Y-12

OAK RIDGE Y-12 PLANT

LETTER REPORT:

RADIOLOGICAL ANALYSIS OF OAK RIDGE Y-12 PLANT GROUNDWATER DATA

MARTIN MARIETTA

June 22, 1995

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Prepared by:

H&R TECHNICAL ASSOCIATES, INC.
Under Purchase Order 90Y-TK532C

for the

Environmental Management Department
Health, Safety, Environment, and Accountability Organization
Oak Ridge Y-12 Plant
Oak Ridge, Tennessee

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Managed By
LOCKHEED MARTIN ENERGY SYSTEMS, INC.

for the
U.S. DEPARTMENT OF ENERGY
Under Contract
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To: Kevin Jago
From: Phil Walsh
Date: June 22, 1995
Subject: Radiological Analysis of Oak Ridge Y-12 Plant Groundwater Data

The Y-12 Plant groundwater radiological data bases have been analyzed to determine whether historical and current data is suitable for unqualified release to various user groups. User groups include those who routinely compare results to reference standards or regulatory levels, conduct hydrogeological transport studies, conduct statistical analyses and conduct risk assessment studies. This analysis will help to inform user groups about radiological caveats and limitations associated with the data.

The overall methodology used for the radiological analysis is to check whether results are consistent with chemical and physical expectations, plant operational history and, where applicable, with results from other sites. For example, the relationship among isotopes in a decay chain are predictable if no unusual sources for a particular isotope in the chain exist, the time history is known, and differential removal or concentration mechanisms for a particular isotope are understood or do not exist. Similarly, background concentrations for radioisotopes (e.g. ^{238}U , ^{234}U , ^{235}U , ^{230}Th , ^{226}Ra , etc.) should be consistent with those obtained in other studies given similar mineralogical or hydrogeological conditions at the Y-12 Plant.

If the analysis results in lack of agreement between results and expectations based on known relationships, plant operations and transport parameters, then results are investigated further. If no explanation can be found for the unexpected results, they are suspect unless they are confirmed by repetition. Confirmed results not in agreement with reasonable expectations stimulate investigation of the entire sample collection and analytical laboratory system. Process and environmental transport parameters may also be reviewed. Radiological analysis is a continuing process. This particular analysis is

essentially a "snapshot in time" and focuses on some main issues. Each issue summarized here and others could be addressed in more detail. No attempt is made to address future changes in regulations or procedures.

Activities at the Y-12 Plant have primarily involved uranium processing at various levels of enrichment in ^{235}U . Therefore ^{238}U and ^{235}U decay series isotopes have been continuously monitored in various media. For a brief period of time (early 1960s) from a historical perspective, reactor fuel elements containing transuranics, activation products and fission products were processed. Also for a brief period of time some thorium processing was conducted at the Y-12 Plant but thorium cycle reactor fuel elements were not processed.

ORNL also conducted biological research and other research at the Y-12 Plant that utilized fission products, transuranics and accelerator-produced isotopes.

Based on these general activities, a wide array of radioisotopes have been monitored and alpha, beta and gamma screening measurements have been conducted. The monitoring history of the Y-12 Plant and DOE, EPA and Tennessee requirements have resulted in procedure changes over the years and to changes in radioisotopes and sites monitored.

Current users of the radioisotope data must consider whether the historical data base is suitable for their purposes. At most sites monitored radioisotope levels are either near variable background levels or so low that counting errors are high compared to mean levels of the isotopes. Reduction of counting errors would require time-consuming sample preparation methods to reduce interferences and longer counting times. Significant reduction of counting error is more a practical level of effort/economics issue than a technical issue. As the number of samples and isotopes analyzed can be reduced, results for the remaining ones can be more precise.

Uranium and Thorium Series Isotopes

An important question is whether background levels of radioisotopes in groundwater based on historical data are reliable. Of particular importance for the Y-12 Plant Site are the natural radionuclides in the ^{238}U and ^{235}U series, which exhibit highly variable natural levels for uncontaminated sites.

Details on the decay schemes for the natural radionuclides are taken from the Radiological Health Handbook or from a chart of the nuclides. For natural radionuclides in geological materials that have not been disturbed, secular equilibrium is often observed among radioisotopes down the chains until a gaseous element is produced (^{222}Rn , ^{220}Rn , ^{219}Rn). For chains that have been disturbed, near equilibrium is observed for isotopes with similar chemistry (e.g. uranium isotopes) or for isotopes which have short half lives relative to their parents and relative to time between processes that may separate them. For radionuclides leached into water, equilibrium may be upset by differential solubility and may not have time to reestablish if water turnover times are less than or of the same order of magnitude as radiological half lives.

Enrichment of fissionable ^{235}U (0.7% of natural uranium on a mass basis) will usually enrich ^{234}U and will result in proportionately much higher specific activities of enriched uranium compared to natural U. Natural U contains about 0.67 $\mu\text{Ci/g}$ of radioactivity (0.33 $\mu\text{Ci/g}$ of ^{238}U and ^{234}U and 0.014 $\mu\text{Ci/g}$ of ^{235}U). Therefore, water containing about 1 ppb of natural U on a mass basis contains about 0.67 pCi/L on an activity basis. Water containing 1 ppb of enriched uranium on a mass basis contains proportionately higher activity levels. For example, water containing 1 ppb of uranium enriched to 95% in ^{235}U by the gaseous diffusion process would exhibit activity levels of about 67 pCi/L. Over 95% of this activity is from ^{234}U which is enriched along with the ^{235}U .

For all the groundwater measurements conducted at the Y-12 Plant Site, discussed further below, a general consistency in results for total uranium, ^{238}U and ^{234}U supports

the conclusion that contamination of groundwater by enriched uranium has not been extensive. The wells exhibiting the highest U contamination levels (the S-3 Site) usually have lower ^{234}U levels than ^{238}U levels. Thus, the uranium is not enriched and may be slightly depleted with lower specific activity than natural U.

Because the U isotopes are alpha emitters, alpha spectrometry is often used to analyze samples. The resolution of alpha spectrometry systems should be adequate to distinguish ^{238}U (4.14 MeV, 25%; 4.2 MeV, 75%), ^{235}U (4.37 MeV, 18%; 4.4 MeV, 57% and 4.58 MeV, 8%) and ^{234}U (4.72 MeV, 28%; 4.77 MeV, 77%). However, the 4.78 MeV alpha from ^{226}Ra could be difficult to discriminate from the 4.77 MeV alpha from ^{234}U . Therefore, radiochemical separation of ^{226}Ra is necessary before counting for ^{234}U in order to obtain accurate results for ^{234}U and ^{226}Ra . Higher concentrations of ^{226}Ra than ^{234}U might be typical because radium is more soluble than uranium. The ^{230}Th alphas (4.62 MeV, 24%; 4.68 MeV, 76%) could also interfere with ^{234}U results depending on system resolution. However, ^{230}Th concentrations in water are generally lower than ^{234}U concentrations because thorium is less soluble than uranium.

Alpha spectrometry results for ^{235}U can easily be confounded because the specific activity of ^{235}U in natural uranium is over 20 times less than for ^{238}U or ^{234}U . If even only small energy straggling of the ^{234}U , ^{230}Th or ^{226}Ra alphas occur as a result of sample matrix effects, then ^{235}U could be completely obscured. In addition, expected ^{235}U background groundwater concentrations are well below current MDAs. Therefore, the Y-12 Plant groundwater data for background ^{235}U is not reliable. More quantitative results for ^{235}U might be obtained by analyzing the 185 keV gamma (54%) using high resolution gamma spectrometry. The gamma detector would have to be selected for high efficiencies for low energy photons.

Values for ^{238}U and ^{234}U , when the ^{226}Ra interference discussed above is accounted for, can be reliably based on alpha spectrometry. With expected background concentrations highly variable and near MDAs for a constant counting time, counting

errors are also variable and high. However a large number of measurements should result in mean values approximating actual background conditions.

Data for the 1986-1990 and 1991-1994 time frames for "background wells" was used to estimate background concentrations for ^{238}U and ^{234}U . Using all data, arithmetic calculation of means and standard deviations in pCi/L were as follows:

1991 - 1994

$$^{238}\text{U mean} = 1.3 \pm 4.1$$

$$^{234}\text{U mean} = 1.2 \pm 4.1$$

1986 - 1990

$$^{238}\text{U mean} = 1.0 \pm 3.0$$

$$^{234}\text{U mean} = 0.6 \pm 5.1$$

Some of the data values were suspect because very high values of either ^{238}U or ^{234}U were not accompanied by high values of the other.

Omitting "suspect" values that could be ruled out statistically as outliers and did not exhibit expected approximate equilibrium between ^{238}U and ^{234}U , the results are in pCi/L are:

1991 - 1994

$$\text{Mean } ^{238}\text{U} = 0.8 \pm 2.6$$

$$\text{Mean } ^{234}\text{U} = 0.6 \pm 1.6$$

1986 - 1990

$$\text{Mean } ^{238}\text{U} = 0.8 \pm 1.2$$

$$\text{Mean } ^{234}\text{U} = 0.5 \pm 3.6$$

Combining all the "corrected" data from 1986 - 1994, the results in pCi/L are:

$$\text{Mean } ^{238}\text{U} = 0.8 \pm 2.9$$

$$\text{Mean } ^{234}\text{U} = 0.6 \pm 3.9$$

and total ^{238}U and $^{234}\text{U} = 1.4 \pm 4.9$ or about 2 ± 7.3 ppb for natural U on a mass basis.

It could be informative to conduct a more in depth statistical evaluation of the data starting with the raw data before subtraction of counter background.

The standard deviations include the variable and high counting error as well as normal variations in background levels. Counting error is often equal to several times the mean value for the analytical system used. Lower detection limits can be obtained by chemical isolation of radionuclides from the sample and by monitoring the sample in a nearby massless form on an alpha counting disc or plate. For a 1 liter sample and 24 hour counting periods, detection limits for alpha emitters can be as low as 0 .01 pCi/L. The effort and cost would be substantial. The costs are probably not justified for routine monitoring given the high natural variation in background levels and the low levels encountered.

The results apply only for the Y-12 Plant data set but it is interesting that the values are in good agreement with the data set accumulated to support the EIS for the LLWDDD program. That data set yielded a value for background total U in groundwater of about 2 ± 4 ppb.

Based on the above results, it would appear that measurements above about 10 pCi/L for total U would allow 95% statistical confidence that the measurements were above background.

Another aspect of this analysis was to investigate whether actual data agreed with expected relationships among isotopes. Several wells at the Y-12 Plant exhibited elevated ^{234}Th (e.g. GW-711, GW-712) and protactinium (several wells in the Chestnut Ridge Regime). The protactinium isotopes were not specified. According to the partial decay chain for ^{238}U ,

elevated levels of ${}^{234}\text{Th}$ and ${}^{234}\text{Pa}^{\text{m}}$ should be accompanied by elevated levels of ${}^{238}\text{U}$ at about the same activity concentrations unless wastes from a process that separates U from Th and Pa has been placed in the waste sites within the last few months before sampling. The fact that these expectations are not borne out by the data make the results for ${}^{234}\text{Th}$ and protactinium suspect. In fact, analytical results for ${}^{234}\text{Th}$ and ${}^{234}\text{Pa}^{\text{m}}$ are often based on alpha spectroscopy of ${}^{238}\text{U}$. Since the ${}^{234}\text{Pa}^{\text{m}}$ is a strong beta emitter (2.29 MeV, 98%), beta spectroscopy might be used to determine ${}^{234}\text{Pa}^{\text{m}}$ and ${}^{234}\text{Th}$ as a method to check the results.

Since the Pa isotopes are not specified, the high Pa values (if real) could result from ${}^{233}\text{Pa}$ which should be approximately in equilibrium with ${}^{237}\text{Np}$ produced by decay of ${}^{241}\text{Am}$ or from neutron capture of uranium isotopes in the uranium fuel cycle. Where comparisons could be made (only a few cases), ${}^{237}\text{Np}$ was very different and lower than protactinium. ${}^{237}\text{Np}$ is a decay product of ${}^{241}\text{Am}$. However, ${}^{241}\text{Am}$, ${}^{237}\text{Np}$ and ${}^{233}\text{Pa}$ values were not given and/or not given together so that it is not possible to compare results to expectations.

${}^{233}\text{Pa}$ could also be produced without ${}^{237}\text{Np}$ via the reaction:

Since thorium fuel cycle elements were not processed at the Y-12 Plant, another process (ORNL?) would need to be identified to support the results.

If ^{233}Pa from the thorium fuel cycle components were significantly elevated, then ^{233}U should be slightly elevated. The ^{233}Pa , unsupported by ^{237}Np , should be gone (half life = 27d) unless it has been placed in waste sites within a few months before sampling. The ^{233}U alphas have energies of 4.78 MeV(15%) and 4.82 MeV(83%), which, similar to the case for radium, are close to the ^{234}U alpha energies. However, given efficient separation of the uranium isotopes and careful sample preparation, an alpha spectrometry system with a full-width-half maximum resolution of 50 keV or better could resolve the 4.77 MeV (72%) ^{234}U and 4.82 MeV (83%) ^{233}U alphas.

Clarification of the complicated picture with respect to "total" Pa measurements would require speciation of the Pa isotopes and measurement of ^{241}Am , ^{237}Np and ^{233}U . This would constitute a special study in addition to the routine measurements already underway.

Fission Products

Uranium fuel cycle reactor elements processing at the Y-12 Plant in the early 1960s resulted in fission and activation product contamination. Those with higher production levels in fuel elements and longer half lives (^3H , 12.33 years; ^{137}Cs , 30 years; ^{90}Sr , 29.12 years; ^{99}Tc , 2.13×10^5 years) are still monitored. They are detected in some wells at the Y-12 Plant in all hydrogeologic regimes.

Background levels, expected to be low, are not well established. Based on 1994 data, which is the most complete set, the mean concentrations in background wells were:

Tritium	-1.64 ± 13.4 (Bq/L)
^{90}Sr	3.3 ± 23.8 (pCi/L)
^{99}Tc	53 ± 64 (pCi/L)

Only a few background values are available for ^{137}Cs . However, even at the most contaminated site (S-3 Site), the ^{137}Cs value was only about 30 pCi/L. The very large variation in the results indicate that the MDAs were not low enough to reliably quantify the background concentrations.

The MCLs (pCi/L) for these isotopes based on 4 mrem/yr with a 2L/d water intake are:

$$^3\text{H} \sim 86,000$$

$$^{99}\text{Tc} \sim 3,770$$

$$^{137}\text{Cs} \sim 110$$

$$^{90}\text{Sr} \sim 38$$

The Safe Drinking Water Act (40 CFR 141.16) values for ^{90}Sr , ^3H and ^{99}Tc are 8 pCi/L, 2×10^4 pCi/L and 900 pCi/L respectively. MDAs at or below these levels should not be difficult to achieve.

The only isotopes exceeding the MCL off-site in 1994 was ^{90}Sr . Off-site well GW-171 had a measured concentration of 267 pCi/L for the 09/27/94 sample and 20 pCi/L for the 11/15/94 sample date. Off-site well GW-230 had a measured concentration of 64.7 pCi/L for the 09/28/94 sample date. The source of these ^{90}Sr values is not clear since the highest measured concentration for any well on site was 103 pCi/L for GW-243 at the S-3 Site for the 03/30/94 sample. Concentrations in GW-243 were 163 and 254 pCi/L on 05/14/92 and 08/19/92, respectively. Similar values were measured in 1991. A shallow groundwater flow divide also occurs between the Y-12 Plant Site and wells GW-171 and GW-230. Groundwater flow in the shallow intervals (i.e., less than 100 ft) should actually be toward the Y-12 Plant from these wells. However, deeper groundwater flow is not well quantified. Values for ^{99}Tc , which should be more mobile

than ^{90}Sr , were reported to be lower than the mean measured background value listed above. These factors make it unlikely that groundwater contamination from the Y-12 Plant Site is the source of the elevated ^{90}Sr .

The only other isotope that was elevated based on 1994 measurements was ^{235}U . Both ^{234}U and ^{238}U were near or below background levels. Although the ^{235}U measurements in background wells are unreliable as discussed above, the measured levels in GW-171, GW-172 and GW-230 are too high to be dismissed without further study. These apparently elevated ^{235}U levels without elevations in ^{234}U or ^{238}U , which are not typical for the Y-12 Plant Site, also indicate that a cause other than groundwater contamination from Y-12 Plant Site may be responsible for the elevated ^{90}Sr and ^{235}U measurements.

It should be kept in mind that the measurements could be erroneous. The highest off-site ^{90}Sr values have not occurred for other time periods. The measurements should be enhanced to include ^{40}K and ^{228}Ra because of possible interference with the ^{90}Sr measurements. Higher natural levels of ^{228}Ra (from ^{232}Th) could lead to interferences with the ^{90}Sr measurements because radium will precipitate with strontium in the analytical procedure. Natural ^{40}K , which is often seen at several hundred pCi/L in groundwater samples, could also interfere if ^{40}K partially precipitates with ^{90}Sr in the analytical procedure. If the wastes are associated with reactor fuel elements, then cesium and barium isotopes may be present. The barium isotopes will also precipitate with strontium. These possibilities may vary from site-to-site because of variations in chemical form and matrix effects. Spiking the sample with a known amount of ^{90}Sr will not correct for interferences unless the contribution of interfering isotopes can be determined.

Sample matrix differences (chemical and physical properties) could also produce changes in separation efficiencies of ^{90}Sr from ^{90}Y which is expected to be near equilibrium with ^{90}Sr in the samples (See April 23, 1993 memo to Kevin Jago from

Phil Walsh). In addition, matrix differences produce differences in energy straggling, which could result in unreliable measurements for ^{235}U as discussed previously in this memo.

According to the general radiological analysis methodology, repetition of the unexpected results should stimulate a more detailed examination of the entire system including process and transport parameters. For the sampling and analytical laboratory results, the ^{235}U results should be checked using the 185 keV gamma in a high resolution gamma spectrometry system. Also, the efficiency of ^{90}Sr separation in the sample matrix from ^{90}Y , ^{228}Ra , barium isotopes, and perhaps ^{40}K should be verified. Monitoring for ^{137}Cs ($^{137}\text{Ba}^m$ will be in secular equilibrium) should be added. An additional barium isotope, ^{133}Ba , may be present in activity concentrations comparable to ^{90}Sr if the ^{90}Sr results are reliable.

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