and must be retained in order for secondary equilibrium of the Pb-214 and Bi-214 daughters to occur. The sample set was then measured at discrete intervals during the 21 day period. The greater the number of times the set is measured over the 21 day period, the better defined the in-growth curve would be.

The Pb-214 or Bi-214 activity concentration (ordinate) in picocuries per gram (pCi/g) was plotted versus time (abscissa) in days. After the in-growth curve was constructed, a correction factor was subsequently applied to actual samples depending upon the time elapsed from the moment the sample was sealed. The advantages of using the Pb-214 or Bi-214 to measure Ra-226 were that both isotopes have significantly higher yields than the Ra-226 line thus giving a better signal-to-noise ratio at a given activity, and they have multiple lines that may be used giving the analyst more options to use lines that are less prone to possible interferences. A disadvantage of using Pb-214 or Bi-214 is the additional error incurred by the error in the activity obtained from the in-growth curve.

For FUSRAP Maywood Superfund Site samples, the mean correction factor was the mean ratio of the activity at 21 days versus the activity at time zero, where “time zero” is defined as a time soon (within approximately 1 hour) after the sample container was sealed. For actual field samples to which the correction factor is applied to obtain the Pb-214 or Bi-214 activity, the correction factor, and therefore the activity, would be overestimated if the sample was counted at a time greater than one hour after being sealed.

DISCUSSION

In an attempt to determine the relative errors and biases associated with the measurement of Ra-226, Pb-214, and Bi-214, data was obtained from 975 soil samples collected from various properties at the FUSRAP Maywood Superfund Site in Maywood, New Jersey. The data were obtained from one of three high purity germanium P-type detectors, closed-end coaxial, with a resolution of 2.0 keV @ 1332 keV. Signal processing is performed using the DSPEC jr TM and software is Gamma Vision Advanced Measurement Technologies, also known as: AMETEK or ORTEC [3].

The Pb-214 data was corrected using a mean in-growth factor of 1.35 obtained from construction of an in-growth curve. The Bi-214 results were also corrected by a factor of 1.35. The Bi-214 data does not have an associated in-growth curve. The in-growth factor for Bi-214 was assumed to be the same as that for Pb-214.

The Ra-226 results were corrected to account for the contribution from U-235. The correction factor of 0.571 is obtained from Giles [1]. Giles [1] shows that for naturally occurring uranium, which contains U-238, U-234 and U-235, and which contains Ra-226 as a daughter in the uranium decay series, three out of every seven gamma rays at (or approximately at) 186 keV are due to U-235. Thus the Ra-226 activity obtained from measurement of the gamma signal at 186.21 keV was corrected by multiplying by 0.571 (4/7).

In addition, 105 of the 975 were determined to be outliers possibly due to the presence of elevated uranium, and were therefore removed from the calculation. Outliers were defined as points whose Ra-226:Bi-214 or Ra-226:Pb-214 ratio fell more than1.5 interquartile range above the third quartile of the data set. These outlier points showed higher Ra-226 values, presumably because the U-235 contribution for these points was higher, and therefore the Ra-226 contribution to the overall 186 keV signal was lower—i.e., the correction factor should have been lower than 0.571 for these points to account for the smaller percentage of Ra-226.

During further analysis of the lab data, it was discovered that the Ra-226 energy line used to obtain this data, 185.99 keV, and its associated yield 3.28%, was outdated. The currently accepted Ra-226 energy line and yield vales are 186.21 keV and 3.59% [2]. Use of the lower yield would have overestimated the Ra-226 by 0.0359/0.0328, or a factor of 1.0945.

All samples are allowed to equilibrate with respect to radon by holding the samples for 21 days to allow ingrowth of daughters potentially lost during the sampling process. Samples are counted within 12 hours after being held for 21 days. To account for the small amount of radon daughters (about 2%) that do not ingrow over 5.5 half lives, an additional correction factor of 1.02 was applied to the data.

The mean, standard deviation, and median values of the activity ratios were therefore adjusted and are shown in Table I.

Table I. Sample Statistics.

Statistic	Ra-226:Pb-214	Ra-226:Bi-214
Mean	1.03	1.08
Standard Deviation	0.29	0.30
Median	0.98	1.02

It's important to note that though the mean and median values for the data set were nearly unity, the standard deviation suggests that the actual ratio does vary somewhat from sample to sample. In practice, the ratios were typically found to be between 0.5 and 1.5. This can be seen visually in Figure 1. The red and green bars represent levels two standard deviations above and below the mean ratio.

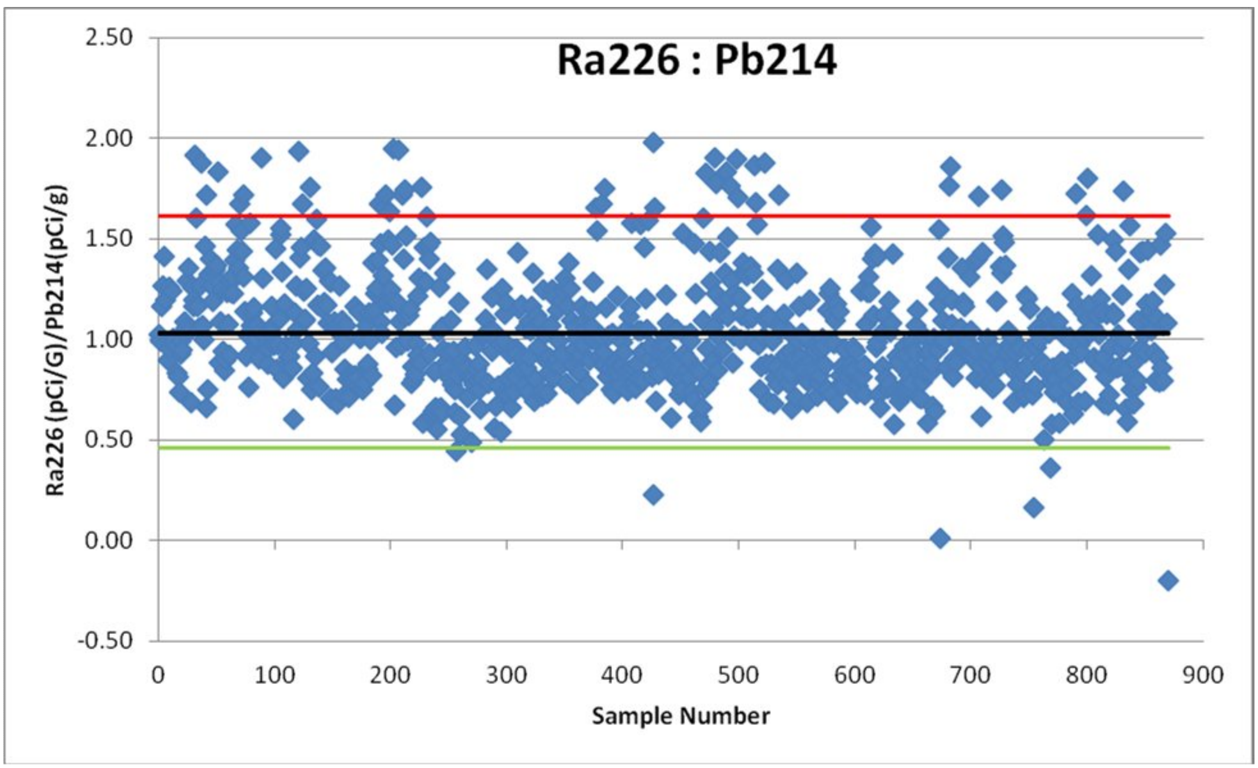

Fig 1.Ra-226:Pb-214.

In order to examine the correlation between data from each of the three radionuclides the data for each component was plotted against each other. A plot of the Ra-226 against the Pb-214 data is shown in Figure 2 and a plot of Ra-226 against Bi-214 is shown as Figure 3.

The slopes of the best-fit line would ideally be unity with an R^2 value of 1, indicating perfect 1:1 correlation between the radionuclides. In practice, the slopes of the best-fit lines were slightly higher, with a value of 1.029 for Pb-214 and 1.041 for Bi-214 indicating a slightly higher bias for the Ra-226 activity. This higher bias may be due in part to elevated U-235, as well as greater susceptibility of the Ra-226 line to Compton interference. It also may be due to a lesser degree to Cesium 137 from nuclear testing fallout backscatter occurring at 184 keV.

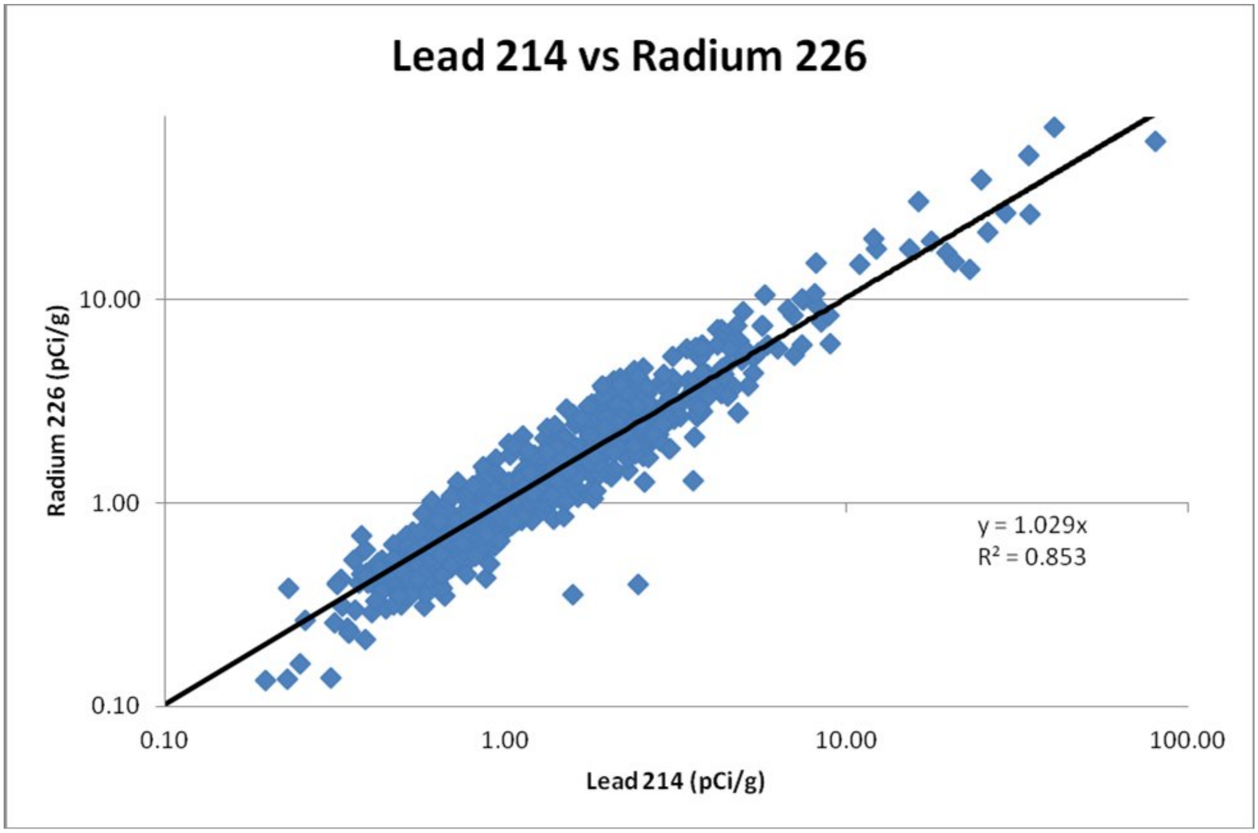

Fig 2. Ra-226 vs. Pb-214.

The correlation between the radionuclides is moderate, with the Ra-226 vs. Pb-214 and Ra-226 vs. Bi-214 displaying correlation coefficients of 0.853 and 0.837, respectively. Though the data shows definite correlation between Ra-226 and Pb-214 and Bi-214, the fact that the correlation coefficients are not closer to unity is likely due to the (relatively) high error associated with Ra-226 measurements, discussed later in this paper, as well as potential additional difficulty in assessing whether high level activity samples truly represent NORM material rather than material contaminated with excess Uranium, which would not be properly accounted for using the correction factors previously discussed.

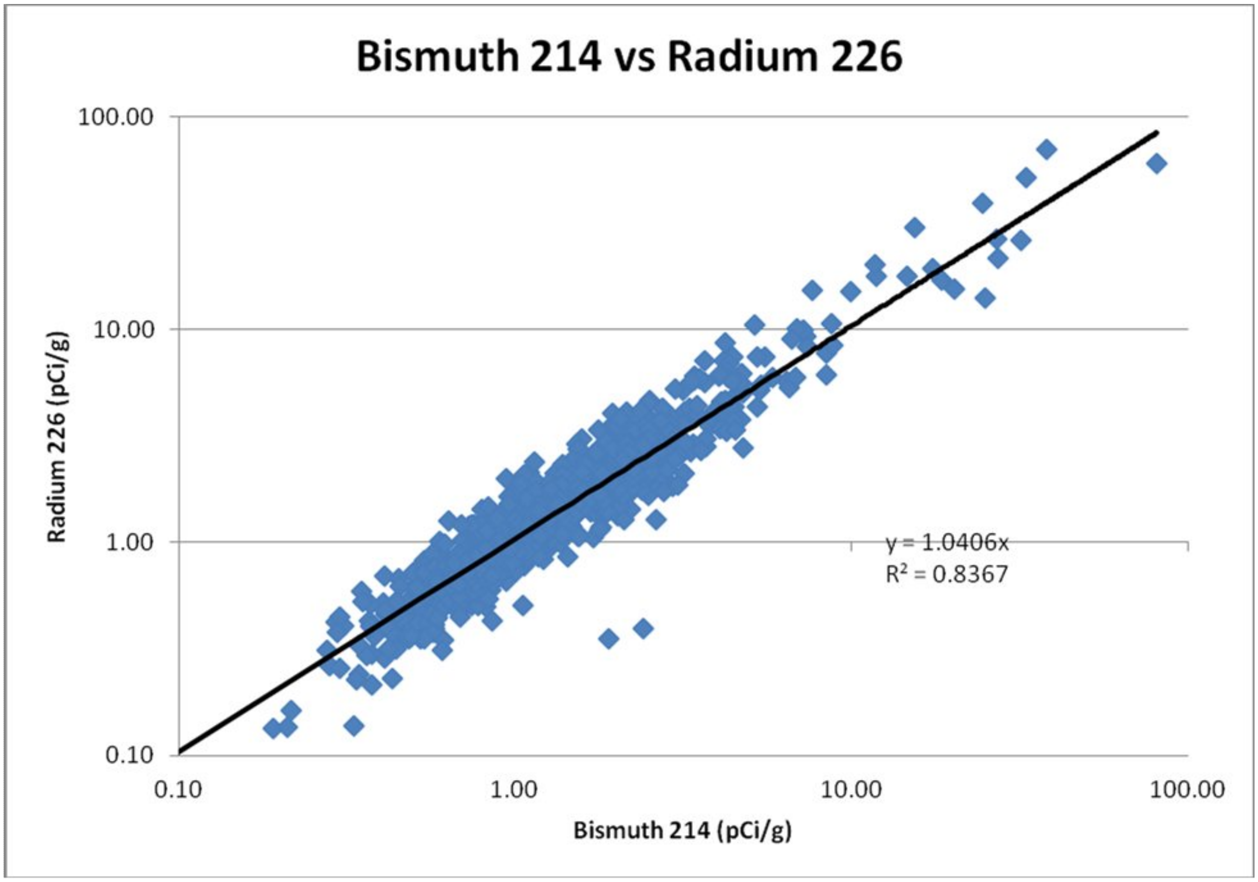

Fig. 3. Ra-226 vs. Bi-214

To check laboratory performance, Pb-214 results were compared to Bi-214 results. Because Bi-214 is a daughter of the short lived Pb-214, the two radionuclides should have essentially identical activities. In order to check this in the Maywood data set, activities of the two radionuclides for each of the samples were plotted against each other. The plot of Bi-214 vs. Pb-214 in Figure 4 shows very good agreement with a slope of 0.9802 and a correlation coefficient of 0.997, which is to be expected.

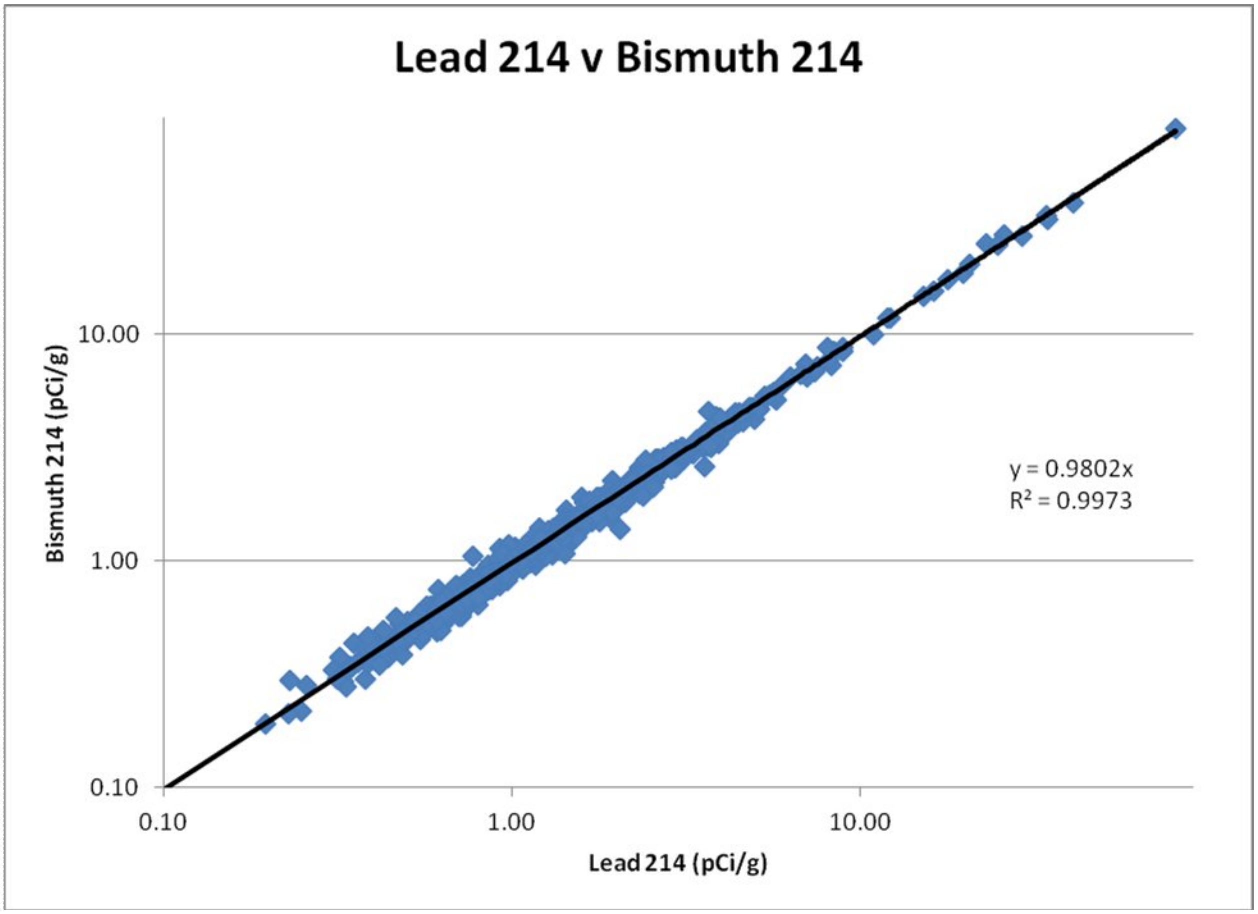

Fig 4. Pb-214 vs. Bi-214

STATISTICAL TESTING

In order to determine whether or not there is a statistically significant difference between data obtained from any pair of radiounclides, a Kolmogorov-Smirnov test was performed for each pair (i.e., Ra-226 to Pb-214, Ra-226 to Bi-214, and Pb-214 to Bi-214). The Kolmogorov-Smirnov test is a nonparametric test used to compare two sample distributions. The null hypothesis in the test is that the samples are drawn from the same distribution. The R statistical software package was used to perform the evaluation. A value of 0.15 was selected as the critical p-value which would cause a rejection of the null hypothesis and show that the data was significantly different. The results of the tests showed that there was no statistically significant variation between the data sets at the 0.15 significance level and as such, the null hypothesis, that all the data appears to have come from the same distribution, could not be rejected. P-values for each pair are presented in Table II.

Table II - Kolmogorov-Smirnov Test Results

	Test Statistic	**P-value**	**Null Hypothesis**
Radium 226 and Lead 214	0.0517	0.1949	*Accept*
Radium 226 and Bismuth 214	0.0483	0.2627	*Accept*
Lead 214 and Bismuth 214	0.0356	0.6387	*Accept*

ERROR ANALYSIS

It should be noted that one significant difference between the Ra-226 186 keV line and the gamma lines from Pb-214 and Bi-214 is that the errors associated with results from the 186 keV line generally tend to be significantly higher than those of the other two. The average and median errors for each line are given in Table 3. As such, even though it has been shown that one may correct for the effects of interference from U-235, the low energy line will still have a greater uncertainty associated with it, and as such may be of less use when evaluating samples with activities near the project action level.

Table III - Associated Errors

Radionuclide (energy)	Average Error	Median Error
Ra-226 (186 keV)	45.4%	31.0%
Pb-214 (352 keV)	14.0%	13.2%
Bi-214 (609 keV)	14.2%	13.4%

CONCLUSIONS

Proper use of correction factors and comparison of the data from three different gamma-emitting radionuclides revealed agreement with expectations and provided confidence that using such correction factors generates quality data.

The results indicate that if contamination is low level and due to NORM, the Ra-226 can be measured directly if corrected to subtract the contribution from U-235. If there is any indication that technologically enhanced uranium may be present, the preferred measurement approach for quantitation of Ra-226 activity is detection of one of the Ra-226 daughters, Pb-214 or Bi-214, using a correction factor obtained from an in-growth curve. The results also show that the adjusted Ra-226 results compare very well with both the Pb-214 and Bi-214 results obtained using an in-growth curve correction factor.

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