

**Report of Sampling and Analytical Activities: Groundwater from the Vicinity  
of the Industrial Excess Landfill, Uniontown, Ohio**

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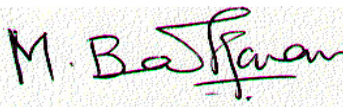
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**I. Sampling Activities.** Groundwater samples were collected in two sampling trips, on July 15, 2005 and October 20, 2005. All samples were collected personally by the investigators (Michael E. Ketterer and Mark M. Baskaran), working in the capacity of paid environmental consultants on behalf of the Concerned Citizens of lake Township (CCLT). Water samples were obtained from existing domestic/residential wells, irrigation wells, and one pre-established monitoring well, all of which were located on private property accessed with explicit permission given to CCLT. Samples from irrigation and monitoring wells (DK, GZ, NB, and MW-25s) were collected using a submersible 12V battery powered pump, equipped with fluorinated ethylene-propylene tubing. The pump head was inserted directly into the well casing, to the screened depth of the well (all wells except NB) and the pump was operated for  $\geq 15$  minutes to sufficiently expel the water contained within the well casing itself. Well NB-1 was not screened, and the pump head was inserted to a depth of approximately 60 feet. Wells DK and GZ consisted of irrigation wells installed by CCLT in June 2005. Well NB is a former domestic well that is no longer being utilized for this purpose. Well MW-25s is a monitoring well previously installed by EPA during previous investigations of the offsite IEL contamination. Samples from residential/domestic water sources (GL, RE, TK) were obtained using wells pre-established by the resident and used for outdoor irrigation; samples were collected from exterior hose spigots, following a  $\geq 5$  minute flush.

The July 15 sampling locations and aliquots collected are as detailed below:

<b>Sample ID/Description</b>	<b>Time</b>	<b>Aliquots Collected</b>
DK-1, irrigation well approx. 45'. Southwest	1045	<b>A, B, C, D, E, F</b>
GL-1, domestic well, inter./deep, ~100', West	1130	<b>A, B, C, D, E, F</b>
GZ-1, irrigation well, shallow, approx. 35' west	1230	<b>A, B, C, D, E, F</b>
NB-1, domestic well, intermediate ~ 85', NW	1445	<b>A, B, C, D, E, F</b>
RE-1, domestic well, approx. 90', north	1540	<b>A, B, C, D, E, F</b>
TK-1, domestic well, approx. 65', northwest	1610	<b>D, E</b>

**A** = 20 liters, unfiltered, preserved with 50 mL of 12 moles/liter hydrochloric acid; used for determination of  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ , and  $^{236}\text{U}$ .

**B** = 20 liters, unfiltered, unpreserved, used for gamma spectrometric analysis of the residue, and  $^{236}\text{U}$ .

**C** = 1 liter, unpreserved, used for  $^{99}\text{Tc}$ , submitted to Eberline Laboratories on 8/19/2005.

**D** = 250 mL, unpreserved, used for U concentrations and  $^{238}\text{U}/^{235}\text{U}$  atom ratios.

**E** = 10 liters, passed through  $\text{MnO}_2$ -impregnated acrylic fiber, used for Ra isotopes.

**F** = 20 liters, unfiltered, unpreserved, collected in the field, then 4 liters was pre-concentrated onto Dowex 1-X8 anion exchange resin and archived for potential future determinations of  $^{99}\text{Tc}$  by a referee laboratory. The archived Dowex 1-X8 anion exchange resin cartridges are now in the possession of Dr. Jerzy W. Mietelski of the Henryk Niewodciznanski Institute of Nuclear Physics, Krakow, Poland. The remaining 16 liters were discarded.

The October 20 sampling locations and aliquots collected are as detailed below:

<b>Sample ID/Description</b>	<b>Aliquots Collected</b>
DK-2, irrigation well approx. 45', southwest	<b>A, B, C, D, E, F</b>
GZ-2, domestic well, inter./deep, ~100', west	<b>A, B, C, D, E, F</b>
CB-1: irrigation well, approx. 45' southwest	<b>A, B, C, D, E, F</b>
GL-2, irrigation well, shallow, approx. 35' west	<b>A, B, C, D, E, F</b>
TK-2, domestic well, approx. 65', northwest	<b>A, B, C, D, E, F</b>
RE-2, domestic well, approx. 90', north	<b>A, B, C, D, E, F</b>

**A** = 20 liters, unfiltered, preserved with 50 mL of 12 moles/liter hydrochloric acid; used for determination of  $^{238}\text{Pu}$ ,  $^{239+240}\text{Pu}$ , and  $^{236}\text{U}$ .

**B** = 20 liters, unfiltered, unpreserved, used for gamma spectrometric analysis of the residue, and  $^{236}\text{U}$ .

**C** = 1 liter, unpreserved, used for  $^{99}\text{Tc}$ , submitted to Eberline Laboratories on 11/7/2005.

**D** = 250 mL, unpreserved, used for U concentrations and  $^{238}\text{U}/^{235}\text{U}$  atom ratios.

**E** = 10 liters, passed through  $\text{MnO}_2$ -impregnated acrylic fiber, used for Ra isotopes.

**F** = 20 liters, unfiltered, unpreserved, collected in the field, then 4 liters was pre-concentrated onto Bio-Rad 1-X4 exchange resin and archived for potential future determinations of  $^{99}\text{Tc}$  by a referee laboratory. The archived resin has been retained in Michael E. Ketterer's custody.

**II. Sample Transport and Custody.** Sample aliquots were maintained under custody of the investigators as follows:

**A, B:** Maintained under Mark M. Baskaran's custody and transported by personally owned vehicle back to the Geology Department at Wayne State University, stored and processed there under Mark M. Baskaran's custody.

**C, D:** Maintained under Michael E. Ketterer's custody and transported by personally owned vehicle to E.R. Ketterer's residence in Fairlawn, OH; kept in a locked foot locker until being transported back to the Chemistry and Biochemistry Department at Northern Arizona University, as checked baggage on a commercial passenger aircraft. After arrival at the NAU Chemistry Department, the samples have been maintained under Michael E. Ketterer's custody. Aliquot **C** samples were shipped via Federal Express to Eberline Laboratories. Aliquot **D** was acidified with 1 mL 16 M aqueous  $\text{HNO}_3$  upon arrival at the NAU laboratories.

**E:** The  $\text{MnO}_2$ -impregnated acrylic fiber was maintained Mark M. Baskaran's custody and transported by personally owned vehicle back to the Geology Department at Wayne State University, stored and processed there under Mark M. Baskaran's custody.

**F, July Samples:** Maintained under Michael E. Ketterer's custody and transported by personally owned vehicle to E.R. Ketterer's residence in Fairlawn, OH; 4 liter aliquots of the total sample volume were kept in a locked foot locker until being transported back to the Chemistry and Biochemistry Department at Northern Arizona University, as checked baggage on a commercial passenger aircraft. After arrival at the NAU Chemistry Department, the samples were processed to retain  $^{99}\text{Tc}$  on an anion exchange resin (shipped to J.W. Mietelski), while the water was thereafter discarded. The samples have been maintained under Michael E. Ketterer's custody.

**F, October Samples:** Maintained under Michael E. Ketterer's custody and transported by personally owned vehicle to E.R. Ketterer's residence in Fairlawn, OH; 4 liter aliquots of the total sample volume were processed with anion exchange resin at E.R. Ketterer's residence for pre-concentration of  $^{99}\text{Tc}$ ; resin and a small volume of water (~ 0.5 L) were kept in a locked foot

locker until being transported back to the Chemistry and Biochemistry Department at Northern Arizona University, as checked baggage on a commercial passenger aircraft. After arrival at the Northern Arizona University Chemistry and Biochemistry Department, the samples have been maintained under Michael E. Ketterer's custody.

**III. Analytical Procedures.** The samples were subjected to analysis for selected radioisotope constituents using the following procedures:

**Plutonium and  $^{236}\text{U}$ -Fe(III) Pre-concentration:** A 5 liter sub-sample of sample aliquot **A** was placed in a large Pyrex beaker; 1.5 mL of  $^{242}\text{Pu}$  spike (0.346 dpm/mL) was added along with 100 mg of Fe(III) in the form of an aqueous  $\text{FeCl}_3$  solution, and 2.0 grams of solid  $\text{NH}_4\text{Cl}$ . The solution was stirred for about 10 minutes using a glass rod, and was allowed to settle for one hour to equilibrate the  $^{242}\text{Pu}$  tracer. Then, aqueous  $\text{NH}_3$  (15 M) is slowly added until a pH of 7 is reached; the precipitate is allowed to settle  $\geq 4$  hours (or overnight). The supernatant is decanted and discarded, and the precipitate is collected on Whatman 42 paper using vacuum filtration. One blank (5 liters of deionized water) was processed along with each of the two (July and October) sample batches. The chemical procedure was conducted under the custody of Mark M. Baskaran and the precipitates were shipped from Mark M. Baskaran to Michael E. Ketterer for further processing.

The precipitates were re-dissolved with 10 mL of 16 M aqueous  $\text{HNO}_3$  and 10 mL of 12 M aqueous  $\text{HCl}$ , then adjusted to 50 mL with water and 10 mL of additional 16 M aqueous  $\text{HNO}_3$ . The mixtures were allowed to stand overnight, and decanted; the undissolved residue consisted of paper fibers and small amounts of undissolved precipitates (most likely originating from  $\text{Mn}^{2+}$  ions indigenous to the samples). Thereafter, 1.0 grams of solid  $\text{NaNO}_2$  was added to adjust the Pu to the Pu(IV) oxidation state; then 0.10 grams of TEVA resin (EiChrom, TE-B-100-S) was added. The mixtures were allowed to stand  $\geq 1$  hour with occasional agitation. The TEVA resin was collected on a 10 mL plastic pipette tip equipped with a small glass wool plug, while the column effluent was collected for subsequent recovery of U (not retained by TEVA). The TEVA resin was rinsed with 10 mL of 2 M aqueous  $\text{HNO}_3$  to remove unretained sample matrix constituents; Pu was eluted with a sequence of 2 mL deionized water, 2 mL of 0.05 M aqueous ammonium oxalate, and 1 mL deionized water. The Pu fraction from the TEVA column

(5 mL of combined water-ammonium oxalate fraction) was analyzed directly by inductively coupled plasma mass spectrometry (ICPMS). The TEVA column effluent, which contains U, was collected and mixed with 0.150 grams of UTEVA resin (EiChrom, UT-B25-S); the solution-UTEVA resin suspension mixture was allowed to stand  $\geq 1$  hour with occasional agitation. The UTEVA resin was collected on a 10 mL plastic pipette tip equipped with a small glass wool plug, while the column effluent was discarded. The UTEVA resin was rinsed with 10 mL of 2 M aqueous  $\text{HNO}_3$  to remove unretained sample matrix constituents; U was eluted with a sequence of 2 mL deionized water, 2 mL of 0.05 M aqueous ammonium oxalate, and 1 mL deionized water. The U fraction from the UTEVA column (5 mL of combined water-ammonium oxalate fraction) was analyzed directly by inductively coupled plasma mass spectrometry (ICPMS). ICPMS was used to measure  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{236}\text{U}$  in the Pu and U fractions from the TEVA and UTEVA columns, respectively. A VG Axiom MC instrument, equipped with a CETAC U-5000AT ultrasonic nebulizer, was operated in the single collector, electron multiplier mode.

For Pu analysis, the instrument was operated in the low resolution ( $R=410$  nominal) mode. The instrument was tuned at  $^{238}\text{U}^+$  using a  $0.05 \mu\text{g/L}$  uranium solution to provide optimal ion response and mass calibration adjustment. Each Pu extract was first analyzed in the magnet sweep mode (mass range 236.5-242.5) to obtain a qualitative spectral scan; thereafter, each solution was quantitatively analyzed using a peak-jump, electrostatic sector scan of narrow mass ranges ( $\sim 0.05$  amu) at the summit of each selected isotopic peak ( $^{238}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{240}\text{Pu}$ , and  $^{242}\text{Pu}$ ). Using a dwell time of 50 msec and 10 points within each summit mass range, data were collected for each solution as three integrations of 150 “E-scan” sweeps each. Total E-scan acquisition time was approximately five minutes for each sample solution. In addition to the samples, the  $0.05 \mu\text{g/L}$  uranium solution was run as a control to develop a “uranium hydride”  $^{238}\text{U}^1\text{H}^+$  subtractive correction factor, which accounts for the well-known interference of  $^{238}\text{U}^1\text{H}^+$  on  $^{239}\text{Pu}$  (Ketterer *et al.*, 2004).

For  $^{236}\text{U}$  analysis, the instrument was operated in the medium resolution ( $R=3440$  nominal) mode. The instrument was tuned at  $^{235}\text{U}^+$  using a  $200 \mu\text{g/L}$  Honeywell uranium solution (devoid of detectable  $^{236}\text{U}$ ) to provide optimal ion response and mass calibration adjustment. Each U extract was first analyzed in the magnet sweep mode (mass range 234.95-236.15) to obtain a qualitative spectral scan; thereafter, each solution was quantitatively analyzed

using a peak-jump, electrostatic sector scan of 2.5 peak widths ( $\sim 0.12$  amu) encompassing the entire profile of each selected isotopic peak ( $^{235}\text{U}$ ,  $^{236}\text{U}$ ). Using a dwell time of 50 msec and 20 points within each peak envelope, data were collected for each solution as five integrations of 150 “E-scan” sweeps each. Total E-scan acquisition time was approximately seven minutes for each sample solution. In addition to the samples, the 200  $\mu\text{g/L}$  Honeywell uranium solution was run as a control to develop a “uranium hydride”  $^{235}\text{U}^1\text{H}^+$  subtractive correction factor, which accounts for the well-known interference of  $^{235}\text{U}^1\text{H}^+$  on  $^{236}\text{U}$ . The data are used to obtain the atom ratio  $^{236}\text{U}/^{235}\text{U}$ , which is useable to establish the absence or presence of  $^{236}\text{U}$  and the atom ratio  $^{236}\text{U}/^{238}\text{U}$ . Further details are given elsewhere (Ketterer *et al.*, 2003).

**Uranium concentrations and  $^{238}\text{U}/^{235}\text{U}$ :** Aliquot **D** (acidified upon arrival at the NAU laboratory) was analyzed directly by ICPMS without any pre-concentration. 10 mL aliquots were spiked with 100  $\mu\text{L}$   $^{242}\text{Pu}$  internal standard solution (approximately 20 picograms, derived from NIST 4334g). Standards of known U concentration (0 and 1  $\mu\text{g/L}$  total U), also containing the same relative amount of  $^{242}\text{Pu}$  internal standard solution, were analyzed for determination of the U concentrations in the unknown samples. A solution, consisting of a natural bottled water (Crystal Geyser) diluted with deionized water, was prepared for comparison purposes in the determination of  $^{238}\text{U}/^{235}\text{U}$ . This isotope ratio is well-known to be constant in Nature with  $^{238}\text{U}/^{235}\text{U} = 137.88 \pm 0.03$  (Arden, 1977). Both the U concentration and the  $^{238}\text{U}/^{235}\text{U}$  data were collected using the same “E-scan” peak jump algorithm as was used in the Pu analysis, with selection of appropriate isotopic peaks ( $^{235}\text{U}$ ,  $^{238}\text{U}$ , and  $^{242}\text{Pu}$ ).

**$^{236}\text{U}$ -Calcium Hydroxyapatite Resin Preconcentration:** Four liter portions of aliquot **B** were decanted and treated in a batch mode with 4.0 grams of a “calcium hydroxyapatite resin”. This proprietary material, developed by Michael E. Ketterer, consists of calcium hydroxyapatite impregnated on a polymeric support. It retains uranium from aqueous solution under neutral pH conditions. The resin-water mixtures were stirred for  $\geq 15$  minutes, then the resin was collected by settling and decantation. The water treatment was done by Mark M. Baskaran and the resins were shipped to Michael E. Ketterer. The calcium hydroxyapatite was dissolved by treatment with 10 mL of 8 M aqueous  $\text{HNO}_3$ ; this solution was next treated with UTEVA resin (20 mg) and the U fraction was prepared by collection of the UTEVA resin on a pipette tip equipped with

a small glass wool plug. After rinsing with 3 mL of 2 M aqueous HNO<sub>3</sub>, the U was eluted with 1 mL deionized water, 1 mL 0.05 M aqueous ammonium oxalate, and 1 mL deionized water. The <sup>236</sup>U analysis was thereafter conducted by ICPMS as described previously.

**Plutonium-238:** 5-L of acidified water samples were taken in acid-cleaned 5-L beakers and 1 ml of <sup>242</sup>U spike (= 0.197 ± 0.001 pCi/ml) was added. The spiked solution was evaporated to ~ 500 ml over a period of about 48 hours and the solution was transferred to a precleaned Teflon beaker. Pu was co-precipitated using Fe(OH)<sub>3</sub> co-precipitation technique. The precipitate was separated from the solution by decanting and centrifugation and was subsequently the radiochemical separation and purification of Pu was done using standard procedures (Baskaran et al., 1996, 2000). The pure Pu was electroplated on stainless steel planchets and counted on high-resolution, low-background alpha spectrometers (Baskaran et al., 1996). Along with the 3 samples, one blank was run to determine Pu derived from reagents and resins.

**Radium:** The pre-concentration method that we employed is similar to the methodology that we have published in peer-reviewed journal articles (Tricca et al., 2001; Reynolds et al., 2003). Briefly, a known volume of unfiltered water sample (aliquot **E**) was passed through the MnO<sub>2</sub>-coated acrylic fluffy fiber cartridges at the rate of ~0.3 L/minute. The used fibers, then, subsequently radiochemically processed and gamma counted in a high-purity Ge well detector coupled to an InSpector (Canberra Inc., Moore, 1976; Baskaran et al., 1993; Tricca et al., 2001; Reynolds et al., 2003). The gamma counter was calibrated with NIST and IAEA primary standards for U-Th series radionuclides. The errors reported are the 1-sigma propagated errors arising from counting statistics, detector calibration, and background subtraction.

**Gamma Residue:** Four liter of aliquot **-B** was dried on a hot plate and the residual material was scraped quantitatively and transferred into a gamma counting vial. The residue was gamma counted in a Ge-well detector coupled to a InSpector (Canberra Inc.) for ~24 hours. The main focus was to determine if any anthropogenic gamma-emitting radionuclides (such as <sup>60</sup>Co, <sup>137</sup>Cs, <sup>134</sup>Cs, etc) are present in the groundwater.



**Technetium-99:** Sample aliquots **C** were filtered using 0.20  $\mu\text{m}$  cellulose acetate membrane filtration units to remove un-dissolved material. This is not anticipated to affect the activity of  $^{99}\text{Tc}$ , since this isotope is present in natural waters as the highly soluble and geochemically mobile anion  $\text{TcO}_4^-$  (Brookins, 1986). The samples were sent in one liter HDPE containers to Eberline Laboratories, located in Albuquerque, NM. Samples were pre-concentrated and  $^{99}\text{Tc}$  was determined using beta liquid scintillation spectrometry (LSC) using well-known procedures and protocols. The samples were encoded as follows: RE-1 = Kett-1; TK-1 = Kett-2; NB-1 = Kett-3; GL-1 = Kett-4; GZ-1 = Kett-5; DK-1 = Kett-6; DK-2 = Kett-7; GZ-2 = Kett-8; GL-2 = Kett-9; CB-1 = Kett-10; RE-2 = Kett-11; TK-2 = Kett-12. The names Kett-1 through Kett-12 appear in Eberline's reports.

#### IV. Results

Sample Location/Date	Findings	
DK-1 July 15, 2005	U = $0.66 \pm 0.02$ $\mu\text{g/L}$ $^{239+240}\text{Pu} < 0.006$ pCi/L	$^{238}\text{U}/^{235}\text{U} = 139.9 \pm 1.5$ $^{99}\text{Tc} = 4.5 \pm 1.6$ pCi/L
GL-1 July 15, 2005	U = $0.274 \pm 0.002$ $\mu\text{g/L}$ $^{239+240}\text{Pu} < 0.010$ pCi/L	$^{238}\text{U}/^{235}\text{U} = 139.7 \pm 1.7$ $^{99}\text{Tc} = 5.1 \pm 1.7$ pCi/L
GZ-1 July 15, 2005	U = $0.258 \pm 0.003$ $\mu\text{g/L}$ $^{239+240}\text{Pu} < 0.03$ pCi/L	$^{238}\text{U}/^{235}\text{U} = 137.2 \pm 0.7$ $^{99}\text{Tc} = 2.7 \pm 1.6$ pCi/L
NB-1 July 15, 2005	U = $0.026 \pm 0.001$ $\mu\text{g/L}$ $^{239+240}\text{Pu} < 0.03$ pCi/L	$^{238}\text{U}/^{235}\text{U} = 138.6 \pm 1.1$ $^{99}\text{Tc} = 2.7 \pm 1.6$ pCi/L
RE-1 July 15, 2005	U = $0.422 \pm 0.003$ $\mu\text{g/L}$ $^{239+240}\text{Pu} < 0.006$ pCi/L	$^{238}\text{U}/^{235}\text{U} = 140.0 \pm 1.5$ $^{99}\text{Tc} = 4.6 \pm 1.9$ pCi/L
TK-1 July 15, 2005	U = $0.0084 \pm 0.0007$ $\mu\text{g/L}$ $^{239+240}\text{Pu} = \text{not analyzed}$	$^{238}\text{U}/^{235}\text{U} = 137.6 \pm 1.6$ $^{99}\text{Tc} = 3.4 \pm 1.3$ pCi/L

DK-2	October 20, 2005	U = 0.51 ± 0.01 µg/L <sup>239+240</sup> Pu < 0.006 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 137.5 ± 1.4 <sup>99</sup> Tc = 4.2 ± 1.6 pCi/L
GZ-2	October 20, 2005	U = < 0.02 µg/L <sup>239+240</sup> Pu < 0.016 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 137.9 ± 1.6 <sup>99</sup> Tc = 6.9 ± 1.7 pCi/L
CB-1	October 20, 2005	U = 0.19 ± 0.01 µg/L <sup>239+240</sup> Pu < 0.008 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 137.3 ± 1.3 <sup>99</sup> Tc = 5.1 ± 1.6 pCi/L
GL-2	October 20, 2005	U = < 0.02 µg/L <sup>239+240</sup> Pu < 0.018 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 137.3 ± 3.3 <sup>99</sup> Tc = 6.5 ± 1.7 pCi/L
TK-2	October 20, 2005	U = < 0.02 µg/L <sup>239+240</sup> Pu < 0.013 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 139.4 ± 2.3 <sup>99</sup> Tc = 6.0 ± 1.6 pCi/L
RE-2	October 20, 2005	U = 0.29 ± 0.01 µg/L <sup>239+240</sup> Pu < 0.017 pCi/L	<sup>238</sup> U/ <sup>235</sup> U = 137.6 ± 1.0 <sup>99</sup> Tc = 5.4 ± 1.7 pCi/L

**Table 1: Radium Data – IEL – Groundwater sampling in July and October 2005**

SAMPLE	Water	Mean <sup>226</sup> Ra	Mean <sup>226</sup> Ra	Mean <sup>228</sup> Ra	Mean <sup>228</sup> Ra
		Dpm/100L	pCi/L	dpm/100L	pCi/L
First Field Sampling	(L)				
DK#1	20.0	<b>47.1±1.7</b>	<b>0.21±0.01</b>	<b>50.4±2.6</b>	<b>0.23±0.01</b>
GK#1	13.2	<b>187.4±2.8</b>	<b>0.84±0.01</b>	<b>189.0±4.0</b>	<b>0.85±0.02</b>
GZ#1	10.0	<b>37.9±2.8</b>	<b>0.17±0.01</b>	<b>30.7±3.4</b>	<b>0.14±0.02</b>
NB#1	10.0	<b>27.2±2.0</b>	<b>0.12±0.01</b>	<b>BD</b>	<b>BD</b>
RE#1	10.0	<b>104.0±3.4</b>	<b>0.47±0.02</b>	<b>76.6±3.6</b>	<b>0.35±0.02</b>
Second Field Sampling					
DK#2	12	<b>44.7±2.5</b>	<b>0.20±0.01</b>	<b>43.8±3.3</b>	<b>0.20±0.02</b>
RE#2	9.5	<b>81.2±3.3</b>	<b>0.37±0.02</b>	<b>67.4±4.0</b>	<b>0.30±0.02</b>
GL#2	10	<b>22.7±2.9</b>	<b>0.10±0.01</b>	<b>24.1±5.6</b>	<b>0.11±0.03</b>
GK#2	10	<b>175.0±3.9</b>	<b>0.79±0.02</b>	<b>81.2±3.2</b>	<b>0.37±0.01</b>
TK#2	9.5	<b>215.7±5.1</b>	<b>0.97±0.02</b>	<b>214.5±6.8</b>	<b>0.97±0.03</b>

CB-1	10	19.9±2.5	0.09±0.01	22.9±4.3	0.10±0.02
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BD: Below Detection Limit

## V. Discussion

The results for U concentrations,  $^{238}\text{U}/^{235}\text{U}$  atom ratios, and  $^{239+240}\text{Pu}$  are in accordance with expected conditions for naturally occurring radioactivity in undisturbed environmental systems. They do not disprove the presence of anthropogenic radioactivity; instead they indicate that the U present appears to be of natural origin, and that Pu cannot be detected at levels above what could be expected in surface waters from stratospheric fallout.  $^{238}\text{Pu}$  was below detection limit using the methodology utilized (detection limit = 0.0002 pCi/L sample size used).

Analysis of  $^{236}\text{U}$  in the CaHAP resin indicates that the  $^{236}\text{U}/^{238}\text{U}$  ratio in all samples and the blank were  $< 2 \times 10^{-7}$ . This indicates that we cannot detect any  $^{236}\text{U}$  in any of the samples. The  $2 \times 10^{-7}$  atom ratio is the lowest possible detectable ratio we can do with our system for reasons detailed in Ketterer et al. (2003).

The data are reported in Table 1. There are no detectable gamma-emitting anthropogenic radionuclides ( $^{60}\text{Co}$ ,  $^{134}\text{Cs}$ ,  $^{137}\text{Cs}$ , etc) in any of the residues resulted from the evaporation of water samples that were analyzed. The mean  $^{228}\text{Ra}$  activity in all the 6 sites varied between below detection limit and 0.97 pCi/L while the  $^{226}\text{Ra}$  activities varied between 0.10 and 0.97 pCi/L. The activities reported here are significantly lower than U.S. EPA Drinking Water Limit.

The  $^{99}\text{Tc}$  results indicate the presence of a fission product in all samples. The second set of samples collected in October 2005 also indicates presence of  $^{99}\text{Tc}$  in every one of the samples. These samples were collected north, northwest, west and southwest at varying depths, shallow, intermediate and fairly deep (~ 100 ft). This isotope is associated with “recycled uranium” and has been found as such at several DOE-related sites where reactor-irradiated uranium has been handled and processed. The activities are relatively low; nevertheless, this isotope would not be expected to be present in a natural, unaffected environmental system. Accordingly, the presence of any  $^{99}\text{Tc}$  is a positive indication of the presence of anthropogenic radioactivity, most likely “recycled uranium”, a source of fission products, or a chemically pure sample of  $^{99}\text{Tc}$  from a past industrial use.

## V. Literature Cited

- Arden, J.W., "Isotopic composition of uranium in chondrite meteorites", *Nature* **1977**, 269, 788–789.
- Baskaran, M., D. J. Murphy, P. H. Santschi, J. C. Orr and D. R. Schink, 1993. A method for rapid in-situ extraction and laboratory determination of Th, Pb and Ra isotopes from large volumes of seawater. *Deep-Sea Research* 40(4): 849-865.
- Baskaran, M.; Asbill, S.; Santschi, P.H.; Davis, T.; Brooks, J.M.; Champ, M.A.; Adkinson, D.; Colmer, M.R.; Makeyev, V., "Pu, 137-Cs and 210-Pb-Excess in Russian arctic sediments. *Earth and Planetary Science Letters* **1996**, 140, 243-257.
- Baskaran, M.; Asbill, S.A.; Schwantes, J.; Santschi, P.H.; Champ, M.A.; Brooks, J.M.; Adkinson, D.; Makeyev, V., "Concentrations of 137-Cs, 239,240-Pu and 210-Pb in sediment samples from the Pechora Sea and biological samples from the Ob, Yenisey Rivers and Kara Sea. *Marine Pollution Bulletin* **2000**, 40, 830-838.
- Brookins, D.G., "Rhenium as analog for fissionogenic technetium: Eh-pH diagram (25 C, 1 bar) constraints", *Applied Geochemistry* **1986**, 1, 513-517.
- Ketterer, M.E.; Hafer, K.M.; Link, C.L.; Royden, C.S.; Hartsock, W.J., "Anthropogenic <sup>236</sup>U at Rocky Flats, Ashtabula River Harbor, and Mersey Estuary: Three Case Studies by Sector ICPMS", *Journal of Environmental Radioactivity* **2003**, 67, 191-206.
- Ketterer, M.E., Hafer, K.M., Jones, V.J., Appleby, P.G., "Rapid Dating of Recent Sediments in Loch Ness: Inductively Coupled Plasma Mass Spectrometric Measurements of Global Fallout Plutonium", *The Science of the Total Environment* **2004**, 322, 221-229.
- Moore, W.S., Sampling of Ra-228 in the deep ocean, **1976**, *Deep-Sea Res.* 23, 647-651.
- Reynolds, B. C., G. J. Wasserburg, and M. Baskaran, The transport of U- and Th-series radionuclides in sandy confined aquifers. *Geochim. Cosmochim. Acta* **2003**, 67, 1955-1972.
- Tricca, A., G. J. Wasserburg, D. Porcelli and M. Baskaran, The transport of U- and Th-series nuclides in a sandy unconfined aquifer. *Geochim. Cosmochim. Acta*, **2001**, 65, 1187-1210.