

The Quantitative Analysis of Uranium Isotopes in the Population of Port Hope, Ontario Canada

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Introduction

The contamination of the civilian population living in the vicinity of nuclear fuel processing plants has been a subject of numerous studies and controversy regarding the adverse effects of internal contamination with uranium isotopes released into the environment. Among many sites in North America, particular interest has been given to facilities such as Fernald, Ohio and Paducah, Kentucky although never followed up by objective research studies of the quantities and ratios of uranium isotopes. Likewise the oldest uranium processing facility in the world, located in Port Hope, Ontario Canada, although being studied by epidemiological research, the objective analytical study of uranium isotopes in the Port Hope population has never been conducted. The purpose of our study was the quantitative analysis of the internal contamination with four uranium isotopes in the population living near the uranium conversion facility in Port Hope, Ontario Canada.

Materials and Methods

The urine samples of subjects presenting with multi-system, non-specific symptoms of immune system alterations, musculo-skeletal, central nervous system, and neoplastic disease were obtained from residents of Port Hope and analyzed in reference to the control samples from residents of other parts of Ontario. The samples were analyzed at the Institute for Mineralogy, J.W. Goethe University in Frankfurt, Germany in a specialized radiochemistry laboratory by mass spectrometry. The analytical methodology included pre-concentration of urine by co-precipitation, oxidation of organic matter, uranium purification by ion-exchange chromatography, and ICP-MS double-focusing Thermo Finnigan Neptune multi-collector.

Results

Our results show 4 of 9 samples containing uranium of non-natural origin. Subject 3 was highly positive for depleted uranium with a $^{238}\text{U}/^{235}\text{U}$ of 147.11 ± 1.42 and a relatively normal abundance of total uranium. This sample contained a concentration of ^{236}U with a $^{236}\text{U}/^{238}\text{U}$ ratio of $4.38 \times 10^{-6} \pm 4.3 \times 10^{-7}$ indicating its reactor origin. Three other subjects (2, 4, and 6) contained detectable amounts of ^{236}U . Subject 6 had a paradoxically high $^{236}\text{U}/^{238}\text{U}$ ratio of $5.53 \times 10^{-5} \pm 3.9 \times 10^{-6}$. Subjects 2 also had a higher than normal concentration of total uranium at 24.8 ng/L. The ^{236}U in these samples indicates its origin as contamination with non-natural uranium. The remaining five subjects were negative for both depleted uranium and uranium-236. Control subjects had no

detectable ^{236}U and a normal concentration of total uranium in their urine. Control subject 2 had a natural $^{238}\text{U}/^{235}\text{U}$ ratio. However control subject 1 had $^{238}\text{U}/^{235}\text{U}$ ratio that was slightly depleted. It was learned after testing that control 1 had visited Port Hope at some time prior to giving their sample.

Table 1: $^{238}\text{U}/^{235}\text{U}$ Isotopic Ratio, Total Uranium, and ^{236}U Concentration

Subject	$^{238}\text{U}/^{235}\text{U}$	2 SD	U ng/L	^{236}U fg/L
1	137.97	0.31	8.5	< 1
2	137.99	0.57	24.8	1.7
3	147.11	1.42	7.0	31
4	138.75	1.12	5.1	< 1
5	139.26	1.52	2.7	< 1
6	137.71	0.67	9.4	517
7	138.22	0.83	8.8	< 1
8	138.49	1.79	3.0	< 1
9	137.34	0.78	3.7	< 1
Control 1	138.74	0.41	5.6	< 1
Control 2	138.15	1.54	2.1	< 1

Table 2: $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ Isotopic Ratios

Subject	$^{234}\text{U}/^{238}\text{U}$	2 SD	$^{236}\text{U}/^{238}\text{U}$	2 SD
1	6.71×10^{-5}	8.88×10^{-6}		
2	5.65×10^{-5}	1.11×10^{-6}	6.53×10^{-8}	8.6×10^{-9}
3	5.17×10^{-5}	5.03×10^{-6}	4.38×10^{-6}	4.3×10^{-7}
4	6.78×10^{-5}	9.43×10^{-6}	7.48×10^{-8}	4.3×10^{-8}
5	6.81×10^{-5}	5.06×10^{-6}		
6	5.97×10^{-5}	4.69×10^{-6}	5.53×10^{-5}	3.9×10^{-6}
7	6.01×10^{-5}	4.50×10^{-6}		
8	5.56×10^{-5}	7.09×10^{-6}		
9	7.07×10^{-5}	3.16×10^{-6}		
Control 1	4.80×10^{-5}	9.82×10^{-7}		
Control 2	4.62×10^{-5}	5.50×10^{-6}		

Natural uranium has a $^{238}\text{U}/^{235}\text{U}$ ratio of 137.88 and does not contain ^{236}U , a man made isotope. A $^{238}\text{U}/^{235}\text{U}$ ratio lower than 137.88 indicates enriched uranium and a ratio higher than 137.88 is consistent with depleted uranium. Background total uranium concentration in the urine of humans is 1 to 7 ng/L (USA NCEH).

Discussion

The inadvertent exposure and toxicology of uranium isotopes in both military personnel and civilians employed in the nuclear industry or living in the vicinity of uranium processing plants has been well documented. Both parenteral and oral administration of uranium isotopes has been studied in animal studies and humans. Of particular interest are inhalational pathway toxicity studies which confirmed significant renal and pulmonary damage with eleven uranium compounds including oxides, fluorides, tetrachlorides, and nitrates in six different animal species as well as humans. Most recent studies of the Gulf War veterans have estimated a significant carcinogenic risk of inhaled depleted uranium. Uranium containing dust has been identified as the most important source of radiation exposure in uranium mining and processing. Toxicity of uranium in the ground waters (Saskatchewan, Canada), higher risk of lung cancer in uranium miners (New Mexico, Arizona), overall cancer risk in workers involved in the uranium processing industry (Ohio, Colorado), and numerous published studies from around the world all point to the realistic probability of adverse health effects of uranium isotopes in the human population living in the vicinity of nuclear processing plants.

Summary

The contamination with depleted uranium has been verified and well documented in the studies on the military personnel in the conflicts in Iraq and Eastern Afghanistan, as well as, in the civilian population. The history of uranium contamination in Port Hope is well documented. Our results provide the first objective analytical study of long-term contamination and possible association with adverse health effects in the current population of Port Hope. These preliminary results warrant additional multidisciplinary studies.

Detailed Methodology

Approximately 500 ml of urine was used for uranium isotope analyses. The urine was first acidified with 50 ml concentrated nitric acid per litre and then transferred to a pre-cleaned polypropylene beaker and left on a stirring hotplate at about 80°C after adding calcium nitrate and 20 pg of an enriched ^{233}U tracer solution. Both the urine and the tracer were precisely weighed ($\pm 0.1\%$). Uranium was co-precipitated with calcium phosphate by adding ammonium phosphate and ammonium hydroxide. The supernatant was decanted and the insoluble phosphate cleaned and extracted by repeated centrifugation with Milli-Q H_2O . The precipitate was wet-ashed with a 3:1 $\text{HNO}_3:\text{H}_2\text{O}_2$ mixture at about 120°C over 48 hours in Teflon vessels in order to destroy remaining organic material. The white inorganic residue was dissolved in 3M nitric acid for uranium purification using a pre-washed ion exchange column with 0.8 ml Eichrom UTEVA resin (particle size 50-100 μm). To minimize sample contamination, the entire procedure was performed in a clean-lab facility and only acids purified twice by sub-boiling two-bottle distillation and deionised Milli-Q water (resistivity $> 18 \text{ M}\Omega$, Milli-Q, Bedford, USA) were used. All reagents and beakers were pre-cleaned and polypropylene beaker and columns with resin were disposed of after use. Two beakers containing Milli-Q H_2O instead of urine and two beakers with an in-house urine standard were processed alongside the samples as procedural blank and reference solutions.

Isotope analysis was carried out using a double-focusing MC-ICPMS Neptune (Thermo-Electron, Bremen) equipped with a retarding potential quadrupole lens and a secondary electron multiplier for ion counting. The Neptune allows simultaneous detection of up to 9 isotopes over a dynamic range of up to 10 orders of magnitude. Eluted uranium was converted to nitrate and dissolved in 1 ml of 2% HNO_3 -0.2% HF. For introduction of the solution, a desolvating nebuliser (Aridus, CETAC Technologies, Nebraska 68144 USA) was used. The limit of detection was constrained by both the instrument and the chemical processing. For the Neptune, the detection on a Faraday cup was limited by the noise on the amplifier which was $< 10 \text{ fgg}^{-1}$ for any uranium isotope in solution, whilst the limit of detection for the ion counter was $< 0.02 \text{ fgg}^{-1}$. For naturally abundant isotopes, the detection limit was compromised of chemical blanks, which were about 24-27 pg of ^{238}U . Careful cleaning of all relevant parts and longer wash steps before running low-level samples allows routine detection limits (3 times the standard derivation of the 2% nitric blank; $n>10$) for ^{236}U below 0.05 fgg^{-1} . Reproducibility of isotope analyses depends mainly on isotope abundance. For a 8 ppb CRM950a solution for instance, the reproducibility ($n=14$) of the $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ ($= 4.5 \times 10^{-8}$) over several days were better than 0.1, 0.4 and 5%, respectively. Instrument sensitivities at the times of analysis were 350-450 Vppm^{-1} or 20000-28000 $\text{cs}^{-1}\text{ppt}^{-1}$ (counts per second per $1 \times 10^{-12} \text{ gg}^{-1}$). Abundance sensitivity at -2 amu , e.g. tailing of ^{238}U at ^{236}U , was $< 250\text{ppb}$. All measurements were made relative to a natural uranium $^{238}\text{U}/^{235}\text{U}$ value of 137.88, a result of application of mass bias correction using the CRM112A natural uranium standard. Each analysis was followed by a 4 min wash and a 5 min blank (2% HNO_3 -0.2% HF) analysis. An 8ppb CRM112A solution was run every 3 unknowns to check machine conditions. Accuracy and precision were monitored using CRM112A and CRM950a as well as internal urine standards of natural uranium composition. The in-house urine standards were prepared from natural urine. Off-line data processing included corrections for drift on ion counter gain (generally $< 1\%$) and instrumental mass bias ($< 1\% \text{ amu}^{-1}$), as well as for tracer impurities and procedural blank. Reported uncertainties (2σ) are the results of quadratic weighted additions of the main error sources, such as uncertainties of all applied corrections, analytical precision and the reproducibility of the 8ppb CRM112A solution.

History of the Nuclear Industry in Port Hope

Canada began mining uranium ores in the early 20th century for their radium content. In 1930, uranium ores were discovered in the Great Bear Lake deposit in the North West Territories and were developed by Eldorado Gold Mines for radium and uranium extraction. The refinery in Port Hope, Ontario was the first facility of its kind built and the only one in North America in the early 1940s that was equipped to refine uranium. Uranium concentrates (yellowcake) were shipped to the refinery where uranium was refined into uranium oxides (UO₂ and UO₃) as well as uranium hexafluoride (UF₆).

From 1941 to 1945, the entire production of refined uranium was supplied to the United States for use in the Manhattan project. The Port Hope facility had hundreds of tons of uranium concentrate on site from years of radium extraction but to meet demand Eldorado reopened the mine at Great Bear Lake which had shut down two years earlier. The facility also refined uranium from ores purchased by the US from Union Minière, a Belgian company that developed a deposit in the African Congo.

Canada's uranium mining and processing industry continued to sell uranium for nuclear weapons until 1959 when United States stopped purchasing uranium from Canada. Production slowed but continued under the Canadian government's uranium stockpiling program until the mid 1980s. Eldorado Nuclear built a new uranium refinery at Blind River, Ontario (early 1980s). The Blind River facility refined uranium concentrate into UO₃ which was shipped to Port Hope. In Port Hope, UO₃ was converted into UO₂ and UF₆. The UO₂ was then sold as fuel for CANDU reactors. The UF₆ was exported to enrichment facilities. The Port Hope facility also produced depleted uranium metals until 1992 and processed enriched uranium from 1966 to 1987. Port Hope also blended enriched and depleted uranium powders to specific isotopic concentrations.

In 1988, Cameco Corporation was formed by the privatization of Canada's uranium industry and the merger of two government owned corporations Eldorado Nuclear and Saskatchewan Mining Development Corporation. Cameco is the only Canadian company and one of only four companies currently providing uranium refining and conversion services to the western world; the other three being Honeywell in the United States, British Nuclear Fuels Limited in the United Kingdom, and Comurhex in France. Cameco is the world's largest uranium producer with four operating mines in Canada and the United States and two new mines being developed, one in Canada and the other in Central Asia. It has about 40% of the capacity in the western world to produce UF₆. It is also the only producer of ceramic uranium oxides for fuel in Canadian-built CANDU reactors.

Port Hope is also home to a facility established in 1965 to develop fuel to support Canada's nuclear energy program. This facility produces fuel pellets from refined UO₂ and assembles fuel bundles for CANDU reactors. In 2006, the plant was acquired by Cameco from Zircotec Precision Industries.



Port Hope harbor back dropped by the Cameco facility, UF₆ drums are visible behind the fence



Street in Port Hope with UF₆ drums just on the other side of the fence



A street, private home, and children's playground in the immediate vicinity of the Cameco facility; a tarp covers uranium tailings



Two UF₆ drums left on a trailer in a publicly accessible parking lot



The laboratory at the Institute for Mineralogy, J.W. Goethe University