Uranium oxide particulate surrounding a former processing facility

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Introduction

The use of depleted uranium (DU) munitions by US and British forces has been highly controversial. On impact with armoured targets, the pyrophoric metal combusts, shedding uranium oxide particulate that can be inhaled into the lungs. Depleted uranium is both weakly radioactive and chemically toxic, and it is frequently cited in the grey literature as a cause of Gulf War Syndrome. However, under the scrutiny of peer-review, no link has so far been made between inhalation exposure and veteran's ill health.

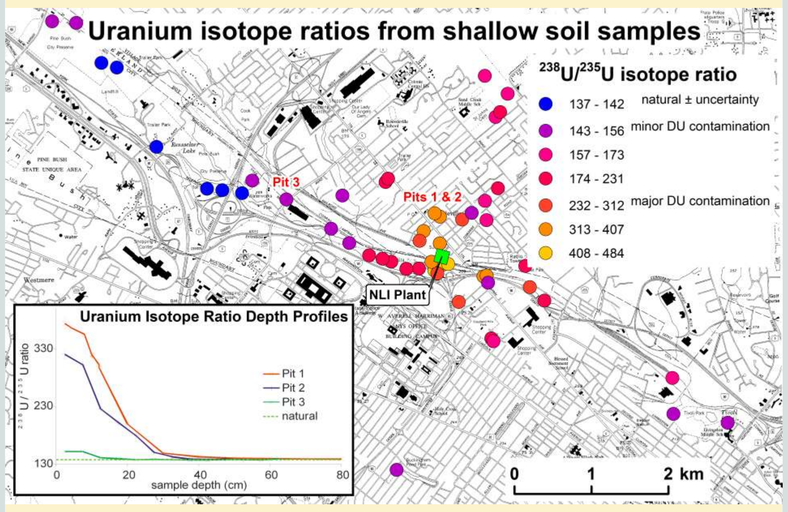
This research project aims to improve understanding of the behaviour of DU particulate in the environment, using a case study of a site that is heavily contaminated by past emissions. The research will help predict the long-term fate of pollution from uranium oxide particulate.

National Lead

National Lead Industries (NLI) operated a plant at Colonie, NY, USA from 1958-1984[1]. Uranium metals were fabricated into radiation shielding, counterweights and kinetic penetrators (anti-tank munitions).

Scrap uranium metal was converted to oxide in a furnace that vented to the atmosphere (left). The plant (below right) was closed by the authorities in 1984 for excessive uranium emissions to the environment, and has now been remediated with the removal of 180,000 tonnes of soil[2] (below left). Uranium contamination is evident in a sediment core from downstream of NLI[3,4].

From pre-existing survey data[5] we estimate that approximately five tonnes of uranium was deposited within 1 km^2 of NLI. This area includes residential and commercial properties.

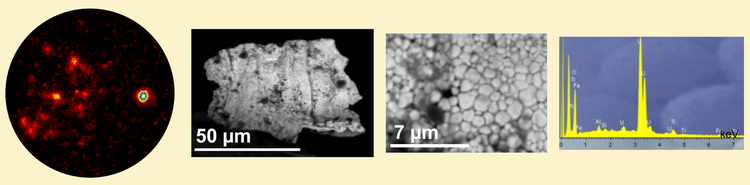


We collected 200 soil and dust samples from the area surrounding NLI. The samples have been analysed by inductively coupled plasma mass spectrometry (ICP-MS), for uranium concentration and isotope ratios. Concentrations close to site exceed 500 mg/kg uranium (natural background soils < 2 mg/kg). Isotope ratios reveal depleted uranium contamination in soil profiles to a depth of 35 cm, and 5.8 km from site (see above). Distribution is shaped by prevailing winds. The isotope ratio data fit a single mixing line between a natural and a depleted uranium end-member ($^{238}U/^{235}U \sim 500$, $^{236}U/^{238}U \sim 3.2 \times 10^{-5}$).

Sample Preparation

Scanning electron microscopy (SEM) grain mounts were made from dust and soil samples, and carbon coated prior to analysis. The mounts were imaged in back-scatter electron mode, to highlight heavy elements. Energy dispersive x-ray (EDX) analysis provides qualitative elemental identification, typically major peaks are from uranium and oxygen (± minor peaks from Al, Si, Fe, Ti).

In order to improve efficiency, dust and soil samples were density separated using di-iodomethane (density 3.3 g/cm^3), followed by magnetic separations. This method effectively concentrates uranium rich particles greater than 20 µm diameter, but smaller particles tend not to settle with the dense fraction.

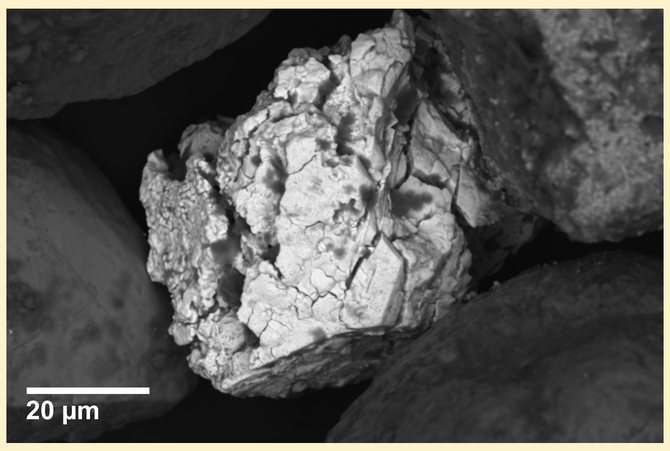


Images from left to right: Autoradiography of density-separated particulate on SEM mount, SEM image of particle highlighted by autoradiography, close-up showing agglomerated texture, EDX spectra from spot analysis.

Equipment, University of Leicester: Hitachi S-3600N SEM with Oxford Instruments Inca X-sight EDX detector (Department of Geology), FEI Sirion 200 FEGSEM (Advanced Microscopy Centre).

Particle Morphology

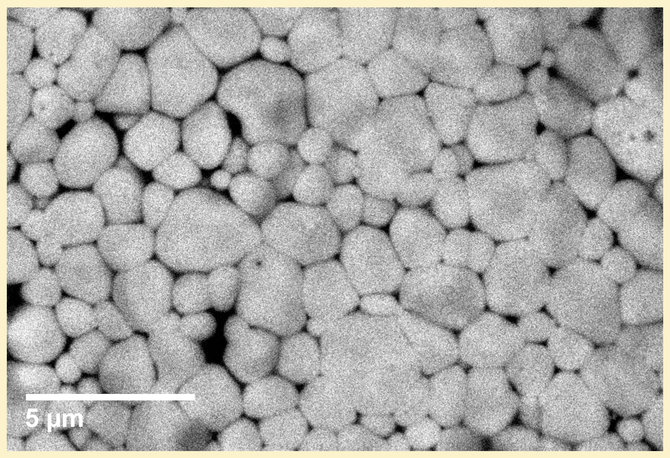
Uranium-rich particles with geometric diameters >0.5 µm have been identified and imaged. Smaller particles exist in these samples, but are hard to resolve with the current methodology. There are a wide variety of morphologies, including agglomerates, rods, cuboids, spheres and well-defined uraninite crystals.



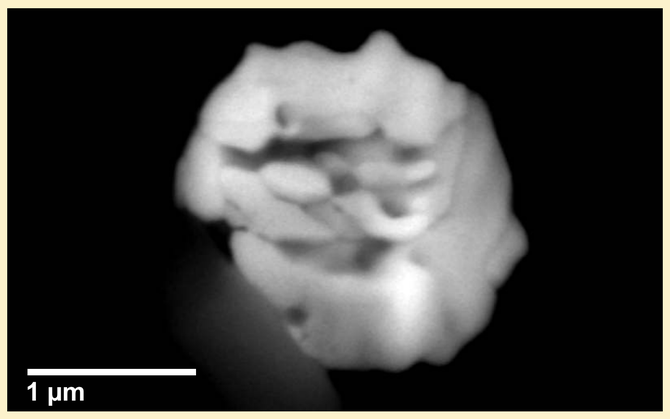
The texture above is comparable to popcorn texture described in McEachern & Taylor[6], a texture from the volume expansion from UO_2 to U_3O_8

Low temperature oxidation of UO_2 proceeds as follows, limited by oxygen diffusion[6]:

$$UO_2 \text{ fi } U_3O_7 / U_4O_9 \text{ fi } U_3O_8$$



Many of the particles are agglomerates of sub-micrometer diameter particulate. Triple junctions are observed between grains in some of the agglomerated particles (above). This could be from compression whilst pliable in the furnace, or from expansion to U_3O_8. Oxidation to U_3O_8 could occur in the furnace, or in the environment.



We estimate that the aerodynamic diameter (d_a) of the particle above is 6 µm. Particles of this size can be inhaled into the lung, and with low probability be deposited in the alveolar region. This is a region of the lung where insoluble particles are not easily cleared, and they may reside there for many years[7].

Several of the particles fractured during sample preparation, and this brittle behaviour has generated smaller, respirable particulate.

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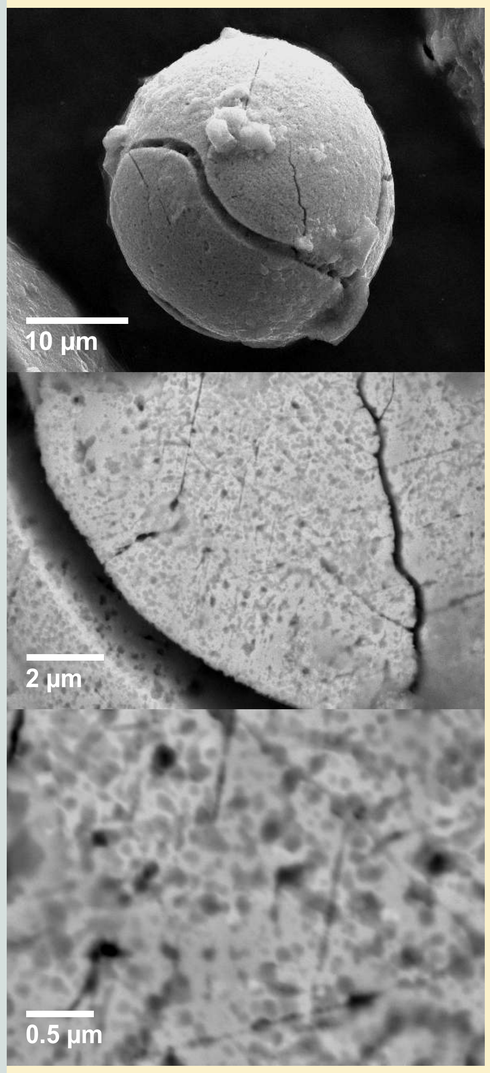
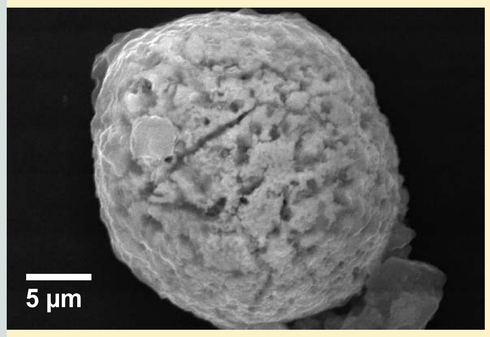
Uranium oxide spheres & environmental degradation



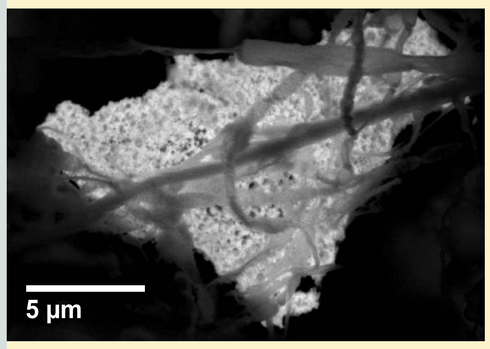
A 28 µm diameter uranium oxide sphere from a wind-blown dirt sample (dirt: 379 ± 21 mg/kg U, $^{238}U/^{235}U$ 469 ± 14). Preserved in a sheltered environment.

Hollow spheres of uranium oxides from sparking metal, appear to form by explosive release of vapour from a freezing shell[8]. Spheres are formed from DU munitions impacting armoured targets[9].

The middle frame shows the surface under high magnification. Surface pitting is common, and may be from corrosion pitting (a process from differential oxygen diffusion through surface water droplets), or possibly etching initiated by alpha recoil damage. The frequency of the larger pits (left) is approximately compatible with alpha recoil damage.



A sphere of similar size was collected in a surface soil sample. The comparatively rough and eroded appearance is attributed to weathering processes, in the exposed and often wet soil environment (soil: 296 ± 16 mg/kg U, $^{238}U/^{235}U$ 472 ± 14).



A uranium bearing particle adhered to the surface of a wooden fence post. It appears porous and sponge like. This could be from advanced degradation in an exposed environment.

The presence of uranium rich particulate, at least 25 years after release into the environment, demonstrates that contamination is long-lived.

Findings

- Depleted uranium contamination surrounds a former processing plant, to a distance of at least 5.8 km.
- Soil and dust samples close to source contain uranium oxide particulate.
- Some of this particulate could be inhaled into the lungs.
- Uranium oxide particulate has survived at least 25 years in the environment.
- Surface characteristics have been related to oxidation and weathering processes. Particulate from exposed, wet environments appears more eroded.
- Uranium oxide spheres are comparable to those from sparking and from munitions impact with armoured targets.
- Uranium oxide particulate is both mobile and durable in the environment.

Future Work

Further experiments are planned to determine uranium isotope ratios, and mineralogy of individual particles. We are looking for comparison materials, and considering micro-anayltical techniques for determining mineralogy.

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