Tronox Response to December 7, 2007 NDEP Advisement Regarding Radionuclide Analyses for Uranium

NDEP comment

As noted to the Companies via e-mail, it has been discovered that there are differences in the preparatory (prep) methods used for isotopic uranium analyses. Specifically, the use of hydrofluoric acid (HF) versus not using HF. This difference has significant impacts on the data and represents a comparability problem.

What has been discovered is as follows:

- 1. The BRC/TIMET background data set was analyzed by STL-Saint Louis (STL-SL) for isotopic uranium. STL-SL uses HF.
- 2. The TRX upgradient data set was analyzed by GEL for isotopic uranium. GEL uses HF.
- The TRX Phase A data and several other BRC data sets were completed by STL-Richland. STL-Richland does not use HF. This results in significant low bias relative to the background data set for isotopic uranium.

Tronox Response

Tronox has reviewed and evaluated the Tronox Upgradient and Phase A data sets with regard to the issues raised.

NDEP comment

All QAPPs shall be edited to specifically identify the prep method that uses HF for isotopic uranium analysis. Please address this issue **by January 11, 2008**.

Tronox Response

NDEP granted Tronox an extension to February 8 to deliver this response. The next revision of the Tronox QAPP will specifically include this requirement. This revision will be complete and submitted for NDEP approval before the Phase B Investigation begins.

NDEP comment

1. The Companies need to identify all data sets that are not comparable and report this to the NDEP. This will also be requested in the letter. Please address this issue by January 11, 2008.

Tronox Response

The NDEP granted Tronox an extension to February 8, 2008 to deliver this response. The Tronox Phase A Investigation dataset for isotopic uranium is not comparable to the BRC/TIMET background study data because a total dissolution prep with HF was not performed prior to the HASL-300 alpha spec analysis. The former STL-Richland (now TestAmercia (TA)-Richland) laboratory has confirmed that only an acid leach without HF was used to digest these samples. TA-Richland has stated that all the Phase A samples analyzed for isotopic thorium by alpha spec were digested with HF in a total dissolution procedure, however Tronox believes the isotopic thorium results are not comparable to the BRC/TIMET dataset based on both the statistical analyses presented in the Phase A report and a subsequent comparison, presented in the attached Table 2, of the results for thorium derived from gamma spectrometry on the same samples.

NDEP comment

 All parties need to work to identify what other radionuclide data may be compromised. Each company should respond to this issue in the January 11, 2008 Deliverable. If additional radionuclide data is compromised additional changes to QAPPs will be required.

Tronox Response

Tronox has not identified any additional radiochemical data, other than the alpha spec isotopic uranium and thorium Phase A results mentioned above, as compromised by prep or analyses so that the data is not comparable in principle to the BRC/TIMET background dataset.

NDEP comment

- 3. All parties need to contemplate how we might salvage the data from STL-Richland for isotopic uranium analysis for use in future background comparisons. Some ideas that have been mentioned thus far are as follows:
 - a. Complete a side by side study of the two methods and develop a correction factor that could be applied to data from STL-Richland. It should be noted that enough uranium (metal) data may exist to develop this correction factor currently. This is important if any of the data will be used for risk assessments. This item can be addressed by the NDEP for the Companies or the Companies can complete this exercise.
 - b. Discard the existing data that is affected by this difference and utilize the total uranium data for background comparisons. It is likely that this is a defensible procedure for addressing background comparisons.
 - c. Utilize gamma spectroscopy for future analyses of isotropic uranium (NDEP does not support this).
 - d. These ideas need to be contemplated for what will be defensible. NDEP is open to additional suggestions.
 - e. Each Company should respond to this issue in the January 11, 2008 Deliverable.

Tronox Response

To salvage the Phase A uranium and thorium data for Phase A Tronox requested that the TA-Richland lab reprocess the raw gamma spec dataset (originally used to measure only the radium) so it included the isotopic uranium and thorium nuclides as well. The exact daughter nuclides and line energies measured were discussed with Dave Gratson at Neptune and are detailed in the attached data validation memo. These gamma spec results are provided in the attached Table 1 and are compared to the original alpha spec results in Table 2.

Ratios of the gamma to alpha spec results for each sample, each nuclide, and the aggregate U and Th isotopes are calculated in Table 2. These results confirm the original Phase A alpha spec data for U and Th were biased low. Moreover the ratios for the U-234 and U-238 nuclides are comparable to the "correction factors" derived by BRC in their comparison of the HF dissolution vs. HNO3 leach prep results for subsamples of the Deep Soil Background and Parcel A/B datasets (see green highlights in Table 2). The similarity of the aggregate U and Th ratios indicates that the alpha spec results for both the U and Th nuclides were biased low even though the lab claims the Th analyses were preceded by total dissolution preparation. Tronox has not been able to determine the exact reason the original Th results also appear biased low.

As discussed in our conference call on January 22, 2008, Tronox has compared the gamma spec data from the Phase A soils at depths from 0 to 10 ft to NDEP-approved background activities, and also evaluated secular equilibrium based on the gamma spec results. The attached statistical analyses using the new gamma spec dataset for U and Th from Phase A soils (0-10 ft deep) corroborates that the gamma data is both more consistent with BRC and COH background datasets and internally more consistent with the assumption of secular equilibrium in the nuclide decay chains. Specific observations based on the comparisons include:

The histograms showing both Phase A soils (0-10 ft) and BRC/COH background data show that the Phase A gamma spec results are consistent with background for Ra-226, Ra-228, Th-228, and Th-230. While the medians of Th-232, U-234 and U-238 appear generally greater than background, the highest activity levels in the Phase A samples are similar to the highest activities in the background samples. The box-plots show the same information in a slightly different way.

- To evaluate secular equilibrium, histograms and box-plots were prepared for the radionuclides in each decay chain. These show a general normal distribution that is similar for all radionuclides in each decay chain, as would be expected from random variability. Similar histograms and box plots were also prepared for the BRC and COH datasets separately.
- In a further evaluation of secular equilibrium, the Phase A data for each decay chain was graphed on a scatterplot. In a world without random errors, all of the points should fall on top of each other, and also on the line representing one-to-one correlation if the samples are in secular equilibrium. Instead, the Phase A data show a clustering of the data points around a central value, as would be expected with random errors. (Note that Th-230 and Ra-226 were measured from the same decay product (Bi-214) and the same emission line, which is reflected in their very high correlation.) Similar scatterplots have been prepared with the BRC and COH datasets.
- In addition, similar scatterplots have been prepared that include error bars based on the uncertainties in the analytical results reported by the laboratory. The uncertainties for the U-238 analyses are relatively high, and show that when uncertainty is considered, the U238 and Th230 activities at any given sample overlap. The uncertainties for the remaining radionuclides are lower, but the conclusions are the same when laboratory uncertainties are considered, activities within each decay chain for any given sample overlap.

Please note that the relationship with respect to background for the U-238 gamma spec data is now more consistent with Phase A comparison of the uranium metal results measured by IPC-MS to the background U metal dataset as well. Tronox believes the weight of evidence suggests the new gamma spec data is reliable and more accurate than the original biased alpha spec Phase A data. Tronox therefore proposes to replace the original data with the new gamma spec data for both isotopic U and Th.

In regards to NDEP's advisement from January 29,2008 Tronox agrees in principle to utilize methods consistent with the BRC/TIMET background study methods for future investigations. The use of gamma spectrometric data discussed above is only to salvage the Phase A radiochemistry data in a manner that is internally consistent and appropriate for background comparisons.