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ISOTOPIC RATIO METHOD FOR DETERMINING
URANIUM CONTAMINATION
by
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The presence of high concentrations of uranium in the subsurface can be attributed either to contamination from uranium processing activities or to naturally occurring uranium. A mathematical method has been employed to evaluate the isotope ratios from subsurface soils at the Rocky Flats Nuclear Weapons Plant (RFP) and demonstrates conclusively that the soil contains uranium from a natural source and has not been contaminated with enriched uranium resulting from RFP releases. This paper describes the method used in this determination which has widespread application in site characterizations and can be adapted to other radioisotopes used in manufacturing industries. The determination of radioisotope source can lead to a reduction of the remediation effort.

Uranium occurs naturally and has been extensively mined from the Coal Creek Canyon area, upgradient of the RFP located along the Front Range of the Rocky Mountains, near Boulder, Colorado. Due to the proximity of the RFP to the natural uranium ore bodies and the depositional environment of the geologic materials at the RFP (alluvial fan), localized accumulations of uranium would not be unexpected.

Weapons production at the RFP over the past 40 years has made use of plutonium, highly enriched uranium, and depleted uranium. Enriched uranium and depleted uranium are manufactured by altering the natural isotopic ratios. The process for manufacturing unnatural forms of uranium for nuclear weapons production occurred at other Department of Energy facilities and transported to the RFP. If even small amounts of either enriched or depleted uranium have been released to the RFP environment through RFP processes, then the natural isotope ratios will have been altered. The natural isotope ratios for uranium are:

- $U^{238} = 0.99283$
- $U^{235} = 0.00711$
- $U^{234} = 0.000054$
- $U^{236} = 0.000006$

The enriched uranium used at the RFP in weapons production typically has the following isotopic ratios:

- $U^{238} = 0.0532$
- $U^{235} = 0.9324$
- $U^{234} = 0.0101$
- $U^{236} = 0.0043$

The depleted uranium used at the RFP in weapons production and other metallurgical processes typically has the following isotopic ratios:

- U^{238} = 0.99772
- U^{235} = 0.00227
- U^{234} = 0.00000596
- U^{236} = 0.00000404

The relative isotopic ratios of these three forms of uranium are graphically shown on Figure 1.

Generally, uranium isotope activities are reported in picoCuries. In order to determine the isotope ratio of U^{234} to U^{238} in a given sample, the number of atoms of each isotope in the sample must be computed. The number of atoms is related to the activity by the equation:

$$Activity = N\lambda$$

Where:
N = number of atoms
λ = decay constant = $0.693/T_{\frac{1}{2}}$
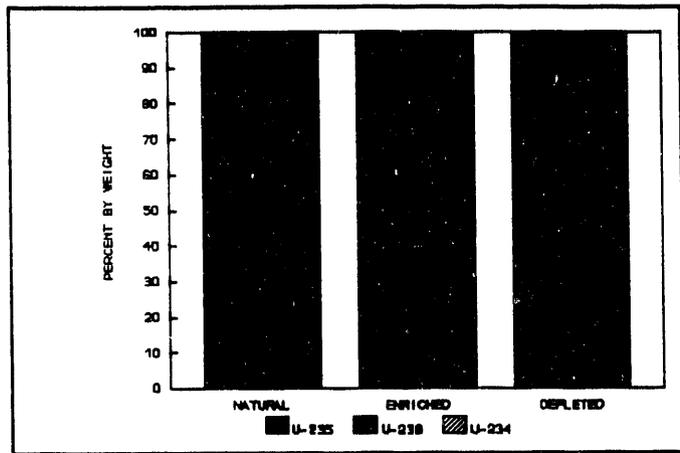
$T_{\frac{1}{2}}$ = halflife constant

Figure 1 Isotopic ratios

The number of atoms of each isotope is given by: $N = Activity/\lambda$

The halflive constants ($T_{\frac{1}{2}}$) for the uranium isotopes are:

- U^{238} = 4.51 x 10^9 years
- U^{235} = 7.1 x 10^8 years
- U^{234} = 2.47 x 10^5 years
- U^{236} = 2.39 x 10^7 years

The corresponding decay constants (λ) are:

- U^{238} = 1.54 x 10^{-10} years^{-1}
- U^{235} = 9.76 x 10^{-10} years^{-1}
- U^{234} = 2.806 x 10^{-6} years^{-1}

N, the number of atoms, is calculated by dividing the activity of each uranium isotope in a single sample, as determined through laboratory analysis, by the decay constant for the corresponding isotope. A ratio of Ns for different isotopes is calculated and compared to the same ratio as natural uranium. The naturally occurring ratio of U^{234} to U^{238} is 5.43 x 10^{-5}. The enrichment process yields a U^{234} to U^{238} ratio of 0.19; four orders of magnitude greater than natural uranium.
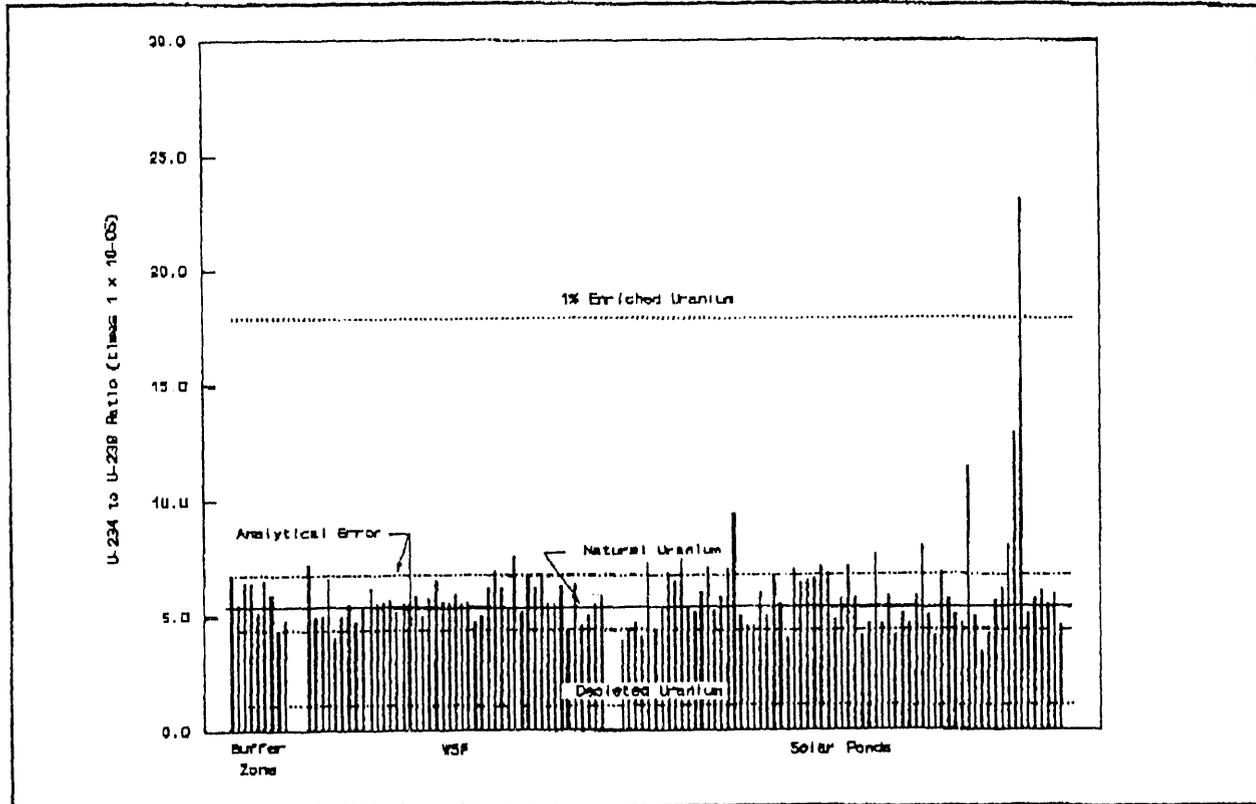

Figure 2 $U^{233,234}$ to U^{238} Ratio per Sample

Using this procedure and activity data collected in the 1986 and 1988 soil sampling programs at the West Spray Field (WSF) area of the RFP, ratios of $U^{233,234}$ to U^{238} were computed. $U^{233,234}$ was used because it was provided from the laboratory analyses. U^{233} is a very small component of uranium because it is not a naturally occurring isotope. Its use at the RFP had been very limited and it is not expected to be present in enriched, depleted, or naturally occurring sources of uranium. Each bar in Figure 2 represents the ratio of $U^{233,234}$ to U^{238} for each sample. The center horizontal line illustrates the natural ratio of 5.34 x 10^{-5}. The upper and lower horizontal lines represent the error inherent in the analytical procedure due to lack of precision. This error range was obtained from the scatter in the data attained from samples collected from the upgradient buffer zone in 1986. It should be noted that the nine samples collected for determining background is small in comparison to the number of samples

that if additional samples were collected for determination of background, the range of analytical error would increase.

Calculations of the amount of contamination resulting from the enrichment process were computed. A one percent enrichment contamination, i.e., one percent of the uranium present is enriched uranium, would result in a $U^{233,234}$ to U^{238} ratio of 1.56×10^{-4}. This line is shown on the graph to indicate how even a very small amount of enriched uranium contamination is dramatically demonstrated by this presentation method.
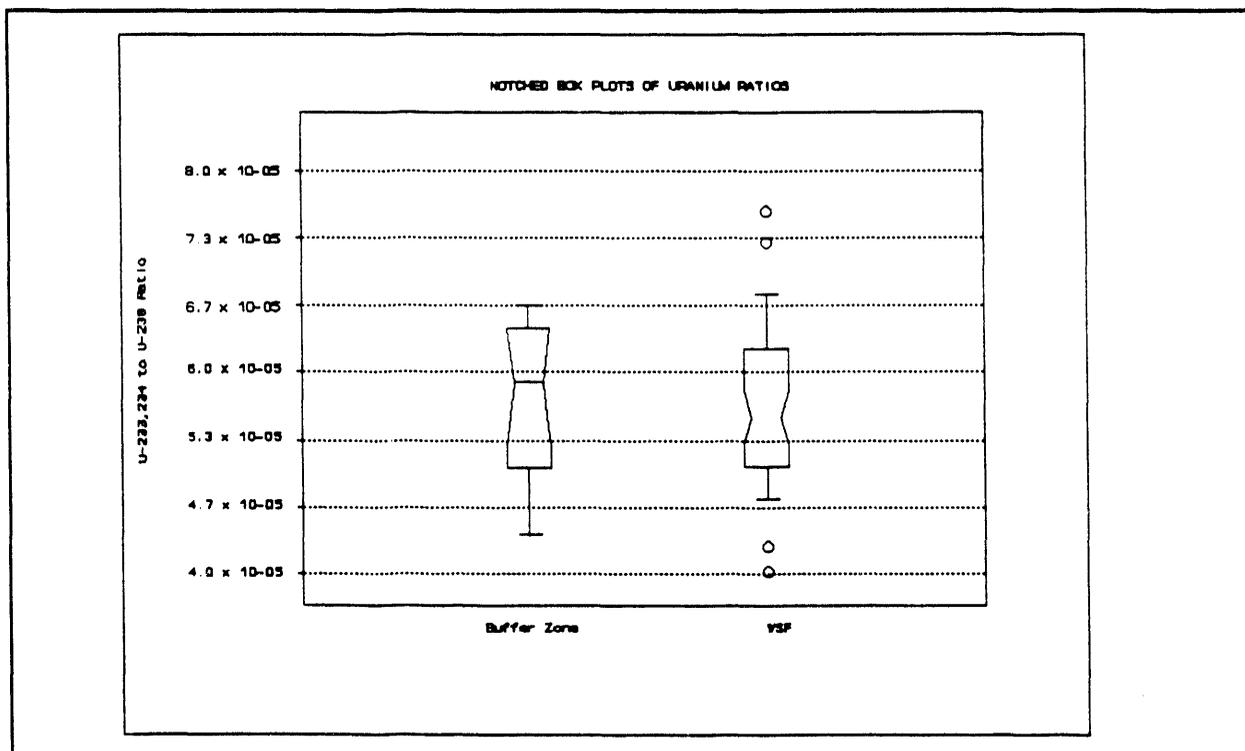

Figure 3 Notched Box Plots

A statistical analysis was performed on these data to numerically identify whether the data collected from WSF are different than the background data collected in 1986. The analysis involved a comparison of median values as opposed to means because medians are not affected by outliers. The probability of having outliers is greater in data collected from the WSF than background because of the number of sample observations (45 and 9, respectively). A notched box plot was produced to graphically show that the medians are not significantly different (Figure 3). The notched box plot was used to summarize the center and spread of the two data sets. Box plots are typically used to compare data that are random in time and space. This is not the case for the data used; however, because both data sets are not random in time or space, the use of a box plot is valid for a side-by-side comparison. The notches of the two boxes overlap which means that the medians of the data sets are the same with a 95 percent level of significance. A 95 percent level of significance is used loosely because the data are not

random. Furthermore, both notches overlap the natural ratio of 5.43 x 10⁻⁵, which suggests that the median values for the buffer zone and the WSF are not significantly different than the natural ratio.

Solar ponds are located in the manufacturing area of the RFP. Uranium isotope ratios from the RFP solar pond area soil samples were compared to the WSF samples for two reasons. First, it is known that the solar ponds received uranium-contaminated liquids (enriched and depleted) during their 35-year use. It is speculated that an unnatural isotope ratio may most likely be seen in soil samples from the solar pond area then from other areas of the RFP. Second, if unnatural ratios are seen in solar pond samples, then unnatural ratios may be expected in the WSF as well because solar pond water was sprayed at the WSF.

The samples evaluated consist of 45 samples from the WSF and 67 samples from the solar pond area. The solar pond samples indicate three samples with enriched uranium contamination levels greater than one half of one percent. However, none of the WSF samples exceed even this very low level of contamination. Therefore, it can be stated conclusively that the soil at WSF contains natural uranium, not enriched uranium.

The RFP produced depleted uranium in addition to enriched uranium. Depleted uranium is by definition uranium which has less of the fissionable U^{235} than the approximate 0.7 percent by weight found in natural uranium. Depleted uranium is rich in the U^{238} isotope. Because the solar ponds received liquid waste from both depleted and enriched uranium processes, the uranium isotope ratios may be reflective of either depleted uranium (very high in U^{238}, very low in U^{234}) or enriched uranium (very high U^{235}, proportionately higher U^{234}, and lower U^{238}). A combination of contamination from both enriched and depleted uranium in a given soil sample would produce an isotopic ratio reflective of the relative amounts of both types of uranium. Although it is theoretically possible to have the exact relative amounts of both depleted and enriched uranium in one sample to produce an overall isotopic ratio that falls within the range of natural uranium, the likelihood of this occurring is extremely low. If both depleted uranium and enriched uranium are present, the ratio of U^{234} to U^{238} would be noticeably different than in natural uranium. As can be seen in Figure 2, the presence of an amount of enriched uranium as small as one percent of total uranium is strikingly noticeable. Up to 30 percent of depleted uranium contamination would be masked by the analytical error with this method of presentation. Isotopic analyses of uranium is sensitive to small variations in the type of uranium present.

The analytical error in the measurement of uranium isotope activities in groundwater is such that the method described above yield inconclusive results. However, the source of unnatural materials at WSF was derived from the spray application of solar pond water. This sprayed water was applied only to the ground surface. Therefore any contamination of groundwater from spray activities must have come from contaminated water percolating through subsurface soil. As demonstrated, uranium present in subsurface soil

is from a natural source. It can be deduced that underlying groundwater could not be contaminated with enriched uranium if the subsurface soil does not contain uranium in enriched form.

This method of isotopic ratio analysis can be applied very quickly and inexpensively. Other radioisotopes can be used in the same manner to help identify the source of radionuclides and more appropriately direct the remediation program.

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