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Depleted uranium contamination by inhalation exposure and its detection after ~20 years: Implications for human health assessment

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ABSTRACT

Inhaled depleted uranium (DU) aerosols are recognised as a distinct human health hazard and DU has been suggested to be responsible in part for illness in both military and civilian populations that may have been exposed. This study aimed to develop and use a testing procedure capable of detecting an individual's historic milligram-quantity aerosol exposure to DU up to 20 years after the event. This method was applied to individuals associated with or living proximal to a DU munitions plant in Colonie New York that were likely to have had a significant DU aerosol inhalation exposure, in order to improve DU-exposure screening reliability and gain insight into the residence time of DU in humans. We show using sensitive mass spectrometric techniques that when exposure to aerosol has been unambiguous and in sufficient quantity, urinary excretion of DU can be detected more than 20 years after primary DU inhalation contamination ceased, even when DU constitutes only ~1% of the total excreted uranium. It seems reasonable to conclude that a chronically DU-exposed population exists within the contamination 'footprint' of the munitions plant in Colonie, New York. The method allows even a modest DU exposure to be identified where other less sensitive methods would have failed entirely. This should allow better assessment of historical exposure incidence than currently exists.

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Abbreviations: DU, depleted uranium, depleted in the ²³⁵U isotope relative to natural uranium; EU, enriched uranium, enriched in the ²³⁵U isotope relative to natural uranium; NLI, NL Industries (formerly National Lead Industries); ICP-MS, inductively coupled plasma mass spectrometry; ICP-AES, inductively coupled plasma atomic emission spectrometry; MC-ICP-MS, multicollector inductively coupled plasma mass spectrometry; U-TEVA, Uranium specific tetravalent actinide ion exchange resin (Eichrom Industries); ng L⁻¹, nanograms per litre; IRB, Institutional Review Board.

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1. Introduction

Depleted uranium (DU) is a by-product of the uranium isotope enrichment process, but aside from its ~40% lower radioactivity than purified natural U, it has similar chemical toxicity to enriched or chemically purified natural uranium. When inhaled or ingested in sufficient doses, DU constitutes a distinct health hazard (Royal Society, 2001, 2002; WHO, 2001). DU has been used in military conflicts primarily as armour-penetrating munitions in the Persian Gulf conflict of 1991 and the Balkans (AEPI, 1995; Royal Society, 2001, 2002; WHO, 2001), and in Iraq primarily in 2003. Its use in other conflicts such as Afghanistan in 2003 and southern Lebanon in 2006 has been suggested but remains unsubstantiated (UNEP, 2007).

Uranium occurs naturally in soil (~1–5 mg kg⁻¹) and water (~0.1–5 µg L⁻¹) and the anthropogenic addition to this natural background is insignificant except near point sources of uranium release. For humans, the aerosol exposure pathway is critical to hazard assessment (Royal Society, 2001) in that inhalation exposure to relatively insoluble DU oxide particles represents a potentially long-term reservoir of internal alpha-decay activity that could cause cell damage. Although considerable quantities of either soluble or insoluble natural uranium are ingested regularly by consumption of food and drink, little of this uranium is absorbed into the blood stream (ATSDR, 1999).

It has been alleged that there is or may be a connection between an individual's inhalation exposure to DU aerosols in the military theatre, and the development of multisymptomatic chronic medical conditions often referred to as Gulf War Illness (Jamal, 1998; Durakovic, 2003). Attempts to assess the significance of DU to health have been complicated in part by the lack of accurate exposure assessments, although it is clear that in laboratory experiments involving animals or cell cultures, high doses of DU induce cell damage and impair certain body functions (Jamal, 1998; Monleau et al., 2005) and can be cytotoxic and clastogenic (Wise et al., 2007). Thus while the widespread use of DU is acknowledged, the lack of evidence for substantial DU contamination of individuals via inhalation–ingestion (notwithstanding the potential inadequacy of existing DU exposure screening) has so far failed to clarify whether DU plays any role in Gulf War Illness. On this and other grounds the relevance of DU to Gulf War Illness remains in doubt (Wesseley and Freedman, 2006; Ismail and Lewis, 2006). Instead it may be more likely that cytotoxic, clastogenic and teratogenic effects are more likely long term outcomes due to long term exposure to low level radiation or chemically toxic effects of DU (Schmidt, 2004; Bernard et al., 2005; Hindin et al., 2005; Wise et al., 2007).

In the health literature, only one study (Durakovic et al., 2002) has claimed to document persistent internal contamination of soldiers by DU from alleged inhalation exposure. However there are many analytical deficiencies to this paper, and the data are unlikely to be reliable, a situation that undermines its conclusion. Most other studies of US or allied soldiers that have DU contamination involve individuals with embedded shrapnel (Hooper et al., 1999; McDiarmid et al., 2000, 2004). Gwiazda et al. (2004) measured uranium isotopes in urine from non-shrapnel-embedded US soldiers that served in the Persian Gulf conflict of 1991 and found some evidence of DU, but the measurements by

ICP-MS lacked sensitivity and reproducibility at moderate to low urinary uranium concentrations, and the study involved a small cohort. More recently, the UK government commissioned both a voluntary screening programme of more than 400 individuals potentially having a DU exposure during the period 1991–1997 (DUOB, 2007) and a study by Bland et al. (2007) that tested for DU in spot urine samples of more than 300 personnel involved in Iraq in 2003. Both studies failed to find evidence for DU contamination in any of the tested individuals and both used high sensitivity methodologies at or close to current state of the art. These studies collectively show that DU exposure may be uncommon to rare in military personnel, but because the magnitude of DU inhalation of tested individuals is unknown, they do not provide a quantitative measure of exposure incidence or magnitude. Thus a critical question that remains is the extent to which a significant inhalation exposure of DU metal or DU oxide could be a source of chemical and radiological toxicity in the body.

The potential relationship between DU exposure and illness has also been highlighted in recent years by reports (Hindin et al., 2005; Al-Sadoon et al., 2002) of significant increases in certain cancers and birth defects in southern Iraq, an area where in 1991 DU was used extensively and where civilian chronic exposure to DU dust is potentially significant. Unfortunately, there are no credible studies of DU contamination of Iraqis and thus this apparent increased incidence of cancers and birth defects remains unexplained, with a connection to DU exposure remaining possible but without direct evidence.

With these limitations in mind, a study of a population demonstrably exposed to inhalation exposure of uranium oxide aerosols over a period of time was undertaken to ascertain the potential for detecting DU contamination in human subjects many years after initial exposure.

2. Scope of study

This study investigates a DU contaminated site and a small cohort of individuals that, between 1958 and 1981, resided near to or worked in a uranium processing plant involved in the manufacture of DU and to a lesser extent enriched uranium (EU), near Colonie (Albany) New York (National Lead Industries, NLI). This plant emitted a distinct DU (and possibly minor EU) aerosol plume arising from combustion of metallic uranium milling waste, over a period of decades until plant closure in 1984 (Fig. 1, constructed using data of Jeter and Eagleson, 1980). The data from this study and from additional 2006 soil samples (Lloyd, unpublished data 2007) were integrated to determine that more than 5 metric tons of DU was deposited, primarily by aerosols, in the first 600 m of radius from the plant, and that soils as far as 4 km from the plant have low level DU contamination. It is probable that between 5 and 10 tons of DU aerosol were historically emitted. This quantity is comparable to the total mass of respirable DU particles produced during the entire 1991 Persian Gulf Conflict, considering the proportion of all expended munitions likely to become aerosolised during hard target impact-related combustion.

The temporal record of pollution from the plant is recorded in sediments of a small reservoir nearby (Arnason and

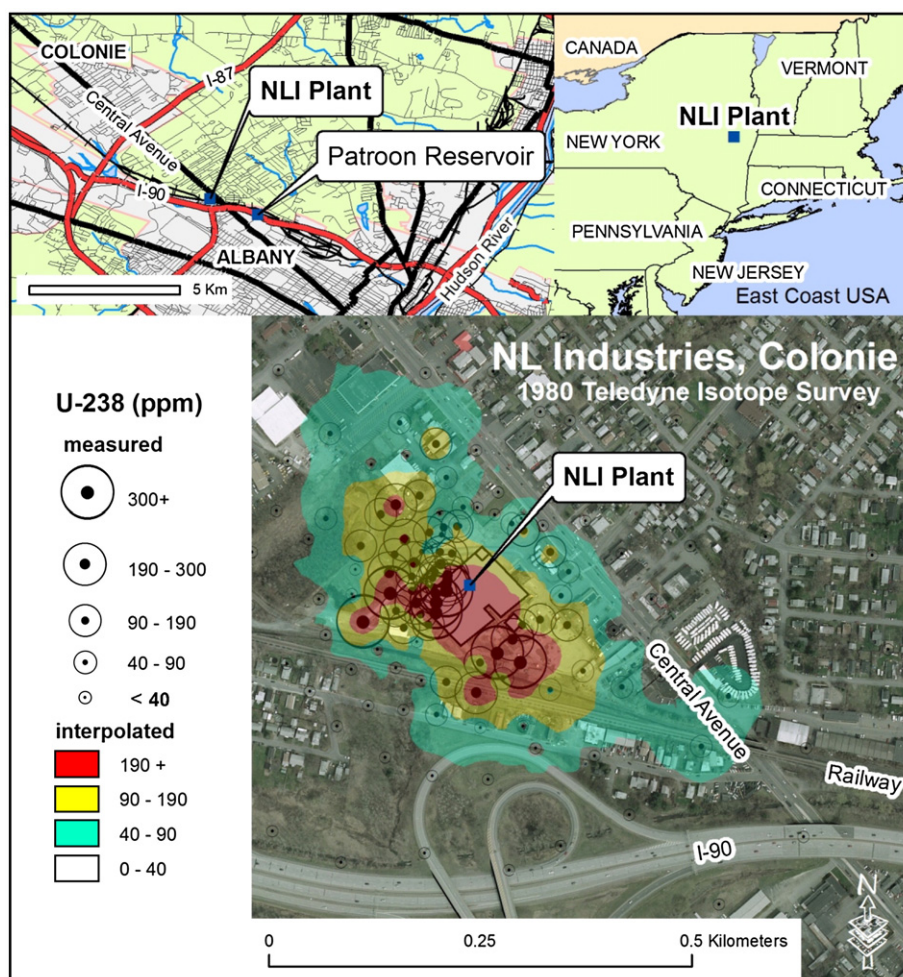


Fig. 1 – Map of the Colonie New York area (in Albany County) showing location, and detailed pattern within the city of the uranium pollution plume from the NLI plant, superimposed upon an aerial view of Colonie. The data used are from the Jeter and Eagleson (1980) study. The figure also uses mapping and photography from New York State public information, <http://www.nysgis.state.ny.us/>.

Fletcher, 2003). We measured uranium concentration and isotope composition for this sediment record and show that the chronic deposition of substantial amounts of uranium took place during the plant's operation. We also isolated and identified DU oxide particles emitted from the plant but now in soils and household dusts to document the presence and nature of the primary aerosol particles.

Against this background of aerosol deposition, individuals were identified that either worked at the plant or lived or worked in close proximity (<1 km) to the site for more than 5 years during its active phase of operation from 1958 to 1981 and who would have had a clear inhalation exposure. These individuals were tested for DU exposure using our method.

3. History of uranium processing at Colonie

The NL Industries (NLI) plant is located in Colonie, New York, less than 6 km from the State Capitol building in Albany. NLI was involved in the reduction of uranium tetra-fluoride to uranium metal, and fabrication of uranium articles from 1958–1984. These consisted mainly of DU projectiles, but with some enriched

uranium for fuel rods prior to 1972 (ATSDR, 2004). A New York State Department of Health draft internal report states that uranium enriched to $\geq 3\%$ ^{235}U was also processed between 1958 and 1968, and that in 1975 a license amendment restricted the plant to possession of depleted or natural uranium. NLI carried out work with the US Atomic Weapons program from 1958–1968 at its Colonie plant (NYS DOH 1979). After 1968 their primary customer was the US Department of Defence, with contracts primarily for DU penetrators (DOE, 2005).

Fabrication processes at the Colonie plant produced chemically unstable uranium scrap metal, which when finely divided can spontaneously combust. The option chosen by NLI to deal with the uranium waste was to convert it to oxide in a furnace with a filtered exhaust stack. In 1979 the New York State Department of Environment investigated claims that the stack filters were bypassed, and subsequently forced the temporary closure of the plant for excessive emissions of uranium compounds to the atmosphere (Romano, 1982). A soil survey in 1980 conducted by Teledyne Isotopes (Jeter and Eagleson, 1980) found considerable depleted uranium contamination (using gamma-ray spectrometry of soil samples) within 600 m of the plant. The plant was permanently closed in 1984 and the

property was transferred to the federal Department of Energy that proceeded to remediate both the site and more than 50 contaminated nearby residential properties (ATSDR, 2004). The site has now been cleared, and is in the process of advanced remediation by the U.S. Army Corps of Engineers, under the Formerly Utilized Sites Remedial Action Program (FUSRAP, 2005).

4. Methods and materials

4.1. Analysis of the Jeter and Eagleson (1980) data

At the direction of state agencies a soil survey was commissioned by NLI in 1980, involving about 240 samples collected in a radius of 600 m of the site, with increasing sampling density closer to the site. Two aliquots of soil were taken for each locality at depths of 0–1.3 cm, and 1.3–5.1 cm and measured by gamma spectrometry for ^{238}U and ^{235}U and expressed as pCuries g^{-1} . We converted these measurements into mg kg^{-1} and contoured the data in the vicinity of the site, as shown in Fig. 1. The minimum integrated deposition of uranium, assuming a dry soil density of 2.0 g cm^{-3} , was $3400 \text{ kg of } ^{238}\text{U}$ and may be more than 5000 kg due to uncertainties inherent in this calculation. This value does not take into account migration of uranium below the sampled soil profile, deposition outside of the 600 m radius, or the removal of U by runoff

during the decades prior to the survey, all of which conspire to increase the estimated mass of uranium pollution.

4.2. Uranium particles and lake sediments

Dry dust and soil samples were taken from domestic locations within 1.5 km of the Colonie site. Uranium rich particles from these samples were pre-concentrated by a combination of magnetic separation using a Frantz LB-1 separator and heavy liquid density separation. Uranium oxide particles were identified at high magnification using a scanning electron microscope; their uranium rich oxide composition was confirmed with energy dispersive X-ray (EDX) analysis at the University of Leicester. The oxidation state of uranium oxide particles is difficult to determine because synchrotron X-ray identification is usually required (Salbu et al., 2007), and therefore the exact composition of the particles, in terms of oxidation state, remains uncertain.

Lake sediment cores (mainly mud and silt) from the Patroon Reservoir downstream from the NLI plant that were studied by Arnason and Fletcher (2003) were re-sampled at 5 cm intervals. Sub-samples were dried and pulverised, and dissolved in acid. Uranium concentration profiles were produced using ICP-AES at the University of Leicester and $^{238}\text{U}/^{235}\text{U}$ isotope signatures using ThermoElemental Excell quadrupole ICP-MS at the British Geological Survey. All data

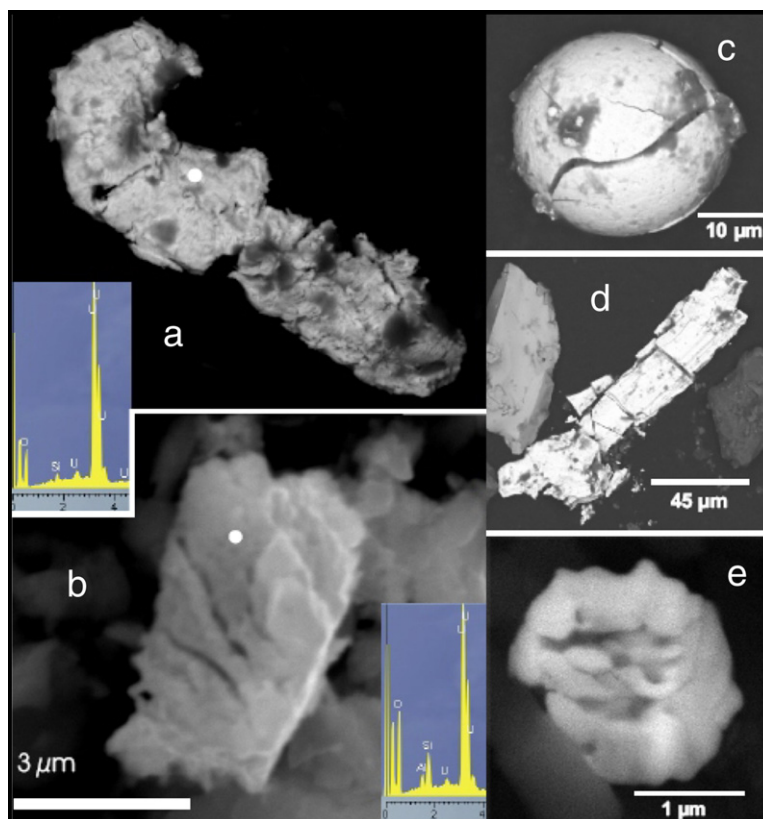


Fig. 2 – Scanning electron photomicrographs of uranium oxide particles from dust samples from residential locations within 400 m of the NLI site illustrating the variety and sizes observed; a,b: energy dispersive X-ray spectrometry (scale in keV) has identified only U, O, and minor Si in the particles (white dot is analysis spot); c, a commonly observed spherical uranium oxide particle suggested to be molten particles quenched in exhaust from the burner stack; d, e: large fragile and very small particles both of uranium oxide.

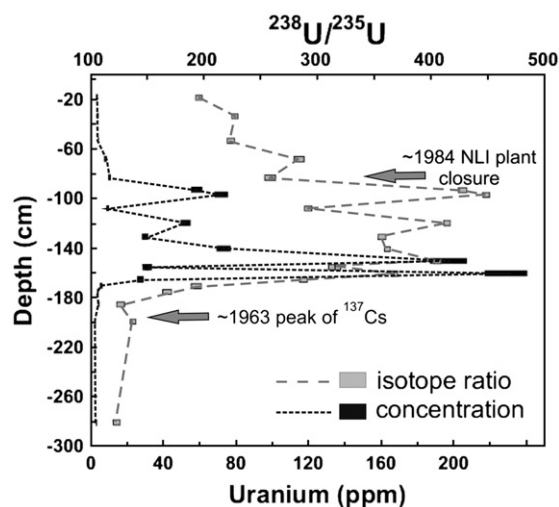


Fig. 3 – Plot of depth (cm) against both U concentration (ppm) and $^{238}\text{U}/^{235}\text{U}$ of the lake sediments. The peak of ^{137}Cs is shown as a time line approximately 1963, and the rapid decline of U concentration at ~ 90 cm is inferred to coincide with the closure of the plant in ~ 1984. The dip in concentration of U between 140 and 110 cm is probably the result of sediment influx during construction of the adjacent interstate highway. See Table 1 for data.

were corrected for blank contributions, mass bias and dead-time effects. Quality control was ensured with solutions of known natural and depleted uranium isotope signatures.

The core has been subjected to ^{137}Cs and ^{210}Pb measurement and sedimentological analysis in order to place age constraints on the core (J Arnason, personal communication 2006). The ^{137}Cs peak, known to have occurred in 1963, can be placed very close to 200 cm depth in the core.

4.3. Water and urine samples

The scope of sampling was limited to 24 individuals that had either worked in the plant or lived in a contaminated area close to the plant for more than 5 years from 1958 to 1981. The drinking water of most of the tested individuals was also sampled. Such water samples were collected from homes using municipal water supplies and a private well, and placed into pre-cleaned HDPE bottles, and treated similarly to urine in terms of shipment and storage.

The individuals were contacted, and the outline and rationale of the project was explained. Participants signed a consent form, provided information about their employment and/or residential history and agreed to provide a urine sample for analysis. The use of >24 h samples allowed calculations of daily excretion rates to be determined, and provided for replicate analyses where appropriate. Samples were sealed and shipped from the State University of New York at Albany to the UK for testing at the NERC Isotope Geosciences Laboratory. Samples were stored prior to analysis in a cold room at approximately 4 °C and were progressively analysed over the course of several months without any signs of sample deterioration. The samples were never frozen. Approximately 700 ml of urine was used for each analysis.

The method is largely the same as that described by Parrish et al. (2006) and involved pre-cleaning of 24 h sample collection bottles, acidification of urine samples, adding a known quantity of ^{233}U tracer, and chemical co-precipitation of uranium with calcium phosphate upon addition of ammonia to achieve pH 9. The precipitate was separated by pouring off the supernate, re-dissolving in ultrapure nitric acid and hydrogen peroxide, and repeated wet-ashing of the sample in quartz beakers to 240 °C to destroy all organic compounds. For water samples the ^{233}U tracer was added, and about 100 ml of water sample evaporated in quartz beakers. The inorganic salts from both urine and water samples were redissolved in 4M HNO_3 and using U-TEVA resin (Eichrom Industries) uranium was purified and separated from other elements, and taken up in ~1 ml of 2% HNO_3 . The chemical procedure was conducted in a class 100 clean laboratory designed for ultra trace analysis. The total procedural blank for the procedure was less than 25 pg U, and its isotopic composition was measured as natural within uncertainty with no detectable ^{236}U . Chemical recoveries varied between 60 and 100%.

Reagent grade nitric acid was sub-boiling distilled in-house using Teflon bottle stills to achieve better than 0.05 pg U/ml blank level. A 99.94% isotopically pure ^{233}U tracer was obtained from the IRMM (Geel Belgium) for isotope dilution determination of U concentration. HDPE urine collection bottles were cleaned with reagent grade nitric acid and rinsed in purified water using a Milli-Q multiple cartridge purification system with RO water as feedstock. Co-precipitating reagents were reagent grade $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4(\text{PO}_4)\cdot 4\text{H}_2\text{O}$ separately dissolved in 4M HNO_3 and cleaned of contaminant uranium by passing through U-TEVA ion exchange resin in 4M HNO_3 (Eichrom Industries). In house sub-boiling distilled HNO_3 and Romil SPA hydrogen peroxide and Romil SPA ammonia were used for wet-ashing and neutralisation, respectively.

Table 1 – Uranium in lake cores

Depth (cm)	U (ppm)	2 SD	$^{238}\text{U}/^{235}\text{U}$	2 SD
17	3.6	0.2	197	3
32	4.3	0.2	229	3
52	4.4	0.2	225	3
67	8.4	0.4	285	4
82	10.7	0.5	260	5
92	58.4	2.9	428	4
96	71.8	3.6	449	3
107	9.7	0.5	293	3
119	52.1	2.6	415	3
130	30.1	1.5	358	3
140	73.3	3.7	362	3
150	196.4	9.8	406	3
155	32.0	1.6	319	3
155	30.5	1.5	314	3
160	227.9	11.4	368	3
165	27.6	1.4	289	3
170	6.3	0.3	194	3
170	5.9	0.3	195	4
175	4.2	0.2	169	4
185	4.7	0.2	129	3
199	2.8	0.1	140	2
281	3.5	0.2	125	3

Purified uranium extracted from urine and dissolved in ~1 ml of 2% high purity HNO₃ was introduced into the double-focussing ThermoElemental Axiom MC-ICP-MS using an Aridus desolvating nebulizer to produce a dry U aerosol carried in a stream of argon gas for sample introduction, thus both improving sensitivity and reducing interfering oxide formation. ICP gas flows were optimised to produce the maximum instrumental sensitivity while maintaining flat-topped peak shapes at approximately 400 mass resolution with clear wide separations between peaks. Uranium standards (CRM950 and SRMU010) were used to correct for mass bias, abundance sensitivity, hydride production, non-linearity of the ion counting detector, and multiplier gain. Peak

switching was employed to measure ²³⁴U, ²³⁵U and ²³⁶U in the ion counting system with other peaks measured in Faraday cups. The measurement of ²³⁵U on both detection systems allowed accurate determination of both major and minor isotope ratios. Purified uranium isotope standards were used extensively for quality control, and an in-house urine sample whose isotope composition was determined to be consistent with the natural value of ²³⁸U/²³⁵U of 137.88 was measured 7 times alongside unknowns using an identical procedure. Repeat measurements of DU-positive samples 6 and 13 were in agreement and the uncertainties quoted for ratios in Table 2 are either the propagated uncertainty of an individual analysis or the weighted mean uncertainty of repeats of the same sample.

Table 2 – Uranium concentration and isotope composition of water and urine

Sample	Weight (g)	[U] (ng/L)	$\frac{^{234}\text{U}}{^{238}\text{U}}$	2 SD%	$\frac{^{235}\text{U}}{^{238}\text{U}}$	2 SD%	$\frac{^{236}\text{U}}{^{238}\text{U}}$	2 SD%	$\frac{^{238}\text{U}}{^{235}\text{U}}$	2 SD%
<i>Drinking water samples of selected residents</i>										
1, Well	98	570	9.81E-05	5.2	7.27E-03	0.2	b.d.	–	137.64	0.15
2, Mains A	98	81.8	7.94E-05	5.2	7.26E-03	0.2	b.d.	–	137.70	0.17
3, Mains A	99	88.1	7.83E-05	5.2	7.26E-03	1.0	b.d.	–	137.72	0.18
4, Mains A	100	81.8	8.01E-05	5.2	7.26E-03	0.2	b.d.	–	137.77	0.17
5, Mains A	102	6.7	1.55E-04	3.7	7.32E-03	2.0	b.d.	–	136.58	2.03
6, Mains A	102	6.5	nd	–	7.28E-03	0.8	b.d.	–	137.42	0.75
7, Mains W	100	103	8.99E-05	3.4	7.25E-03	0.1	b.d.	–	137.93	0.14
<i>NLI plant workers</i>										
1	755	122	1.01E-05	3.6	2.18E-03	0.09	2.5E-05	0.6	458.65	0.09
2	774	80.4	1.39E-04	3.6	1.40E-02	0.04	6.6E-05	0.6	71.65	0.04
3	760	63.7	9.71E-06	10.2	2.16E-03	0.6	3.0E-05	2	463.87	0.56
4	761	65.8	1.02E-05	6.9	2.20E-03	0.5	2.6E-05	2	454.27	0.54
5	738	66.0	1.24E-05	7.5	2.49E-03	0.6	3.3E-05	5	401.88	0.55
<i>Residents and other worker</i>										
6	723	2.08	7.92E-05	33.2	6.97E-03	1.2	1.4E-06	59	143.39	1.20
7	748	1.89	8.38E-05	3.9	7.25E-03	0.4	b.d.	–	138.01	0.44
8	751	3.40	8.48E-05	3.7	7.25E-03	0.5	b.d.	–	137.95	0.47
9	758	4.13	7.35E-05	10.2	7.25E-03	0.6	b.d.	–	137.93	0.55
10	764	5.42	9.88E-05	10.2	7.24E-03	0.6	b.d.	–	138.08	0.57
11	737	0.94	9.24E-05	10.4	7.21E-03	0.6	b.d.	–	138.61	0.62
12	685	1.85	8.55E-05	11.2	7.18E-03	2.9	b.d.	–	139.25	2.91
13	702	3.74	6.68E-05	6.9	6.61E-03	1.8	4.0E-06	14	151.34	1.75
14	775	2.48	8.46E-05	10.2	7.25E-03	0.6	b.d.	–	137.95	0.59
15	660	1.36	7.02E-05	8.6	7.22E-03	0.9	b.d.	–	138.57	0.93
16	673	0.91	8.36E-05	8.1	7.20E-03	0.6	b.d.	–	138.91	0.60
17	706	5.17	7.29E-05	6.9	7.24E-03	0.5	b.d.	–	138.04	0.53
18	742	2.10	8.42E-05	6.9	7.29E-03	0.5	b.d.	–	137.25	0.55
19	744	2.51	7.94E-05	6.9	7.25E-03	0.5	b.d.	–	137.98	0.54
20	755	1.53	9.49E-05	6.2	7.24E-03	0.9	b.d.	–	138.17	0.89
21	739	1.96	5.44E-05	5.9	7.37E-03	1.2	b.d.	–	135.67	1.20
22	750	1.43	8.86E-05	4.8	7.23E-03	0.6	b.d.	–	138.27	0.57
23	752	4.71	7.05E-05	0.8	7.26E-03	0.1	b.d.	–	137.83	0.13
<i>Internal standard (urine)</i>										
1	742	8.7	2.25E-04	6.0	7.26E-03	0.81	b.d.	–	137.65	0.81
2	250	11.0	2.70E-04	5.2	7.24E-03	0.62	b.d.	–	138.21	0.62
3	250	9.5	2.83E-04	6.4	7.23E-03	0.55	b.d.	–	138.24	0.55
4	250	11.0	2.72E-04	7.3	7.21E-03	0.66	b.d.	–	138.70	0.66
5	250	10.5	2.58E-04	2.0	7.27E-03	0.33	b.d.	–	137.52	0.33
6	265	12.7	2.73E-04	4.1	7.25E-03	0.79	b.d.	–	137.93	0.79

Notes:

n.d, not determined; bd, below detection (see text).

Uncertainty on U concentration estimated at 4% (2SD).

Mains A; mains water supply of part of Albany.

Mains W; mains water supply of part of Watervliet.

5. Results

5.1. Nature of primary aerosols

By subjecting accumulated dry household dusts (with up to $\sim 300 \mu\text{g g}^{-1}\text{U}$) and contaminated soils to density and magnetic separation techniques followed by imaging using scanning electron microscopy, we identified primary aerosol particles of U oxides in the size range $<1\text{--}40 \mu\text{m}$ diameter. These cross both the respirable particle size range ($<10 \mu\text{m}$) and the 'hand to mouth' contact ingestible size range ($<250 \mu\text{m}$). Many are irregular and/or pitted although some are spherical and resemble fused metal globules, consisting now of primarily oxides of uranium (Fig. 2), consistent with their origin by combustion.

5.2. Anthropogenic uranium isotope signatures of lake sediments

In the U concentration profile in the core (Fig. 3, Table 1), there is a marked drop in concentration between higher values in 100–140 cm depth range; this could be explained by an increase in sedimentation rate that diluted the flux of uranium runoff related to the plant, but this is only one explanation.

In the sediment core, the concentration of uranium generally correlates with isotopic composition (Fig. 3). The highest uranium concentrations, however, have a $^{238}\text{U}/^{235}\text{U}$ isotopic ratio between 360 and 400 rather than a value closer to ~ 500 which is considered typical for current end-member DU. This occurs in the section of the core deposited most likely in the late 1960s and earliest 1970s, and could be explained by a mixture of a minor component of enriched uranium mixed with dominant DU. The highest isotope ratio is found between 90 and 120 cm depth in the core and in this section the contaminant may be closer to pure DU with an end member composition close to ~ 500 . The greatest mass of DU appears to have been deposited between 1963 and plant closure in 1984. Since closure the concentration of uranium has dropped to close to background values, but the isotopic composition demonstrates that a significant proportion of the uranium is environmentally "recycled" DU, presumably from runoff derived from already contaminated soils.

5.3. Identification of DU by isotope measurement

Natural uranium has a very specific isotope composition, the value of $^{238}\text{U}/^{235}\text{U}$, $^{235}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$, and $^{236}\text{U}/^{238}\text{U}$ being 137.88, 0.0072527, 0.00003–0.0002, and $<10^{-10}$, respectively, with only the $^{234}\text{U}/^{238}\text{U}$ having any natural variability. Enriched uranium has $^{238}\text{U}/^{235}\text{U}$ much lower than 137.88, and DU much higher, generally close to 500. ^{236}U is effectively absent in natural uranium. The uranium isotope measurements are sufficiently sensitive that if the uncertainty band of a measurement indicates the $^{238}\text{U}/^{235}\text{U}$ is 139.0 or larger, we are confident the sample is DU-positive, this assessment being based upon approximately 400 urinary uranium measurements of DU-negative samples as part of a related large study (DUOB, 2007). Similarly, when $^{236}\text{U}/^{238}\text{U}$ has a value larger than 1×10^{-6} , we are confident that it contains either DU or EU due to the fact that both DU munitions and reprocessed

EU contain ^{236}U originating from reactor-related neutron capture by ^{235}U .

5.4. Water samples

Table 2 and Fig. 4 show that drinking water samples contain natural uranium, since ^{236}U is absent (i.e. below detection) and the $^{238}\text{U}/^{235}\text{U}$ is indistinguishable from natural uranium (with a value of 137.88) within 95% confidence limits. The data fall into two different concentration groups of approximately 85 and 6.6 ng L^{-1} , reflecting two distinct sources of municipal water in the Albany, NY area. Other samples are local supplies outside of the immediate vicinity of Albany, with one from a private well, and contain uranium at 570 ng L^{-1} . These data indicate that in spite of the widespread presence of DU in the Albany, NY area, DU contamination is not detectable in the water supply of the city. Because drinking water is regarded as the dominant source of uranium ingestion (Kurttio et al., 2005), it can reasonably be inferred that any anomalous isotopic composition discovered in urine cannot arise from recent ingestion of water.

5.5. Former workers of the NLI plant

Urine samples from five former employees were tested with results shown in Table 2. These individuals worked at the plant for between 5 and 22 years during the active period of uranium processing in jobs ranging from plant floor worker to office worker. None lived near the plant, and so any exposure to uranium is almost certain to have arisen during employment. Their uranium isotopic compositions are highly anomalous, with $^{238}\text{U}/^{235}\text{U}$ ratios from 72 to 464, the lowest of these clearly including a component of enriched uranium (Table 1). Concentrations of uranium in workers' urine range from $64\text{--}122 \text{ ng L}^{-1}$, much higher than the range of residents' urine ($0.9\text{--}5.4 \text{ ng L}^{-1}$, summarised below), which is a finding consistent with uranium contamination as the dominant contribution to

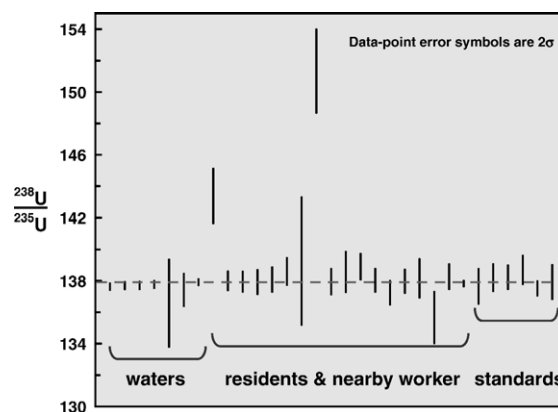


Fig. 4 – Plot of $^{238}\text{U}/^{235}\text{U}$ of drinking water and resident urine samples and 'standard urine samples' measured in this study, omitting those from factory workers that are off the scale of the diagram (see Table 2). The 'standards' refer to repeat measurements of an internal urine sample known to be of natural isotopic composition, and are shown to illustrate reproducibility.

excreted urine. The predominant source of their drinking water is from municipal sources.

The values of $^{236}\text{U}/^{238}\text{U}$ for four of the five workers range from $2.5\text{--}3.3 \times 10^{-5}$ and are close to the measured composition of DU penetrators as shown by analyses of DU shrapnel ($^{238}\text{U}/^{235}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ of DU of ~ 500 and $2.5\text{--}3.0 \times 10^{-5}$, respectively, McLaughlin et al., 2003; Trueman et al., 2004). On the $^{236}\text{U}/^{238}\text{U}$ vs. $^{235}\text{U}/^{238}\text{U}$ plot shown in Fig. 5, the workers' measurements are similarly distinct from natural uranium.

DU dominates the contamination budget in spite of one worker with evidence of EU with a $^{238}\text{U}/^{235}\text{U}$ ratio of 72. For example, a mixture of ~ 2 parts uranium enriched to 3% (a typical value) and ~ 3 parts DU would produce this value.

5.6. Residents/worker in close proximity to the NLI plant

Eighteen individuals were tested who lived in close proximity (1 km) to the plant, or in one case who worked nearby in employment unrelated to NLI. Repeated analysis of a control urine sample with natural isotope composition and similar concentration was also undertaken to demonstrate reproducibility. With a few exceptions, all tested individuals lived or worked near the plant for 10 years or more during the active period of aerosol emissions from 1958 to 1981. Concentrations of urinary uranium vary from 0.9 to 5.4 ng L^{-1} and fall within the normal range for humans. Fourteen individuals returned isotopic ratios that could not be distinguished from natural uranium while four (individuals 6, 11, 13, and 16 in Table 2) had $^{238}\text{U}/^{235}\text{U}$ values ranging from 138.9 to 151.7, though two of these four are only marginally distinguishable as containing DU (Table 1, Fig. 4). Of these four, only individual 13 lived near the plant while undergoing testing, 11 and 16 moved some distance away by 1986, and individual 6 worked until recently ~ 200 m from the plant but never lived nearby. These observations suggest strongly that the main DU exposure was via inhalation during the active period of the plant, though some amount of additional exposure by dust resuspension cannot be ruled out. Mass balance calculations using

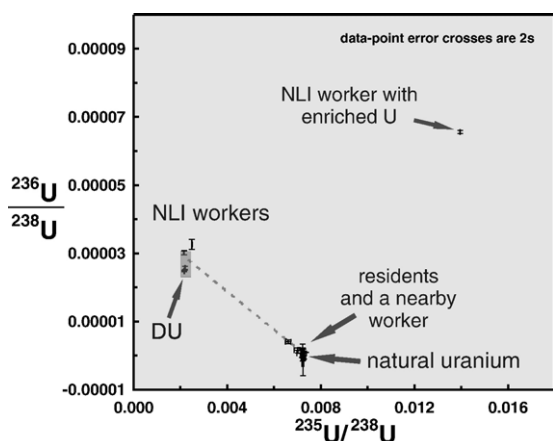


Fig. 5 – Plot of $^{235}\text{U}/^{238}\text{U}$ vs. $^{236}\text{U}/^{238}\text{U}$ of tested individuals. The end member composition of DU and the mixing line between natural uranium and DU is shown. Any mixture of two distinct compositions will define a straight line on this plot. Natural uranium contains no ^{236}U and plots as shown.

end-member DU indicate that DU constitutes between 1 and 12% of the excreted uranium in these four contaminated individuals.

The two higher measurements have $^{236}\text{U}/^{238}\text{U}$ of $1.5\text{--}4.0 \times 10^{-6}$ whereas all other urine samples had no detectable ^{236}U . When plotted in Fig. 5, it is clear that these DU-contaminated individuals fall on an array or mixing line between the natural isotope composition and end member DU as represented either by the cluster of workers or the measured composition of DU shrapnel. Although most 'residents' did not have detectable DU, they potentially were contaminated, but to an extent that has not been detected by our measurement threshold of approximately $0.02\text{--}0.05 \text{ ng L}^{-1}$ of DU, or approximately 1% of the excreted uranium in urine. What level of historic aerosol DU contamination this measurement threshold might represent is discussed below by reference to biokinetic models.

6. Discussion

This study documents residual internal DU contamination in all five former employees and in 10–20% of the cohort of individuals who either lived or worked in close proximity to the plant for at least 5 years during its active phase of emissions. The low number of individuals tested in our cohort precludes a quantitative extrapolation to the nearby population as a whole; this can be done only by testing a larger cohort. However, the detection of anomalous uranium in 100% of workers and up to 20% of our 'residents' cohort is in itself significant, since no previous study has documented evidence of DU exposure to aerosols more than 20 years prior.

The exposure pathway of aerosol deposition in the residential area surrounding the NLI plant occurred from 1958 to 1984, with a major drop in emissions in 1981 when NLI largely stopped manufacturing operations prior to closure in 1984. During the ~ 23 years of active uranium emissions, many tons of fine uranium, mostly in the form of combusted oxide particles settled downwind from the plant. We have documented DU contamination 5.8 km from the plant using spot soil samples, and it is likely to have travelled even further (Lloyd, unpublished data 2007). Inadvertent inhalation exposure would have been inevitable and may have affected many thousands of people during a period of chronic rather than acute exposure.

The urine from NLI workers is, even now, almost entirely dominated by a combination of DU and EU derived from their exposures while working at the plant. The persistence of high excretion rates of uranium in urine in workers, more than 20 years since active exposure, indicates that the body burden of uranium must still be significant, whether retained in lungs, lymphatic system, kidneys or bone.

The study also detected DU in up to 20% of the 'residential' cohort of 18 individuals. Their route of exposure is likely to have been dominated by inhalation since aerosols were the main source component, but other routes, including ingestion of contaminated soil or dust, may have played an additional role. In the individuals with a DU signature, the DU comprises $\sim 1\text{--}12\%$ of the total excreted uranium, the remainder originating from ingestion of natural uranium contained in food and water. The analysis of Albany drinking water clearly

shows that it is not contaminated with DU and that it cannot be linked to the DU contamination.

With the exception of uranium workers (like those in uranium mining and milling, and those employed at NLI), there is little or no evidence of the persistence of any anthropogenic inhalation exposure to uranium in the body beyond 10 years, and even that is poorly documented. Our study clearly shows that a sensitive non-invasive method is available to prove that DU contamination of the body can persist for more than 20 years.

6.1. Health implications

For many years there have been persistent concerns regarding the risk to human health from uranium and other heavy metal pollution in the vicinity of the NLI site, from its airborne uranium emissions and waste dumping. These concerns have been covered by the local media, noted by non-profit organizations, and reinforced by a recent US government Health Consultation assessment of risk (ATSDR, 2004). However, that ATSDR Health Consultation concluded that further investigations were unjustified because it would be impossible to determine the incidence of DU contamination after such a long period of time since the inhalation hazard no longer existed. In contrast this study shows that this is feasible. The results of this study suggest that testing a larger cohort could better determine the incidence of DU contamination in nearby residents and potentially place limits on original exposure quantity. This is a critical piece of information needed to design an appropriate follow-up study to assess the potential health outcomes of the nearby population.

6.2. Estimation of initial inhalation dose

In any analysis of exposure to a toxic substance, it is important to quantify the exposure, if at all possible. For DU, this can be estimated in a model calculation using the (1) rate of excretion of DU, (2) time since exposure, (3) solubility function of inhaled DU particles. By way of illustration using the biokinetic model adopted by the Radiological Protection Board in the UK, as summarised in Royal Society reports (Royal Society, 2001, 2002; also see DUOB, 2007), an initial inhaled dose of oxidized uranium after 10,000 days (~27.4 years) should give rise to a daily uranium excretion of the original amount divided by 10^7 ; for example an excretion rate of 1.0 ng DU d^{-1} would imply an intake of 10 mg DU 10,000 days earlier. If it is assumed that the individuals' exposure to aerosols can be approximated as taking place around the time of maximum aerosol emission in the period ~1976–1979 (ASTDR, 2004), approximately 10,000 days prior to testing, one can calculate initial exposures using the measured 24 h DU excretion rates. Using the means of 24 h DU excretion for the four DU-positive residents of 0.3 ng DU d^{-1} and for the five workers of $95 \text{ ng DU+EU d}^{-1}$, the calculated cumulative exposure in 1977 would have been approximately 3 mg DU and 950 mg DU+EU , respectively. Given the variability in individuals and a probable variation in DU excretion of an individual from one day to the next, a considerable uncertainty exists for these calculated exposure estimates. However, their general magnitude falls into the Level II and Level I categories of exposure, respectively,

referred to by the Royal Society (2001) and are sufficiently high to justify an investigation of the health implications in more detail and scope than has been undertaken to date. The limit of detection of measurements on urine from individuals exposed ~20 years earlier, in combination with this biokinetic model, means that our method should detect virtually all Level I and Level II inhalation exposures, but not most Level III exposures. Of course these predictions of exposure quantity are entirely dependent upon the applicability of the biokinetic models used.

The assumption made in the calculation that intake occurred in a single event in 1977 is meant to illustrate the magnitude of the cumulative initial exposure, rather than detailed estimates applicable to each individual. Individually-tailored calculations based upon known history of exposure would vary but the variation would not materially affect the general magnitude of DU exposure estimation.

It is interesting to compare these results to those of a separate study completed recently in the UK (DUOB, 2007) that measured all (including ^{236}U) uranium isotopes in urine of 466 individuals, mainly veterans of the Persian Gulf conflict of 1991, using methods similar to this study. That study failed to find a single demonstrable DU-positive sample, though the extent to which those tested were actually exposed to DU was not known. It seems a reasonable conclusion that if DU cannot be identified in urine by sensitive methods after a period of 10–20 years, then the exposure for such a tested cohort cannot be assumed to have been significant.

7. Conclusions

The NLI plant in Colonie (Albany), New York emitted many metric tons of uranium aerosols, mainly combusted milling waste, into a mixed residential — commercial area of more than 10 km^2 over a period of 25 years from 1958 to 1982. Inevitably, residents, commercial workers, and NL plant workers were subjected to U inhalation and possibly ingestion exposure. Uranium pollutants comprised EU and DU, the latter being dominant. High sensitivity isotope measurements were made on urine samples from 23 individuals known to have lived or worked over many years in close proximity to the source of emissions to ascertain the extent to which the anthropogenic uranium signal could still be detected. Five factory workers continue to excrete high amounts of uranium dominated by a DU isotopic signature. Of eighteen individuals that either lived or worked near the plant for many years, we have detected DU in up to four, with DU being 1–12% of the excreted uranium. Ingestion of DU-contaminated water can be ruled out as a source of the DU excretion. Estimates of the initial inhalation dose of DU-positive individuals range from up to ~6 mg DU for residents to nearly 1 gram DU for workers. Inferred doses smaller than ~2 mg DU 25 years prior appear at the limit of detection of the methodology. Individuals exposed to substantial quantities of DU aerosols are likely to retain a DU-positive signature for the rest of their lives.

These findings cast new light on an important recommendation of a previous Health Consultation by the US Agency for Toxic Substances and Disease Registry (ATSDR, 2004). That

study concluded that, although plant emissions posed a real health risk, further health assessments would not be justified because of a lack of demonstrated DU exposure in the population. In contrast our method could provide estimates of the incidence and magnitude of DU aerosol inhalation exposure of the residential population, critical data needed in the interpretation of mortality and morbidity data.

A comparison of these data with two recent larger testing programmes of both UK veterans of the 1991 Persian Gulf conflict and the recent conflict in Iraq is revealing. In these UK studies of more than 800 individuals (DUOB, 2007; Bland et al., 2007)) no DU-positive urine sample was found. In the case of Colonie where urinary DU is documented in exposed individuals after 25 years, the simplest conclusion is that if an individual is significantly exposed (i.e. Level II–Level I exposures; Royal Society, 2001), the urine isotope signature will persist for decades.

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