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### **Plutonium in the 2003 Second Quarter FAS Composite (REVISED)**

The activity of  $^{239,240}\text{Pu}$  in the WIPP effluent air composite sample for the second calendar quarter of 2003 (Q2-2003) was above its detection limit ( $\sim 0.01$  dpm). This is the first time CEMRC has detected Pu in a sample of WIPP effluent air. This document has been prepared to review the methods used for the effluent monitoring studies and to discuss the steps taken to evaluate the possibility that the Pu detected was the result of contamination of the filter during the sample retrieval or analysis process.

#### **Background**

CEMRC commenced sampling of the WIPP exhaust air at Station A on 12 December 1998. There are three shrouded-probe aerosol samplers at Station A; these located on three separate sampling skids (skids A1-A3). The airstream sampled by each skid is split among three legs such that three concurrent samples can be collected from a single skid. On 15 January 2000, the CEMRC sampling operations were moved from Skid 2 (west skid), leg 1 to Skid 1 (east skid), leg 2 to facilitate more direct data comparisons among the three organizations sampling the effluent air. Since that time all groups (CEMRC plus Westinghouse/Washington TRU Solutions and the Environmental Evaluation Group, EEG) have sampled from the same skid.

The aerosol sampling operations at Station A have at times been hampered by filter clogging, and in a few instances, the flow rates fell below optimal. As a result, CEMRC and the other organizations began changing filters twice daily Monday through Friday starting 24 January 2000. In most cases, a single filter was collected over the weekend. In April 2001, primary sampling operations were transferred from Skid 1 (east skid) to Skid 3 (south skid) to reduce problems associated with water infiltration into the exhaust shaft. On 28 November 2001, the sampling frequency for all groups was returned to once daily except for weekends owing to a trend towards lower mass concentrations and improved flow rates. However, occasionally more than one sample per day is still collected, that is, if the flow rate on any of the sampler legs drops below 1.8 cfm, a low-flow alarm on the sampler is activated and WTS personnel change the filters.

#### **Methods**

The aerosol samples of the WIPP effluent air are collected using a shrouded probe, commonly referred to as a fixed air sampler (FAS). The FAS collects bulk samples (passing efficiency  $\sim 1$  for  $10\ \mu\text{m}$  particles). The aerosol samples used to prepare the Q2-2003 composite were collected daily except on weekends (the weekend samples run from Friday to Monday so the coverage is continuous).

Detailed descriptions of the sampling and analytical methods used by CEMRC have been included in the CEMRC Annual Reports. Briefly, after a sample filter is removed from the FAS at Station A, it is placed in a clean Petri dish and returned to the laboratory where it is weighed to determine the mass loading. Next the filter is counted for gross alpha/beta activity using a gas proportional counter. The filters from each week are then digested as a batch in separate vessels, using a mixture of acids and a microwave digestion unit. The filters in each batch are then combined to form a weekly composite. Elemental (ICP-MS) and gamma-ray analyses are conducted on weekly composites of the filters, and quarterly composites are prepared from the weekly composites: these quarterly composites are used for the determination of actinide activities. Only one half of the quarterly composite sample is routinely used in the determination of the actinide activities. The remaining sample is archived. The actinides are separated and purified using co-precipitation on  $\text{Fe}(\text{OH})_3$  and a series of anion exchange and extraction chromatography steps. Am, Pu, U and Th are then prepared for alpha spectrometry using rare-earth micro-coprecipitation. The sequence of sample preparation and analytical steps for the FAS filters is shown diagrammatically in Figure 1.

## **Results**

$^{239,240}\text{Pu}$  was detected in an aliquot of the composite FAS sample from the second calendar quarter in 2003.

Batch 1278:

Aliquot Size = 953.0 grams of composite

$^{239,240}\text{Pu} = 0.131 \pm 0.011$  dpm

Minimum detectable concentration (MDC) = 0.014 dpm

Although the quality control samples analyzed with this aliquot of the composite sample gave no indication of a problem with the analysis, a second aliquot of the same composite was prepared and analyzed to confirm the unexpected presence of Pu. The  $^{239,240}\text{Pu}$  activity in the second aliquot was similar to that in the first.

Batch 1289:

Aliquot Size = 951.4 grams of composite

$^{239,240}\text{Pu} = 0.112 \pm 0.009$  dpm

MDC = 0.008 dpm,

If one assumes that the Pu actually was in the exhaust air, two extreme scenarios can be used to reconstruct the corresponding  $^{239,240}\text{Pu}$  activity concentrations (activity per unit volume of air) in the exhaust air. The two scenarios are (1) all the  $^{239,240}\text{Pu}$  is concentrated in one daily sample vs. (2) the Pu activity is spread throughout all samples collected in the quarter. The first of these scenarios would represent the maximum activity concentration and the second the minimum. There is no way to distinguish between these two extremes or any intermediate case (follow-up calculations show that the activity would not have been detectable by gross alpha/beta counting).

The typical volume of air sampled for each daily FAS filter is  $\sim 82 \text{ m}^3$  ( $57 \text{ l min}^{-1}$  for 24 hr), and the actual volume of air sampled for the quarterly composite was  $7006 \text{ m}^3$ . The maximum and minimum activity concentrations can be calculated from these flow volumes and a  $^{239,240}\text{Pu}$  activity (weighted by data for the two aliquots) of 0.27 dpm ( $0.27 \text{ dpm } ^{239,240}\text{Pu} = 4.5 \text{ mBq}$ ) as follows:

$$\begin{aligned} \text{Maximum activity concentration} &= 4.5 \text{ mBq}/82 \text{ m}^3 \\ &= 0.055 \text{ mBq m}^{-3} \end{aligned}$$

$$\begin{aligned}\text{Minimum activity concentration} &= 4.5 \text{ mBq}/7006 \text{ m}^3 \\ &= 0.00064 \text{ mBq m}^{-3}\end{aligned}$$

In comparison, the maximum  $^{239,240}\text{Pu}$  activity concentration for TSP ambient aerosols collected from three stations above ground over 4 to 6 week periods was  $70 \text{ nBq m}^{-3}$  (Arimoto et al., 2003). Thus, one can show that the  $^{239,240}\text{Pu}$  activity for the FAS composite, when averaged over the quarter, was less than 10 times higher than the highest observed activity concentration in ambient air.

After the initial finding of detectable Pu in the FAS quarterly composite was made known, a second set of FAS filters, which were collected from the back-up skid during the second quarter of 2003, was made available to CEMRC for confirmatory analysis. Expedited results of the analysis of the back-up samples also showed detectable  $^{239,240}\text{Pu}$ , with a concentration for the back-up composite of 0.56 dpm; this is approximately twice the amount of activity that was in first quarterly composite.

A most important follow-up finding is that the third quarter FAS composite did not have detectable  $^{239,240}\text{Pu}$ .

## Discussion

The detection of  $^{239,240}\text{Pu}$  in the WIPP exhaust air for the first time was expected to raise concerns, and therefore other results and related data were examined to determine whether the Pu present in the quarterly composite may have been the result of contamination introduced during either the sample retrieval or analysis steps. The first possibility evaluated was that the sample was contaminated in the field, but this appears unlikely for two reasons. First, no  $^{241}\text{Am}$  was detected in the composite<sup>1</sup> and second the Al concentrations were in a normal range. If for example, a filter had been dropped and contaminated in the process, one would have expected detectable  $^{241}\text{Am}$  and high Al based on prior observations showing relationships among these substances in ambient aerosol samples (see for example the CEMRC Annual Report 2003).

If the  $^{239,240}\text{Pu}$  activity in the FAS composite were from the same sources that affect ambient aerosols, the  $^{241}\text{Am}$  activity should have been  $\sim 0.036 \text{ dpm}$ , which is well above the  $^{241}\text{Am}$  MDC. Note that  $^{241}\text{Am}$  is not a daughter of  $^{239,240}\text{Pu}$ , which is what was detected in the FAS sample, but rather of  $^{241}\text{Pu}$ . Typically however,  $^{241}\text{Pu}$  and  $^{239,240}\text{Pu}$  are found together in nuclear waste, and given the observed activity of  $^{239,240}\text{Pu}$  in the composite sample, one would have expected  $^{241}\text{Am}$  to be detected but it was not.

Similarly, the elemental data for the weekly FAS composites showed no evidence for elevated aluminum concentrations. The data for Al can provide insight into possible sources for the Pu because prior studies of ambient aerosols (Arimoto et al., 2003) have shown that the activity of  $^{239,240}\text{Pu}$  is correlated with aerosol Al, which is taken as an indicator of mineral dust. Other radiochemical analyses for the composite sample showed that the uranium and thorium activities are about twice what they were in Q4-2002 and Q1-2003, but the concentrations of these two nuclides actually were lower

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<sup>1</sup> A more intensive analysis of the planchet prepared for  $^{241}\text{Am}$  confirmed the absence of detectable activity. For this re-analysis, the same planchet produced from the quarterly composite was used, but it was counted closer to the detector to increase sensitivity. The results are:

Batch 1278:

$^{241}\text{Am} = 1.40\text{E-}03 \text{ +/- } 2.19\text{E-}03 \text{ dpm}$

Minimum detectable concentration =  $6.39\text{E-}03 \text{ dpm}$

than in the second quarter samples from earlier years (Figures 2 and 3). None of these results show any evidence for unusual levels of substances that would suggest contamination had occurred.

The next step in the analytical sequence where contamination could have occurred was when the filters were weighed to determine aerosol mass. This is the one aspect of the handling of the Q2-2003 filters that was unique relative to all other FAS filters, that is, several batches of filters from Q2-2003--and only that quarter--were weighed in the CEMRC count room. This was necessary because several of the CEMRC labs, their contents, and the operations performed in them, were being shuffled to accommodate the LANL and WTS groups. After the filters were weighed, they were sealed to allow short-lived, unsupported radon daughters to decay away. The filters were then counted for 20 hours apiece on a gas proportional counter (GPC) to simultaneously measure gross alpha and gross beta activity. A typical MDC for gross alpha activity is about 0.25 dpm/filter. If 0.1 dpm of  $^{239/240}\text{Pu}$  was deposited on a single filter, it could not be detected, and would be indistinguishable from the naturally occurring radioactive material (NORM) also deposited on the filter. For instrument control checks, the GPC uses pure  $^{239/240}\text{Pu}$  and  $^{90}\text{Sr}$  sources. After the sources are counted, a 60-minute background count is performed. Before FAS filters are counted, the instrument has to meet the efficiency and background controls criteria. We note that although the count room does contain solid sources of essentially pure  $^{239,240}\text{Pu}$ , the sources were not stored or handled on the bench used to weigh the filters, and as discussed below there is no evidence that contamination was introduced in the weighing or gross alpha/beta counting steps.

Quality assurance/quality control (QA/QC) samples are routinely processed with each batch of samples, and the data for these samples showed no evidence of contamination. Associated with each weekly batch of FAS filters are two blank filters. These blanks, although not removed from CEMRC and taken to WIPP, are subjected to most of the same handling steps as the FAS filters. The blank filters are weighed on the same balance and counted on the gas proportional counter along with the weekly FAS batch. One of these blank filters from each batch is archived while the other filter is digested (using the same microwave as the FAS filters) and used as a blank for the elemental analyses. These blanks are not normally analyzed as QA/QC samples for the actinide determinations. Instead the radiochemistry (RC) group prepares a separate blank (matrix blank) and analyzes it with the FAS filter sample. The RC matrix blank that was processed alongside the Q2-2003 composite showed no evidence of contamination.

To further investigate the possibility of contamination of the FAS filters occurring while at CEMRC and where it might have taken place, the a special study of FAS blanks was conducted. For this study, what remained of the Q2 digested metals blanks was composited and delivered to radiochemistry for analysis. In addition, the archived Q2 blanks were digested, composited, and processed for radiochemical analysis. These two blank samples were batched (batch 1296) with the Q3-2003 FAS composite, along with a matrix laboratory control sample, a matrix blank, and a reagent blank. None of these blank samples had detectable activities for any of the nuclides of interest (Am, Pu, U or Th). In addition, the laboratory control sample recoveries were well within limits. These results thus show no evidence that the FAS sample was contaminated when the filters were weighed, when they were counted on the gas proportional counter, when they were digested in the EC laboratory, or when they were prepared for actinide analysis.

The fact that  $^{241}\text{Am}$  was found to be below detection, along with results of the EC analyses showing no unusual levels of dust or other inorganic materials, supports the idea that the  $^{239,240}\text{Pu}$  was from a purified source. One would expect that the most likely source of Pu contamination, if it occurred, would be in the RC laboratory or count room because  $^{239,240}\text{Pu}$  standards and sources are used there. However, the fact that similar  $^{239,240}\text{Pu}$  activities were measured for the two aliquots of the quarterly

composite sample plus the composite prepared from the back-up samples indicates that the sample was not likely to have been contaminated while it was being prepared for actinide analysis. There are several reasons why this is so. First, the two sub-samples were prepared several weeks apart in time, and second different reagents, labware, columns etc. were used to prepare the two aliquots for alpha spectrometry. Furthermore, the composite made from back-up samples was prepared several months after the first composite, again using different reagents, etc. This means that the chances of introducing similar amounts of purified  $^{239,240}\text{Pu}$  during the processing of the various aliquots and samples would be vanishingly small.

Thus, to briefly summarize, two aliquots of the FAS sample (batch 1278 and batch 1289) were separately analyzed and they showed virtually the same Pu concentration. These results were confirmed through the analysis of a composite prepared from a back-up set of samples. All QA/QC samples analyzed with these batches were within limits (blanks were below their MDC and laboratory control samples met data quality objectives). Therefore, although it is not possible to rule out an error in the laboratory, that is, prove the negative, contamination of the sample appears unlikely.

One question that may be raised is “How much Pu is involved?” and we hasten to point out that the amount of  $^{239,240}\text{Pu}$  detected could be contained in a single hot particle. If one were to take one of the planchets prepared for alpha analysis and strip off all of the Pu, the mass of Pu would be:

$$\begin{aligned} &^{239}\text{Pu}: 0.7 \text{ pg (assuming all activity due to } ^{239}\text{Pu)} \\ &^{240}\text{Pu}: 0.2 \text{ pg (assuming all activity due to } ^{240}\text{Pu)} \end{aligned}$$

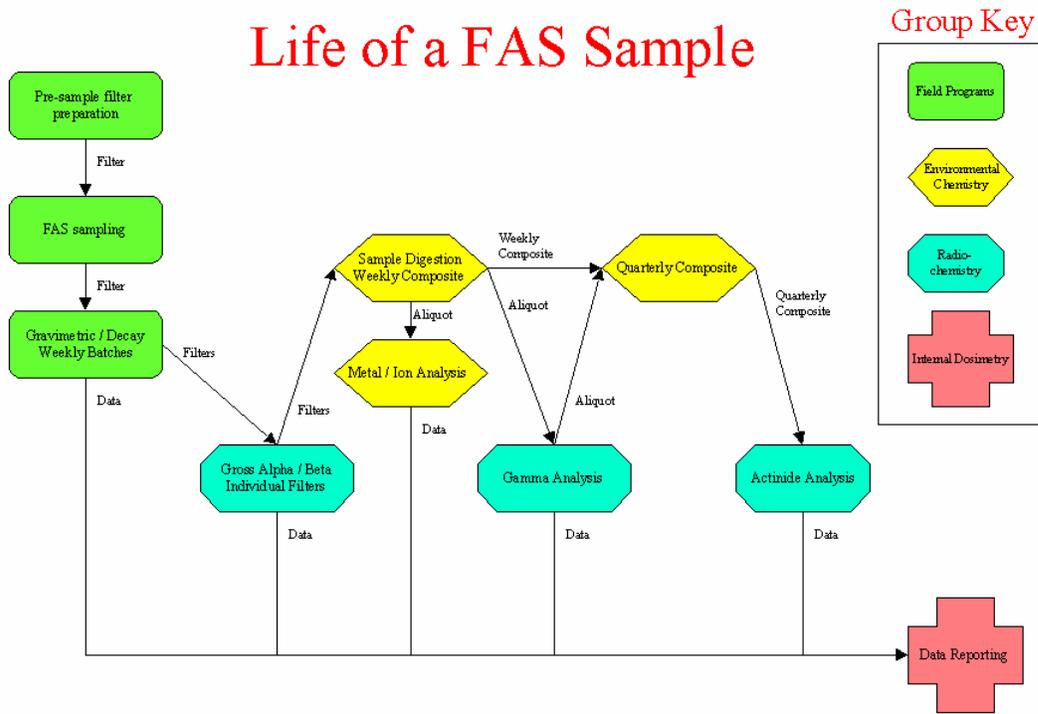
These values would have to be doubled to reflect that fact that two planchets were prepared from the quarterly composite. Even so, a cube of solid Pu equivalent to this amount of mass would be ~1 micrometer on a side and thus invisible to the unaided eye. For further perspective, if this amount of Pu were digested in 5 ml of solution, it would be below the limit of detection by the ICP-MS, which can detect ~ 1 part per trillion (1 in  $10^9$ ) of Pu in solution.

While it is important to be alert to future trends in the FAS data, it is even more important to emphasize that the amount of Pu involved is extremely small, of the order of approximately picogram total. To put this amount of Pu in further perspective, one might compare it to the quantity of Pu that has been produced for military and industrial applications. Hecker et al. (2000), for example, estimate that more than 100 tonnes of Pu were produced by the nuclear weapons complex in the United States alone, and these authors also estimated that the civilian sector had an inventory of over 1000 tonnes of Pu worldwide. Finally, 4.5 mBq of  $^{239,240}\text{Pu}$  is arguably insignificant compared with the  $1 \times 10^{16}$  Bq of plutonium, americium and other nuclides that already have been emplaced in the WIPP (as cited by Webb et al., 2004). Thus more than anything the detection of  $^{239,240}\text{Pu}$  in the FAS sample attests to the extraordinary sensitivity of the methods used by CEMRC to monitor the WIPP effluent.

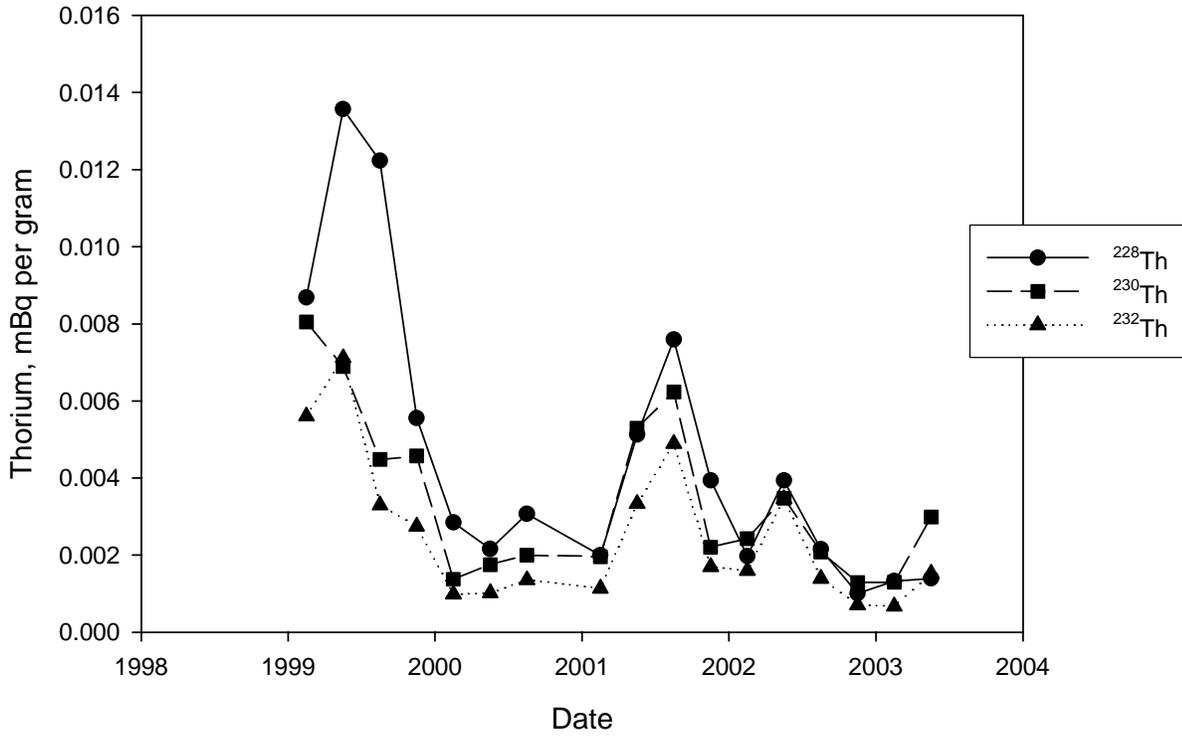
#### Literature Cited

- Hecker, S. S., (with the Los Alamos Science Staff), Plutonium—A Historical Overview, Published in Los Alamos Science, Challenges in Plutonium Science, Volume 1, pp., 2-47, 2000.
- Webb, S. B., Klein, T. M., Anastas, G., Allen, L. E., Concerns relating to effluent air sampling for the WIPP exhaust shaft (unpublished manuscript).

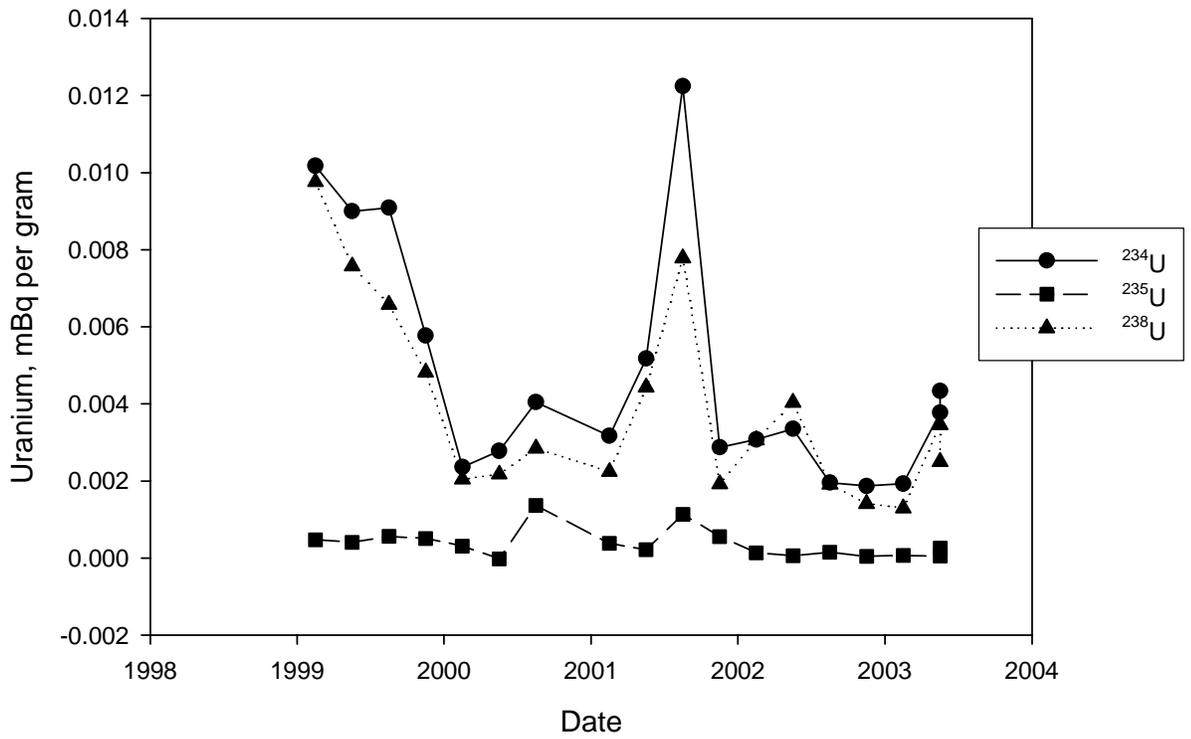
# Life of a FAS Sample



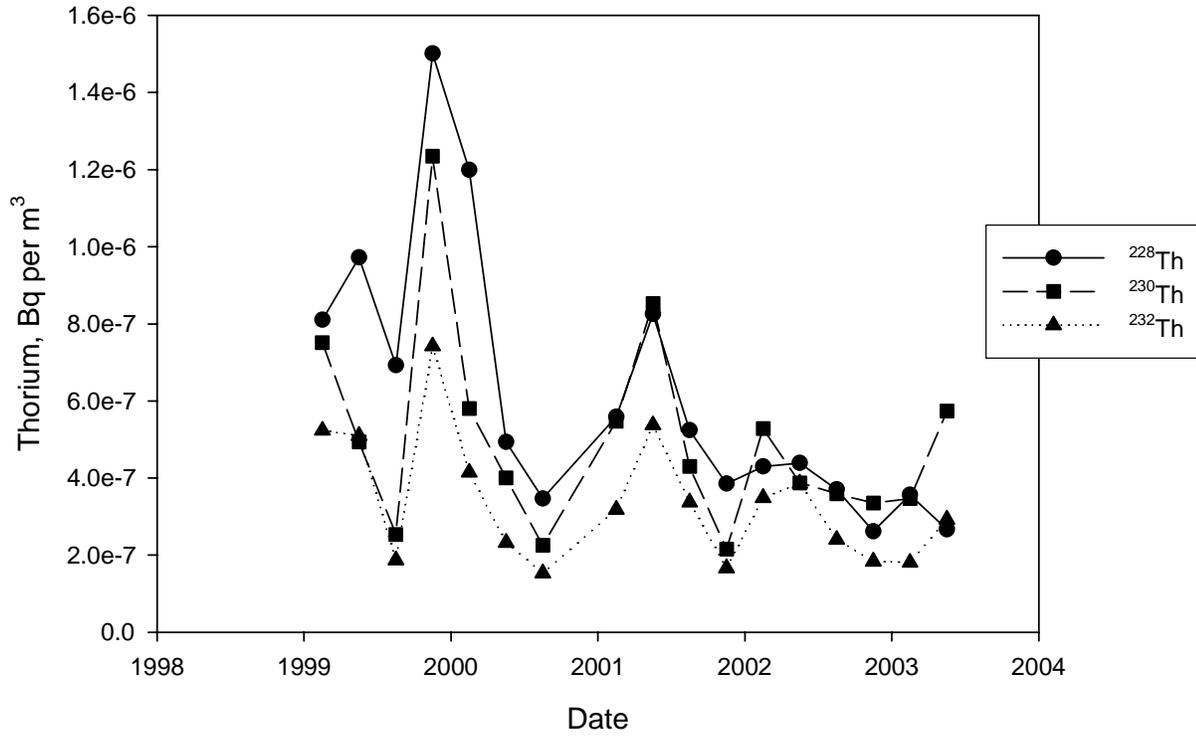
### Thorium Activity Density



### Uranium Activity Density



### Thorium Activity Concentration



### Uranium Activity Concentration

