Testimony of Prof Randall Parrish for the Subcommittee on Investigations and Oversight of the Committee for Science and Technology, US House of Representatives, Washington

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Summary

National Lead Industries (NLI) contracted with the Department of Energy and processed uranium at Colonie NY in the period 1958-84, but in its latter years was environmentally negligent, badly polluting with depleted uranium aerosols the surrounding site and community. The amount of Depleted Uranium (DU) aerosol emissions were comparable to the total respirable DU released in the entire 1991 Gulf War, highlighting the significant pollution issue. In 2003-04, the ATSDR conducted a relatively superficial examination of the health consequences of the pollution of this site. The report lacked depth and substance, failed to address community concerns with adequate scientific data and explanation, it conducted no new research at the site, and presented a confusing picture of the toxic hazards. It did not draw upon the best science available. The site was remediated (completion 2007) by the Army Corps of Engineers, costing more than $190M. The ATSDR consultation significantly concluded that there was a real and significant health risk to the public from depleted uranium oxide emissions from the plant stack during its active years (1958-1982), but it decided not to pursue any environmental surveying or health surveillance activities for poorly articulated reasons. Planned actions related to uranium were not done subsequent to the report's publication. The liaison with the local community appeared to be relatively poor, delivering little in the way of satisfactory communication, and no perceived benefit. No new insight on the situation was presented that was not already apparent and the nature of uranium toxicology was not well balanced. In several respects it failed to take advantage of the best science available to address the issues at the site. It offered little in the way of comment on how to redress the health concerns of the community. In most respects other than providing information on toxins, it failed to deliver its remit for the Colonie site.

My UK research group, beginning in 2004, investigated the nature of the uranium aerosols, made isotope measurements that documented the isotope characteristics of the source emissions, studied particle dissolution in the natural environment – a parameter relevant to their solubility, extended the survey of uranium pollution much more widely, and studied the mobility of uranium in soils and plants, all in order to gain a better understanding of the environmental pollution. We also worked closely with the community to identify former workers and residents who lived or worked in or near the plant for many years during its operation, in order to gather oral history of events and practices in the

plant and to identify part of the exposed cohort for potential health screening. ATSDR evidently decided that this type of approach was not possible or would not be a productive activity. It was instead feasible and useful, and not particularly costly. We had already developed a urine uranium isotope test that was capable of detecting trace depleted uranium in urine. We then tested a small cohort of residents and former workers and clearly showed that our method was capable of identifying a substantial exposure to depleted uranium aerosols more than 20 years after exposure. This clearly offered a way forward to link health outcomes to exposures at Colonie, something ATSDR in 2004 decided was not possible.

There is a breath-taking lack of environmental and community justice in the Colonie situation. While the polluter, National Lead Industries, was absolved two decades ago by the US Government of responsibility and while the Army Corps of Engineers spent nearly £200M on site cleanup, no federal government monies have been spent on even a modest-scope targeted health study to identify what if any health outcomes have occurred for the exposed cohort of people who for years lived near or worked in the site during its active years of uranium pollution. The community has been left with no research, no credible way forward, little or no redress, and a significant environmental pollution legacy with a reasonable probability of some consequences to health of those affected.

Much could have been learned about the environmental health issue of aerosol depleted uranium emissions had ATSDR acted differently; this could have informed US Government policy as it pertains to Veterans' Health related to DU munitions exposure in the battlefield (Gulf Wars I and II) and potentially helped provide vital data to test any potential connection between Gulf War Illness and depleted uranium exposure. It would certainly have improved the medical knowledge database on the inhalation hazard of respirable uranium oxide particles, a relatively rare toxicological pathway which does not currently have benefit of any systematic study of an exposed population, to my knowledge. The need for additional research at the Colonie site is as acute now as it was in 2003-04 when the ATSDR conducted its Health Consultation.

My remit – instructions from Congressional subcommittee

The Subcommittee has asked me to do two things: summarise my investigations into the National Lead Industries (NLI) Colonie NY site and critique the 2004 Colonie ATSDR report and suggest how to improve its environmental health assessments in the future. My contribution herein is largely concerned with the uranium issues at Colonie, not the full menu of pollution-related toxins.

Background and current position; summary of expertise

I am Randall R Parrish and occupy a joint position of Professor of Isotope Geoscience, University of Leicester (UK) and Head of the UK Natural Environment Research Council Isotope Geosciences Laboratory, a national isotope research and analysis facility serving the UK scientific, mainly the academic scientific community. I have occupied this joint post since 1996. More details on my expertise, skills, publications, research and so forth is contained in the CV and biography provided as part of the requested testimony.

I conduct research in many areas of geo- and environmental science, but have a particular expertise in analysis of uranium and lead isotopes using high sensitivity mass spectrometry and am a recognised authority in this area. I have published extensively using such methods, mainly in geoscience in the field of geochronology – the determination of the age of rocks and minerals using radioactive decay of Uranium. Although most of my research has been and continues to be in earth science, since 2003 I have applied this expertise to environmental health research on topics that relate to the issue of depleted uranium (DU) pollution and health. Our work has had some impact on how the UK government approaches its duty of care to the UK soldiers that may have been exposed to depleted uranium munitions and its environmental consequences. I developed a keen interest in this problem because of the lack of thorough relevant studies, its novelty, and the fact that it was and still is an issue in dire need of sound scientific data to combat the huge amount of media and political noise surrounding 'depleted uranium' and its potential relationship to Gulf War Illness.

The wider justification for study of the Colonie site

The overriding reason that I got involved in research at the National Lead Industries Colonie NY site was to try to solve a long-standing problem: how long does inhaled DU oxide reside in the human body and what relationship, if any, does such an exposure have on human health and how might it be quantified? In spite of notions to the contrary, this problem has not been solved because ***no cohort of people exposed by inhalation to this particular toxin has been adequately studied***. As it turns out the NLI Colonie NY site is virtually unique in its relevance to this issue, quite apart from the intrinsic need to address the environmental stewardship and potential health issues of this highly polluted site. My role has been to provide the analytical and environmental science to address this problem. I hope my testimony will clarify your understanding of the problem and the perspective I have on the 2004 Colonie ATSDR Health Consultation.

Some observations about the Colonie situation

- The uranium pollution at Colonie originated at the former National Lead Industries site; all agencies appear to accept that there is no other credible source for the uranium pollution there. From my knowledge base, I agree.
- The uranium pollution is primarily composed of depleted uranium oxide aerosol particles, which have a distinctive isotope composition with some limited variability; we have measured this extensively in our studies. My PhD student published an article on this just last week – it is appended in these documents.
- The uranium pollution at Colonie occurred as a result of environmental negligence of National Lead Industries through inadequate filtration and capture of combusted depleted uranium metal waste.
- The period of active pollution was ~1958-1982 and aerosol pollution ceased with plant closure, though re-suspension of polluted soil undoubtedly occurred after plant closure.

- Our recent research has shown that household dust may have unacceptably high levels of DU; this may be a risk to health if disturbed – a potential health issue, and certainly a perceived concern of the community at the present time.
- ATSDR's 2004 principle conclusion of merit was that the level of airborne radioactivity emitted from the plant represented a distinct health risk during plant operation. The ATSDR report's lack of recommendations concerning past risk to health was a puzzling omission from the report and an obvious source of frustration to the community.
- The ATSDR 2004 report has an overemphasis on ingestion exposure to DU by comparison with the acknowledged more hazardous inhalation pathway, because the latter may lead to long term internal radiation whilst the former is likely to be cleared quickly in the intestinal tract. This is all the more important since our recent research has shown that the uranium aerosol pollution at Colonie is very weakly soluble, and contains a significant proportion of respirable particles. This de-emphasis of the inhalation exposure pathway is a significant weakness of the report.
- In the assessment of health risks and exposures, what is important is getting at an estimate of the cumulative inhalation uranium exposure of workers and residents; this is not simple. It needs to be appreciated that it is entirely *wrong* to conclude that because urinary uranium levels are relatively low *now* that there was/is no health issue. In this 'historic exposure situation' the comparison of current excretion levels in relation to the overall population is a flawed basis for health risk assessment.
- The task of calculating a cumulative historic inhalation uranium oxide dose is complex, but can be modelled using existing, relatively well accepted bio-kinetic models along with a range of solubilities of DU oxide particles, using experimental data, and estimates of excretion of inhaled DU. The US Army Capstone (~2004) report specifically investigated this issue; the ATSDR report was apparently unaware of it and in any case chose not to pursue this avenue of investigation. A fairly thorough discussion of this topic was available in the period 2000-2004 and for example is contained in the Royal Society report on DU (2001). I have included an explanation of this later in the written testimony explaining how current excretion levels of DU can be used to calculate the much larger quantities of inhaled uranium during an historic exposure.
- The detection of depleted uranium as a component of the urinary uranium excreted by affected people is a challenging but feasible measurement; it was feasible in 2003-04 (via for example the UK DUOB website) when ATSDR concluded there was no method available, but it had yet to be published in the refereed literature.
- The quantity of inhalable DU oxide deposited in the vicinity of the Colonie Plant is comparable to the total aerosolised inhalable DU oxide produced in the entire 1991 Gulf War conflict; in Colonie, >95% of this quantity was deposited within 2km radius of the NLI plant; in the 1991 Gulf conflict, the area of dispersion in Iraq-Kuwait was very much larger and partly in sparsely inhabited areas along the Basra Road. Thus the environmental pollution and health risk is likely to have been much higher for Colonie residents than for

Gulf War veterans. This sobering perspective has never been appreciated or recognised and is all the more unbalanced when considering how funds have been spent on research into DU and health.

- No credible well-designed health assessment has been funded or conducted at Colonie; yet, >$190M has been spent on the NLI cleanup within its perimeter fence, not to mention funding allocated to ATSDR for its Health Consultation and that dedicated to other DU-Health research such as the Capstone study of the US Army. This whole funding situation appears perverse, mis-directed, and lacking a natural sense of balance (one could say fairness & justice), in my opinion.
- In my opinion the 'zip code' based cancer occurrence 'studies' cited by the ATSDR Health Consultation and conducted by NY State agencies were unlikely to accurately identify any significant rise in illness that might have arisen from long term significant inhalation exposure to DU from the NLI plant of a cohort of heavily exposed workers or residents. The movement of people with time in and out of the area, the lack of tracking of the most exposed few hundred individuals, and the study of former workers unlikely to have lived nearby meant that this type of study was doomed from the beginning of delivering insight. Why ATSDR opted to not design a more targeted study or to more intelligently discuss the shortcomings of these NY state studies is baffling to me, and no doubt a serious source of frustration to the community.
- The studies that I and my team have conducted at Colonie, both urinary testing (on a small scale) and environmental surveying, have been modest in scale and cost, and were entirely feasible at the time of the 2004 ATSDR Consultation; the ATSDR paper made no recommendations to undertake any such study.
- Unfortunately the 2004 ATSDR Health Consultation undertook no new researchand seemed uninterested in such followup work; while clearly recognising the inherent health risk of the plant, the paper concluded without recommending any way of redressing the community concerns about uranium pollution, whether well-founded or not. It is no wonder that the report satisfied few.
- I have solicited feedback about the 2004 report by the Community Concerned about National Lead; their comments are very critical of ATSDR. This is primarily because while the health hazard was clearly admitted, no recommendations for new research or health screening were made, for reasons that were poorly articulated and justified. As a scientist, I too find a puzzling lack of credible justification for the lack of action arising from the report. The report has therefore made little if any contribution to knowledge or public understanding of the scientific and health issues of the Colonie site that were not already available.

Our research at Colonie 2004-2009

With information from several sources, in ~2004 I recognised the unique situation of significant historic uranium aerosol inhalation exposure of a large urban population in Colonie, a mixed industrial-residential part of Albany NY. Its attributes of interest were:

(1) there was a great amount of uranium pollution;

(2) the nature of the pollution was primarily by aerosol deposition of combusted uranium oxide particles;

(3) it took place over a long period of time but ceased more than 25 years ago;

(4) many individuals who had lived through the active period of aerosol deposition were still living in the area; and,

(5) it seemed certain that if individuals living there also had aerosol-contaminated soil, then they would have inhaled the toxin over a long period of time.

It thus appeared to be a well-controlled experiment where one had an opportunity to address the health impacts of those exposed to inhaled DU, and that such study might have a bearing on the larger issue of inhaled DU and Veterans' Health. Though this latter problem falls outside of the remit of ATSDR, I think it is important for members of the Committee to gain a perspective on how the Colonie example could benefit and contribute to other scientific issues of acute interest to the American government, namely the health of Gulf War(s) Veterans.

Chronological perspective on DU research and the Colonie site

To provide a better perspective, I will outline the pertinent events leading up to the present that bear on my research at Colonie, DU and Health, and the ATSDR consultation.

In chronological order, they are:

- 1958-1982: Colonie site uranium pollution;
- ~1984; US Government accepts responsibility of site from the polluter, National Lead; DU munitions production shifts to other US plants.
- 1982-2007: Assessment of site and major remediation by Army Corps of Engineers within the former National Lead Industries site costing >$190M.
- 2001: publication of the WHO and Royal Society papers on Depleted Uranium and Health, during a period when DU was a major issue in the American, Canadian, and UK media.
- 2001: UK government established the Depleted Uranium Oversight Board (DUOB) to oversee and undertake a voluntary programme of testing of veterans who may have been exposed to DU through service primarily in the 1991 Gulf Conflict. The minutes of this Board were available.
- The DUOB undertook to establish a reliable urinary DU exposure test that could potentially detect a milligram-sized inhaled DU dose after 10 years had passed, in order to satisfy the concerns of potentially exposed veterans. This test was available as of late 2003. This was to be a much more sensitive test than was available any where else in the world. The programme of testing took place between 2004 and 2006. To my knowledge this capability currently exists only in the UK and possibly Germany.

- The NIGL laboratory of which I am Director was one facility offering this test and it was engaged in the analysis of many hundreds of urine samples during this period. I played a key role in this development and testing.
- The Final Report of the DUOB testing programme (published eventually in 2007) showed that no individual tested in the programme was DU-positive.
- Because of the preponderance of DU-negative results, even in 2004 part way through the programme, I felt that there were two explanations possible for these results:

  (1) Some of the veterans were significantly exposed to DU but the passage of time had ensured that residual DU contamination was undetectable; thus health harm may have occurred without a DU-positive test.

  (2) The veterans with DU-negative test results were not significantly exposed to DU.

  Unfortunately there was no study available at the time to quantify the residence time of inhaled DU oxide particles, and both alternatives remained viable explanations of the data; the debate in the UK concerning DU exposure and Health therefore could not yet be fully resolved.
- In the period around 2001-2004 unpublished information became available from Iraqi medical officials of an apparently progressive and significant rise in unusual cancers and birth defects throughout the 1990s; this was not clearly verified but Iraqi and some western medical officials attributed this to DU exposure. This added some anecdotal evidence that there might be a DU-Health connection even though other reports were suggesting that the connection between DU and Gulf War Illness was weak.
- In 2004 I learned of the Colonie site; as noted earlier in this testimony, it appeared to involve a significant aerosol DU oxide pollution footprint in an urban area, with the implication that it was likely that many people had a DU oxide inhalation exposure; thus it to me seemed worth pursuing since it offered a way to resolve the alternatives expressed above about the interpretation of the DUOB DU-negative results.
- With considerable anticipation of new insight, I read the ATSDR 2004 report, and while pleased to read of its conclusion that the uranium emissions during the plant's active period was hazardous, I was quite disappointed with its lack of new data/research and its lack of tangible actions and recommendations for the future. To my knowledge no follow up work was done by ATSDR related to uranium.
- In 2004 I initiated a research project at Colonie, aimed at providing (1) a modern environmental study to document the nature and mobility in the environment of the DU oxide aerosols and (2) urinary tests of potentially significantly exposed individuals (former workers of the plant and residents who had lived nearby for years) to determine whether any urinary DU could be detected. A PhD student (Nicholas Lloyd) was given the environmentally-oriented project, while I undertook the urinary testing. We cooperated in these studies with colleagues at the University at Albany (Dr David Carpenter

and Dr John Arnason). Funding for this work was provided by the British Geological Survey and the UK Natural Environment Research Council.

- In latest 2004 the analysis of the Colonie urine samples showed that it was possible to detect DU in humans more than 20-25 years following exposure (eventually published in 2008). This allowed one to favour one interpretation of the DUOB-tested Gulf War veterans - that they had not acquired a significant DU inhalation dose. We knew in latest 2004 that our method of testing offered a way forward to identify and potentially quantify the cumulative inhalation dose of DU for the Colonie exposed population; this conclusion had very important implications for any follow-on actions arising from the 2004 ATSDR report.
- Our environmental study data was progressively completed in the period 2005-2008; it had several important conclusions, namely:

  (1) DU in soil profiles has very limited mobility, indicating a lack of rapid dissolution of DU in the natural environment;

  (2) Particles of DU oxide aerosol could be located and studied in contaminated soil, and in household dry dusts, and after study (using a synchrotron X-ray source), it was confirmed that UO_2 was the principle chemical component, a finding that is expected in thoroughly combusted material; UO_2 is the least soluble of any uranium oxide.

  (3) UO_2 particles form a minor component of the man-made metal oxide aerosol particles contained in soil; the bulk of the remainder mainly consists of lead particles.

  (4) Particles of UO_2 within soil were found to have suffered minor (generally <10%) dissolution by being subject to natural weathering for more than 25 years; this confirms that the combustion product aerosol emissions from Colonie were relatively insoluble.

  (5) Samples of trees, plants, berries, etc. growing on contaminated soil contain DU; this indicates that some component of DU is soluble and taken up in plants.

  (6) No sample of soil collected to date, including those up to 7 km (~5 miles) from the NLI site, is free of DU; the pollution plume is much larger than was originally thought.

  (7) With our data, a calculation of the total mass of DU emitted from the plant was made, the resultant quantity being approximately 10 metric tons (give or take a few). This is comparable to the total aerosolised DU oxide produced by the Allied Forces in the entire 1991 Gulf Conflict, demonstrating the relative magnitude and concentration of DU in the Colonie site.
- 2008: Publication of the Parrish et al. paper on the Colonie site in Science of the Total Environment; this study when combined with the efforts of the Community Concerned about National Lead (CCNL), resulted in a renewed effort to obtain NY State funding for a credible targeted follow-up health study of affected residents/workers of the NLI site; this activity is ongoing.

Critique of the ATSDR Health Consultation

Prior to making some criticism of the document, it is important to note the strengths of the 2004 ATSDR Colonie Health Consultation, namely:

- It provided a good review and summary of the history of the site and all previous investigations, and brought together information from a variety of sources.
- It used measurements of emissions of radioactivity from the site available from environmental monitoring to conclud that there was a significant health risk to those who lived nearby during the period of active emissions.
- It made an effort to have meetings with the community to present its findings, take note of concerns before preparing its final report.
- It recommended two specific actions related to the NLI plant, namely,

  (1) ATSDR will work with local physicians and provide information on taking patients' environmental exposure histories. ATSDR will also make available resources related to environmental exposure, including contaminant-specific case studies and fact sheets.

  (2) ATSDR is evaluating the feasibility of conducting a study that would compare the mortality rates of former NL workers to the mortality rates of the general public. Former workers likely received the highest exposures to depleted uranium from 1958 to 1984 during operation of the facility. Currently, ATSDR is determining whether relevant past worker records exist.

Unfortunately it also had many shortcomings. I will outline what I feel are the most important problems rather than undertake a detailed critique.

- The study presents a skewed and narrow portrayal of the potential hazards of DU in that it over-emphasized the ingestion-related pathway and under-played the inhalation hazard. This may have been influenced by the lack of published literature on health impacts to cohorts exposed to inhaled DU – a situation arising because of the rarity of such incidents. The report appears to have used the lack of literature to downplay the importance of this problem instead of undertaking a credible analysis of the inhalation hazard with available data and models. This should have been done, but was not. The analysis of the Royal Society (2001), WHO (2001) and Depleted Uranium Oversight Boards (website 2001 onwards) had fairly thorough treatment of this issue, but these sources of information evidently failed to influence the report.
- The discussion on pages 15-16 concerns the health risks of exposure, pathways of exposure, and health survey design analysis. It has undoubtedly left members of the public confused because it contains inconsistencies, is partly wrong, lacks detailed logic and explanation, and is sort of a shopping list of assertions and conclusions without satisfactory elaboration.

  This section should have explained the inhalation hazard and its consequences in detail, since this was the main exposure pathway for the Colonie area (i.e. by

breathing aerosols during the plants operation). In my opinion, addressing the health hazard of DU oxide inhalation exposure is the single most important reason to have conducted this Health Consultation. Therefore it should have noted the relative magnitude of pollution of the site – one of the larges concentrations of DU aerosol pollution in the world, if not the largest. It should have explained that the consequences of inhalation of respirable particles of DU oxide would lead to long residence times in the lungs, on the order of years, with consequent internal organ irradiation by alpha emitters and the likely illness that a major dose of such radiation could have led to. It should have sharply contrasted the differences between the inhalation and ingestion pathways and their implications of short (with ingestion) and long (with inhalation) residence times in lungs. It should have mentioned the consequences to subsequent urinary testing of these two ingestion and inhalation scenarios. It could have and should have summarised biokinetic models that are in theory capable of modelling (i.e. predicting retrospectively) the magnitude of cumulative inhalation dose if the time elapsed since exposure was known and if the daily excretion of DU can be determined. It should also have outlined generally the method of detection (i.e. explained what bioassays methods were available, especially the isotope tests) and their detection limits, to explain to the public whether or not tests available at the time were capable of detecting such residual DU in urine. It should have acknowledged that a urinary measurement made more than 20 years after exposure would be expected, even with very large initial exposure, to be orders of magnitude lower in concentration than it would have been initially. There is much missing in this section; only ATSDR officials can provide the rationale for such a superficial treatment of some of these issues. The section appears to avoid dealing with the main issue.

- The statement on top of page 16 states that if DU had been found in urinary tests, that such tests would be incapable of indicating 'where the DU came from'. This is largely wrong; isotope analysis is a very powerful technique to establish plausible links (or refute them) between sources and exposures. This is all the more surprising since they discuss the NLI plant as the only source of DU for the uranium pollution of the site (on page 19). There is essentially a dismissal of the role that isotope analysis of uranium could play in testing this link. The report shows a lack of insight and understanding of this whole area of measurement. This is all the more surprising since analytical laboratories within CDC itself are conducting research into such measurements of uranium in urine. Perhaps there is a lack of joined up communication within CDC in this regard. One could be forgiven for concluding that they just were not interested in recommending any kind of urinary uranium testing.
- Pages 16-17 discuss the issue of existing health surveys and the possibility of a new health assessment. I found this an exceptional frustrating aspect of the study and the single most disappointing part of the paper. Having concluded already that there was a significant health risk from uranium aerosols during the plant's emission history, they use these two pages to first explain why the earlier zip code surveys of NY state officials could not have worked in identifying any possible excess of cancers arising from the plant. I would have thought this would have prompted them to explain how a well-designed health

survey ought to be designed for this situation, but they failed to do this. Instead, on page 17 the report appears to signal a resignation that no possible survey could be designed that might identify whether or not excess illness might have arisen in the cohort of exposed individuals. This is not a satisfactory outcome of a Health Consultation of this type.

To provide a satisfactory basis for doing nothing, they needed to explain why it would have been impossible to conduct a survey to locate former workers at the plant and individuals who lived in close proximity to the plant for many years. These people could have been ranked in terms of potential exposure by duration of exposure, and proximity to areas of very high uranium in soil (as a proxy for the aerosol uranium concentration).

Ironically the Concerned Citizens about National Lead group was able to gather a lot of this sort of information and had some of it at the time of the report's writing. In our work we used their information effectively. In my time dealing with the Colonie site, I have had conversations with residents of a street adjacent the site in the heavily exposed pollution halo who communicated an alarming number of health issues (mainly cancers) and deaths in the past 25 years in houses in that particular area. Precautionary instincts suggest this ought to be investigated as a priority. No questions of this type were asked by the Consultation. This to me seems a major oversight.

- Part of the reason not to pursue further health assessments appears to have been predicated on the perceived inability to detect a low percentage of excess cancers that might be attributed to the pollution in a much larger cohort population (thousands of people). I fully agree that to use the thousands of people in a current zip code as the 'exposed population' is a poor experimental design for a health assessment of the Colonie situation. Such an approach stands no chance of succeeding in being insightful for the Colonie situation where only a relatively small number of individuals (probably less than 1000) was likely to have suffered a significant inhalation dose. This is in essence the flaw with the former NY State surveys. However, to do nothing and recommend nothing in the face of this is not a satisfactory option or outcome.

  Instead, the report should have recommended conducting a survey on the most exposed group of people; it should have located the several hundred most heavily exposed individuals, wherever they might now live, in addition to collecting death statistics from cancer (for example) from those who formerly lived near the site during its active years. This type of systematic census work is both necessary and feasible. The health issues with this targeted cohort could have been studied to either (1) discover any alarming illness pattern(s) relative to the general population, or (2) show that nothing was identifiably anomalous. Had the survey identified excess illnesses, then a campaign of appropriate-sensitivity uranium isotope testing could have been commissioned to see whether DU could be identified as part of the excreted uranium, in order to provide quantitative data on possible past exposure to DU. This is the sort of investigation that would have been a satisfactory outcome to the ATSDR report; it needn't have been hugely expensive or

undertake the work.

- The ATSDR authors were aware of inhalation exposure computer models that could be used to make predictions on exposure of an inhaled compound using particle grain size, airborne concentration at the point of emission, density of particles, and meteorological data. They could have made assumptions about particle size and density and used existing meteorological data to do this, but they did not. Give the relative ease with which our own research was able to isolate particles from contaminated soil or household dust, and study their general size, shape and composition, the lack of interest or awareness of this avenue of investigation represents a significant oversight, and may indicate a lack of interest in pursuing a credible, reasonably in-depth investigation into the DU pollution.
- On pages 30-31 in addressing direct concerns of the community the report provides a misleading answer by failing to mention the dangers of internal alpha radiation (in lungs in inhalation exposure) after noting that airborne emissions were the main hazard; the report obfuscates the issue here by appealing to the benign nature of alpha radiation to skin, which mixes up internal and external doses. This confusion was entirely unnecessary.
- On page 35 in addressing the 5th concern of the community, the report explains the challenges in designing a health survey and attributing any outcomes to NLI pollution. A lot of the reason the report recommends that no health survey would work is because the report concluded there was no means of establishing a distinct exposure to DU. The authrs would have known that standard existing uranium bioassays and uranium isotope urine tests had defined limits of detection that would limit the ability of these tests to detect DU. They should have realised that significant progress had been made on method improvement and that further improvement in reducing detection limits would be likely. They should have noted this in the report and recommended that should methods become available that could potentially quantify the past exposure via a urine test, that this whole issue should have been revisited. They should have recommended this be done.
- On page 37-38 are the conclusive recommendations and 'planned actions' arising from the Consultation. No recommendations are made with regards to DU exposure at all. In the planned actions are mentioned the following two items:
    1) ATSDR will work with local physicians and provide information on taking patients' environmental exposure histories. ATSDR will also make available resources related to environmental exposure, including contaminant-specific case studies and fact sheets.
    2) ATSDR is evaluating the feasibility of conducting a study that would compare the mortality rates of former NL workers to the mortality rates of the general public. Former workers likely received the highest exposures to depleted uranium from 1958 to 1984 during operation of the facility. Currently, ATSDR is determining whether relevant past worker records exist.

I am not aware that there has been any progress on these two 'planned actions'; I have also checked with CCNL, the main community group and they agree that no action on these was done following the publication of the Consultation. This has increased the sense of frustration by the community and is to say the least, puzzling. ATSDR should comment on this lack of follow up actions, if in fact this is the case.

Scientific Recommendations to address environmental health issues at NLI Colonie NY site

The ATSDR report has failed to resolve any of the outstanding environmental health issues arising from NLI pollution at Colonie. A sensible course of action for ATSDR for the future would be to embrace the shortcomings of its report and take a new approach putting in place a number of actions to make some substantial progress. For example,

- Community consultation in light of this hearing and recent research
- Establish funding for limited health assessment study
- Exposure screening of cohort with highest likelihood of significant inhalation exposures – workers and residents, perhaps several hundred individuals
- Design and implement targeted health assessment of cohort, including investigation of death statistics of those likely to have had a relatively heavy exposure
- Evaluate health data using precautionary ethos given the small cohort size
- Investigate further cleanup of indoor and outdoor properties where re-suspension of heavily contaminated dust could be a problem.

Comments on the ATSDR mission/remit and its performance

The remit of ATSDR Health Consultations is articulated in the ATSDR website is to "serve the public by using the best science, taking responsive public health actions, and providing trusted health information to prevent harmful exposures and diseases related to toxic substances".

At Colonie, while noting the useful case history of the site and especially its main conclusion that there existing a substantial health risk from uranium emissions during the active years of the NLI plant, the agency in my opinion has failed to locate, present, and apply the best science to Colonie, and when combined with the lack of any identifiable responsive health actions arising from its investment of resources, it is hard to conclude that in this case, it has come anywhere near fulfilling its mission.

Recommendations to Congress concerning ATSDR

ATSDR's remit forms an important component of public health policy and mitigation in the United States by undertaking prompt assessment and recommending a course of action to mitigate toxic hazard risks and derive new knowledge concerning unusual toxin situations. The work is important and needs to be highly credible and to reflect the best knowledge available anywhere.

The Colonie example shows that ATSDR needs to work considerably harder in order deliver credible assessments and solutions commensurate with its remit.

In cases like Colonie where it appears it had insufficient experience with an unusual hazard (in this case the inhalation hazard of uranium oxides) it needs to ensure that it taps into the best knowledge available, not just the in house expertise. The Colonie consultation could have been miles better if it had acquired an up to date knowledge of concurrent activities taking place on this same hazard in other government agencies (US Army research on DU inhalation; CDC uranium isotope measurement; National Academy of Sciences reports on DU) and in other countries (UK DUOB screening programme, Royal Society biokinetic models of inhaled uranium exposure and health risks for example). They appear to have failed to 'leave no reasonable stone unturned' in the Colonie study.

Governments (and certain industries) may fear what they might uncover by doing a thorough study into a politically-charged issue like depleted uranium. My view is that it is best to be transparent, face up to the risks of doing the credible science where it appears justified both fiscally and scientifically, do it well, and communicate clearly the issues, risks and conclusions. I think it is likely that the science will put some issues to bed instead of letting them fester without resolution for years. The public deserve this transparency, and responsible environmental stewardship dictates that we should understand the environmental consequences of industrial processes (and negligence) and assess risks properly in order to decide how best to find credible solutions to these issues.

Other Supporting Documents

Summary of current community concerns

The following is a letter with concerns of the community submitted to ATSDR arising from the Health Consultation. It is my impression that most if not all of these concerns are still current because they were not addressed in the report or in any followup actions. I have relied on Anne Rabe of the Community Concerned with National Lead for this input.

Citizens' Environmental Coalition

Aimee T. Treffiletti
Environmental Health Scientist
Division of Health Assessment and Consultation
ATSDR, Mailstop E-60
1600 Clifton Road, NE
Atlanta, GA 30333 November 3, 2003

Re: Colonie, New York NL Industries Site, EPA Facility ID: NY0890137854

Dear Ms. Treffiletti:

The following are the comments of Citizens' Environmental Coalition (CEC) in response to the August 15, 2003 ATSDR Health Consultation regarding the former National Lead (or NL) Industries site, located at 1130 Central Avenue in Colonie, New York. Also attached is a petition letter to ATSDR signed by 89 people—most of whom are residents living near the NL Industries plant—which states, *"We strongly urge ATSDR to conduct a comprehensive health study of the community impacted by NL Industries pollution, with input from a community-appointed Citizen Advisory Committee."* We also note that at the last public hearing over 200 people raised their hand when asked if they wanted ATSDR to conduct a community health study. We hope you will respond to each of the residents who signed the letter petition. Thank you.

CEC agrees with the ATSDR statement on page 1, "that in the past, the uncharacterized emissions from the NL plant were a public health hazard to the community surrounding the Colonie Site."

An article in the *Schenectady Gazette* on February 6, 1980, reported that NL's uranium emissions for January 2-23, 1980, exceeded 417 microcuries. On page 11 of ATSDR's report, in bold print, there is a section heading, "How much DU was released in air emissions from the NL plant?" The answer to that question is extremely important but not provided nor is any estimate made. Can ATSDR provide any quantitative answer as to how much uranium NL might have emitted over the years? Would it be a gram, an ounce, a pound, one hundred pounds? Also, what is the range of the size of the uranium particles NL emitted? What is the shape(s) of these particles? How does the size and shape of the particle inhaled impact health?

Did ATSDR consult with the US Department of Energy, the US Army Corps of Engineers, Albany County Health Department or former NL Industries employees to determine if uranium air emission data for the years 1958-1979 exists? What happened to it? Where is it now located? Did ATSDR contact NL Industries to determine if the company has retained any stack emission records, employment records, or other information that might help quantify the uranium emissions?

On page 12 of the report, ATSDR stated: "Based on the levels of DU found in soil, and the fact that the NL plant scaled down operations during the late 1970s and early 1980s (USDOE 1989b), the earlier (pre-1979) air emissions were probably

higher." It is our understanding based upon news reports from 1979-1982 and interviews with former NL workers, that NL operations were at their peak in late 1979 and early 1980.

Can ATSDR quantify the amount of total stack emissions based on the amounts of uranium found in the soil on-site and in the surrounding community? We request ATSDR expand its exposure evaluation by doing a computer model to estimate air emissions based on the levels of DU found in the soil. This has been done at other sites, such as the Kelly site. It is critical that additional research be done to much more accurately estimate the exposure to the community. ATSDR should contact NL Industries, DOE, the Albany County Health Department, the Army Corps of Engineers and any consultants to legally request all their NL emissions information. It should also conduct an exposure evaluation on the likely air emissions based on the levels of DU found in the soil.

The ATSDR report does not comment on the exposures children might have had because of the inhalation or ingestion of DU particles that landed on the ground and then were resuspended in the air. This is a very important omission that should be corrected. There were scores of children and teenagers who lived in close proximity to the NL facility for much or all of their early years. For example, a child born in 1958 who lived within a block of the NL Industries facility until 1980 would or might have been exposed to 21 or 22 years of air emissions. How many particles of ceramic uranium oxide or other types of uranium might that person have inhaled and retained in his or her lungs? How many particles must be inhaled to cause injury? Could the inhalation of as few as one particle cause cancer or other illnesses?

ATSDR noted on page 12 of its report that the Department of Energy (DOE) regulatory soil cleanup limits "were decided for the purposes of remediation and not based on health risk or dose." DOE obviously did not remove all of the uranium NL emitted. Does the uranium that remains in the soil off-site pose a health risk to humans? This is an important question. There are many people who never walked or played on or near the NL property but who live or used to live a half-mile or a mile or two miles away from the NL site. Some of these people desire to know if there is a health risk to them from either the uranium particles they might have breathed in during the years NL operated or from any uranium that remains in the ground now. Leonard Dietz has demonstrated that uranium particles emitted from the NL factory were transported via air currents to a distance of at least 25 miles from the NL factory.

The ATSDR report stated, "Little scientific information is available regarding how touching DU or DU-contaminated soil can affect health" but then downplayed concerns about this phenomenon. (Page 12.) If little information is available, how can ATSDR be so confident that there is little risk? Children played in the dirt, played football on the NL property, sat on the ground, splashed in puddles, waded in stream, swam in the pond, dug holes in the ground and touched interesting looking and unusual objects. Having spoken to many people who lived in the NL neighborhood for part or all of their childhood and teenage years, we are aware that many children and teenagers played with pieces of radioactive debris that NL buried or discarded in the neighborhood. (We informed ATSDR of this concern in our meeting with agency officials.) If children had open wounds, cuts or scrapes in the skin, or if the DU came in contact with their eyes, nose, ears, or mouth, they could

have absorbed or inhaled DU. We believe both children and adults had substantial exposure to DU through inhalation, ingestion, and skin exposure for many, many years. Many children spent parts of many days playing on or near the NL property. These people had repeated exposures to the soil contamination in addition to the 1958-1984 air emission exposures.

Another key concern is that many children—who are the most sensitive and vulnerable to toxic chemicals—ingest soil while playing in the dirt. ATSDR stated that contacting DU contaminated soil is not expected to cause illness. However, ATSDR grossly underestimated children's exposures to soil contaminated with DU and lead by ignoring important soil ingestion studies by Dr. Edward Calabrese of the University of Massachusetts. His study found that 62% of the children at a day care center ingested 1 gram of soil a day; with 33% of the children ingesting over 10 grams of soil a day. ATSDR bases its assessment on the assumption that children ingest a much smaller amount of soil—500 or 100 milligrams per day. We request a reassessment of the health risk based on 1 and 10 grams of soil ingestion per day assuming 373 milligram per kilogram for lead and 600 picocuries per gram for DU contaminated soil.

We note that the precautionary recommendations for people concerned about not exposing themselves or their children to lead and DU contaminated soil is buried in the report. On pages 18, 19 and 27, ATSDR states that children should be tested for lead exposure and people can prevent exposures by ensuring children wash their hands after playing in dirt and peeling vegetables. Approximately 710 children 6 years and younger live within 1 mile of the NL site. ATSDR should provide clear, understandable recommendations for parents in Fact Sheets and in the beginning of the report.

Depleted uranium is radioactive. It is well known that any increased exposure to radiation causes an increased risk of cancer. Radiation exposure can also cause birth defects and weaken the immune system. ATSDR has not included many medical journal references on the hazards of radiation in its health assessment literature. ATSDR has substantially downplayed the health risks of cancer and birth defects from exposure to DU uranium. We request that ATSDR correct its report to fully include the hazards of DU radiation in its health assessment. Environmentally induced cancers can take 5 to 40 years to show up. The inadequate evaluations by the ATSDR (health consultation) and the Department of Health (cancer cluster investigations) do not do justice to addressing the community's concerns and question—what did NL's pollution do to my health? It is interesting that the priority community concern was not included in the ATSDR summary. Our organization and numerous residents told ATSDR officials that a community health study was the priority action that everyone wanted. This was not mentioned in the community concern summary in the report.

Has ATSDR attempted to speak with the hundreds of people who lived near the NL site from 1958 (when the uranium emissions began) through the 1980s (when the emissions ended and the DOE removed some of the uranium from some of the neighborhood properties?)? These residents and former residents can provide vast amounts of information about their activities, which ATSDR could use to determine uranium exposures. Some of these people also worked at NL Industries. As part of

the health consultation, ATSDR might benefit from conducting a public hearing or a series of hearings where people could provide oral and written testimony about their exposures, their knowledge of NL's operations, and their health concerns.

Did ATSDR make any effort to contact former NL Industries employees to obtain information about the day-to-day practices and manufacturing processes at the NL facility? The ATSDR report provides only skimpy and superficial information about what actually was taking place at the NL facility. Based on what ATSDR knows about NL operations, does the agency think production workers were heavily exposed to uranium? We believe there is substantial evidence that this occurred. We also believe a health study of the surviving workers is warranted. We request that ATSDR contact NIOSH and recommend that NIOSH undertake such a study. NIOSH did investigate the NL Industries plant in the 1980s and was concerned about health risks to workers.

We are concerned about the homes that have contaminated VOC vapors in their basements *above* the federal guidance levels. We request that ATSDR recommend immediate action be taken by the Army Corps to address this health risk.

In summary, we request that ATSDR redo the Health Consultation to expand and improve on the report so it provides an accurate assessment of the community's health risks. The agency needs to fully address the radioactive hazards posed by DU. The agency needs to substantially improve the emissions estimates and exposure scenarios. We also support the comments of Leonard Dietz, William Kelleher, Assemblyman Robert Prentiss and Thomas K. Simpson, and urge ATSDR to incorporate their recommendations in a new report as well. In addition, we request that ATSDR include a recommendation for a Community Health Surveillance investigation to fully evaluate exposures and adverse health outcomes or increases in illnesses, and issue recommendations to adequately address health risks and adverse health outcomes. A community-appointed Citizen Advisory Committee should have full input into the design and implementation of the health surveillance study. Thank you for considering our comments. We look forward to hearing from you.

Sincerely,

Tom Ellis
Board Chairperson
Citizens' Environmental Coalition

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(518)-453-8874

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Representative
Citizens' Environmental Coalition

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Castleton, NY 12033
(518)-732-4538

Enclosures: Letter Petition (5 pages)

Other materials/research relevant to the Colonie site.

- Illustrations of aspects of the Colonie site, urine testing, particles emitted by the NLI plant, etc.
- 2003 DUOB extract – summary and annex on biokinetic models
- 2006 Health Physics paper on the measurement of uranium isotopes in urine.
- 2008 Science of the Total Environment on the Colonie site and urine tests there
- 2009 Journal of Atomic and Analytical Spectroscopy paper on the Colonie uranium oxide particles and their isotope composition.

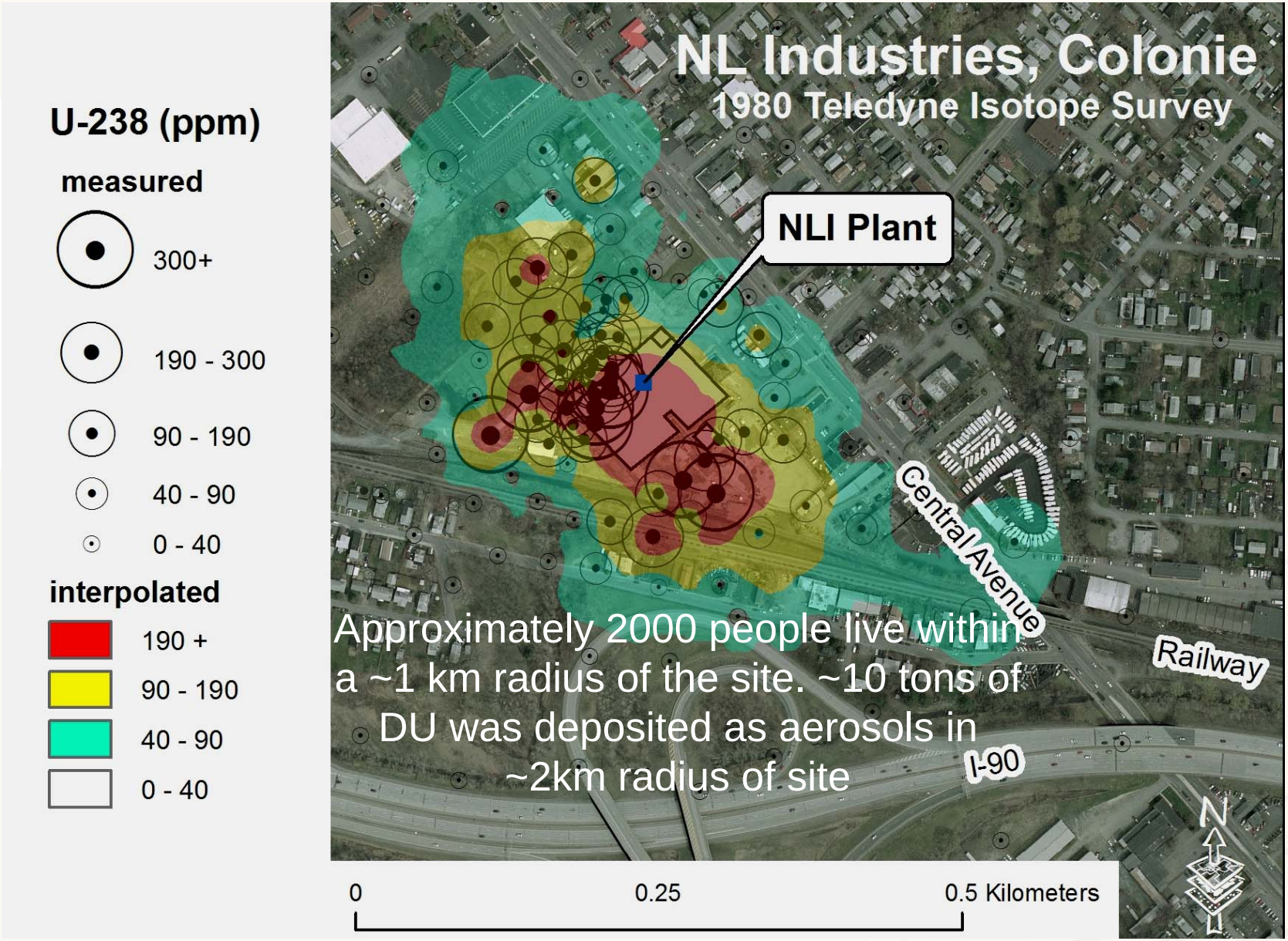
Depleted uranium (DU) and environmental health : The former National Lead Industries Colonie NY site

Prof. Randall Parrish

Natural Environment Research Council
Isotope Geoscience Laboratory (NIGL),
British Geological Survey

& Department of Geology, University of Leicester (UK)

Illustrations in support of 12 March 2009 testimony



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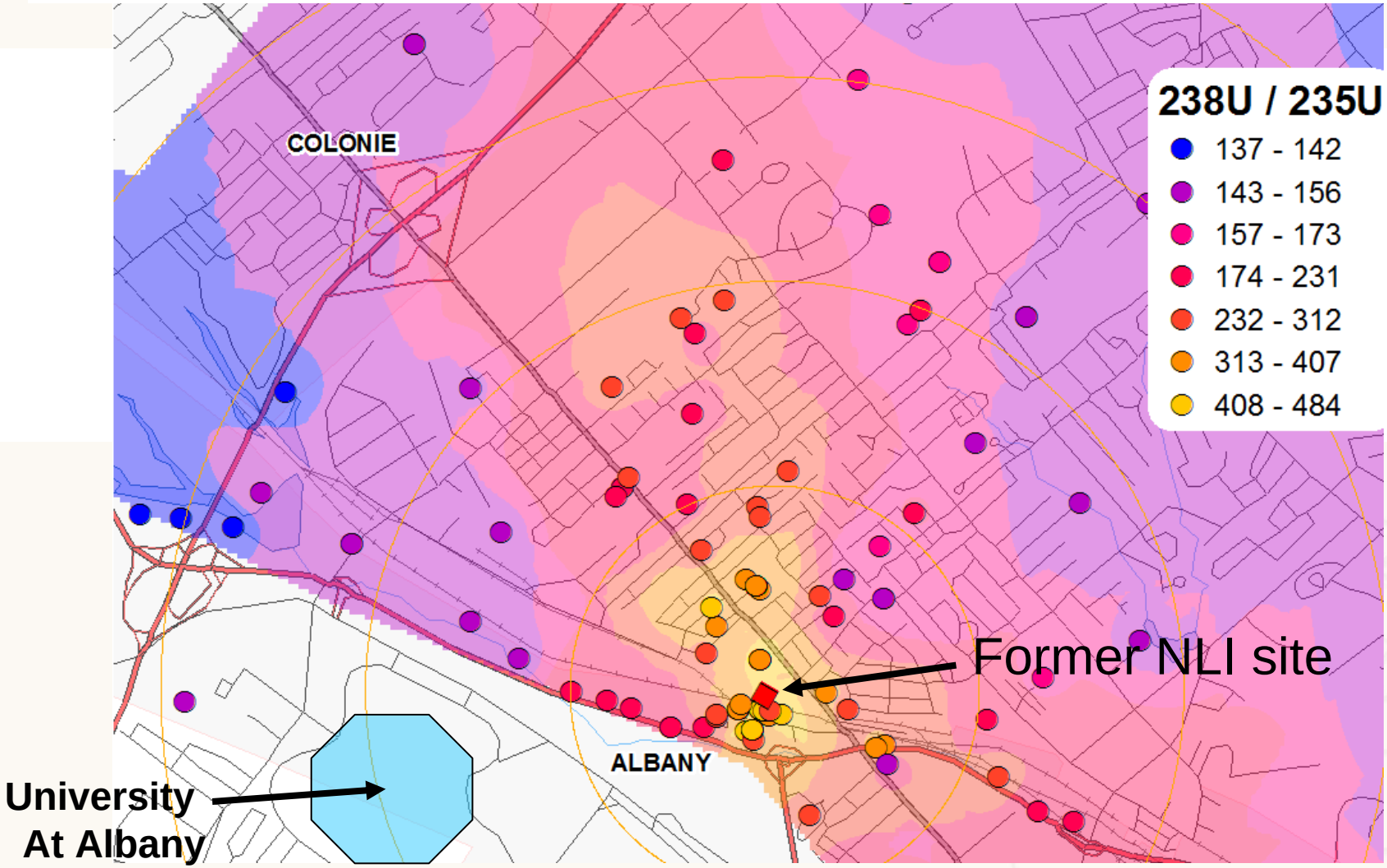
Contamination mapping by isotope ratio



The ratio in natural uranium is 137.88; data courtesy N Lloyd

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The Colonie, NY site during its operational period pre-1947 –1982, prior to decommissioning in the 1990s.

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The Colonie NL site in ~2006 in final stages of remediation by ACE

Huge amount of contaminated building material and soil shipped to radioactive waste disposal sites in western US

DU particles are found in attics, basements, bark, soil near the site in community

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$190M has been spent remediating the site, an amount far larger than the combined resources for DU research worldwide

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A stream containing plant runoff has flowed into Patroon Lake and accumulated for more than 80 years, and it contains an archive of pollution for this time.

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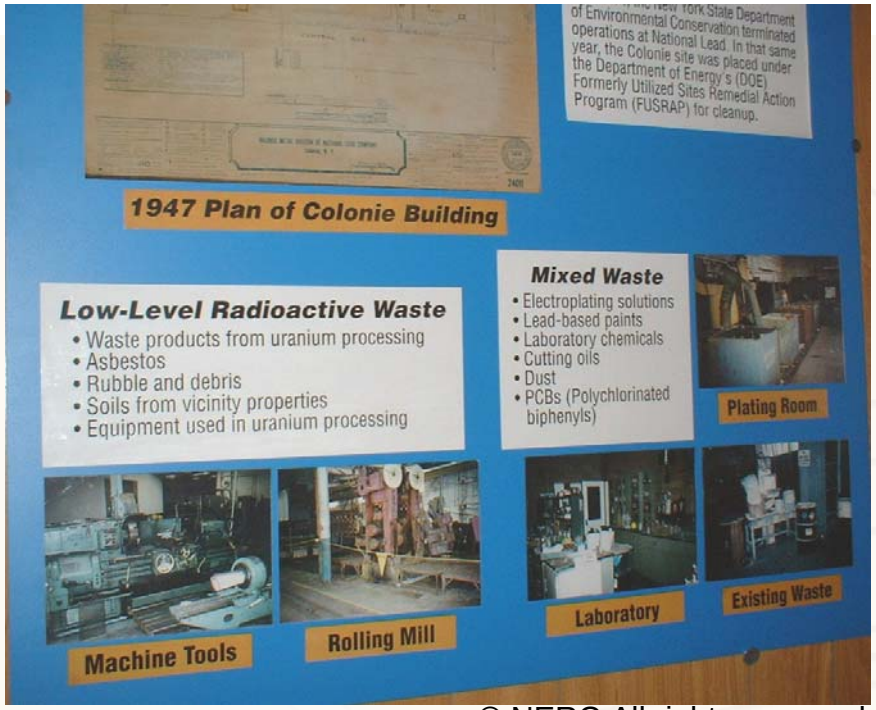
Some photos of the Colonie, NY site and its activities, from archival materials on site, ca. 2006



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Urinary uranium isotope method at NIGL:

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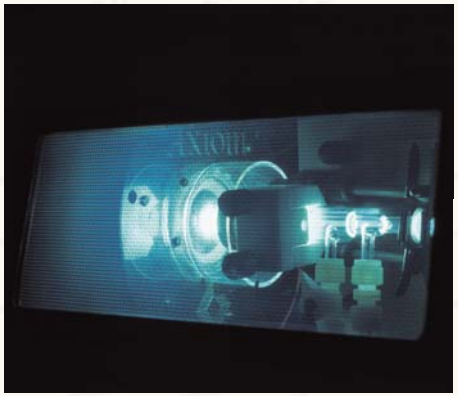
Urine collection in pre-cleaned bottle, away from dust sources

Multicollector ICP-MS analysis

Chemical processing in clean laboratory



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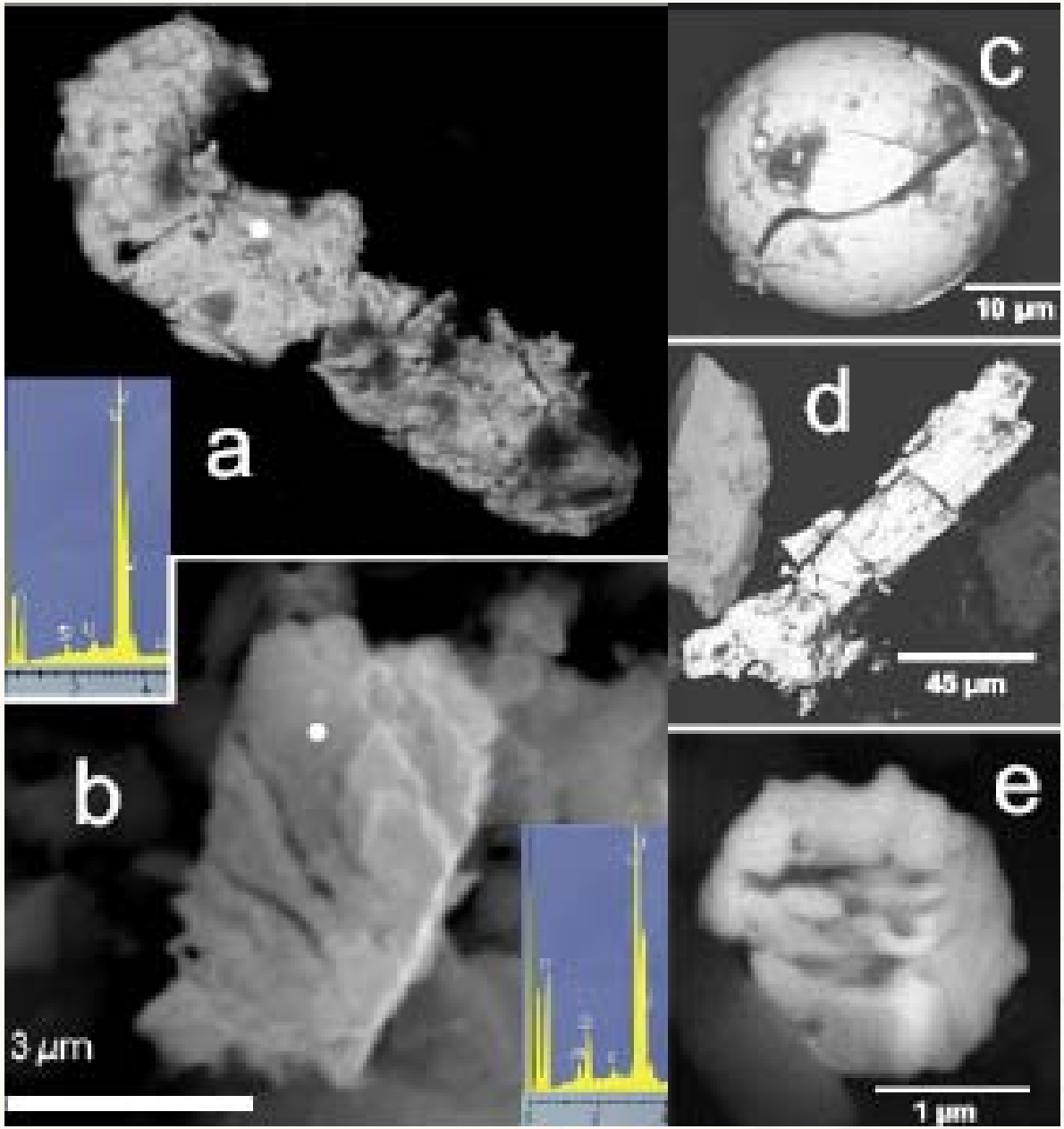
DU oxide particles originating from the NLI plant and recovered from dry household dusts, and identified using scanning electron EDS analysis.

These particles are respirable and are sufficiently small to lodge deep in the lungs.



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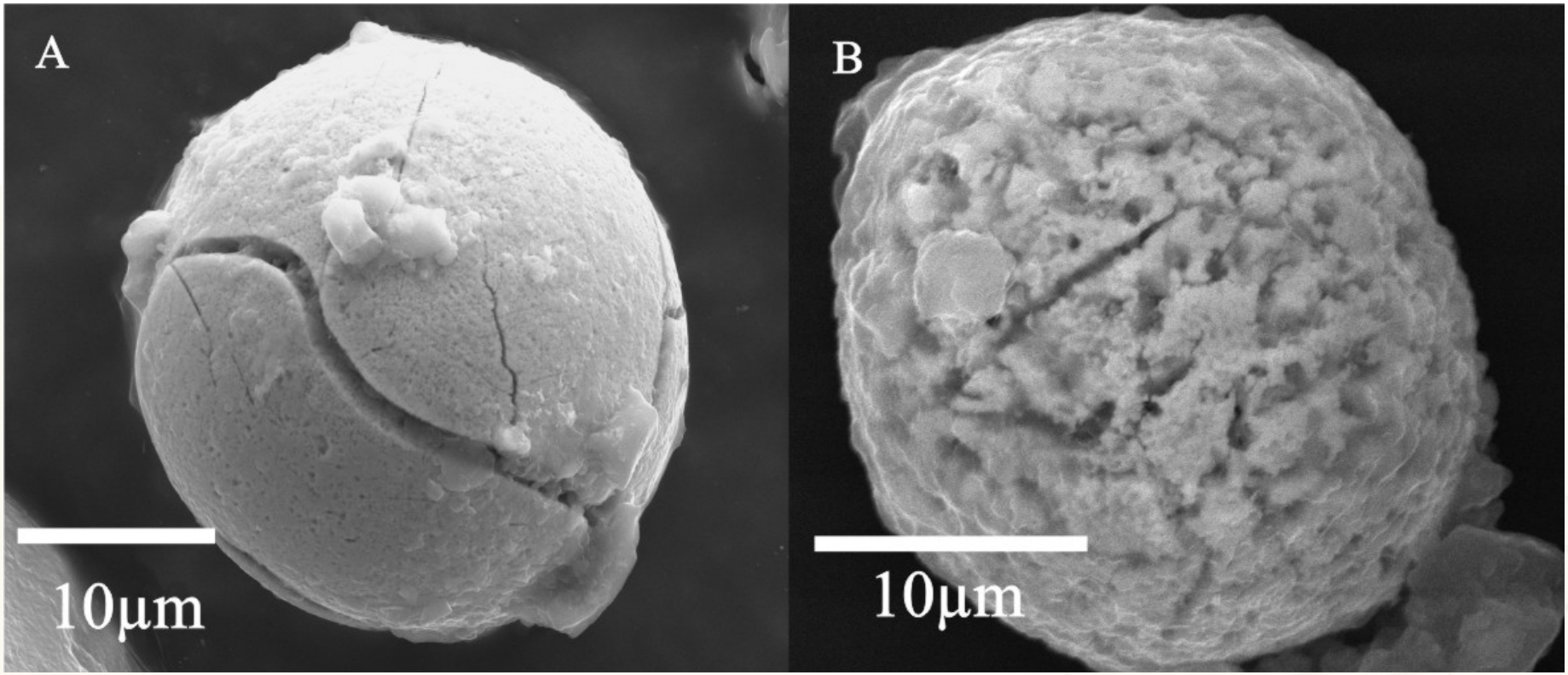
Images of DU oxide particles –
left: house dust (dry, undisturbed)
(right) from soil <10% dissolved after ~25 years
Courtesy Nick Lloyd (PhD student, U Leicester)



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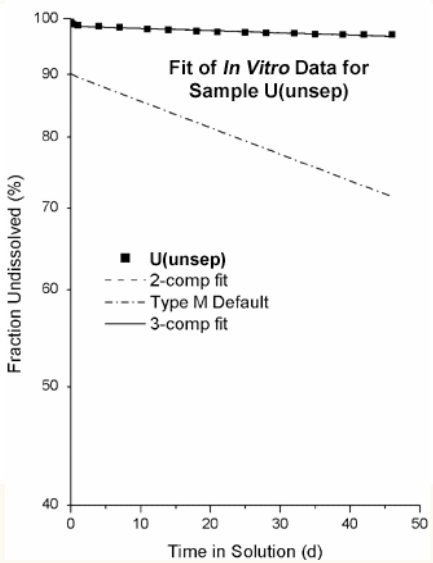
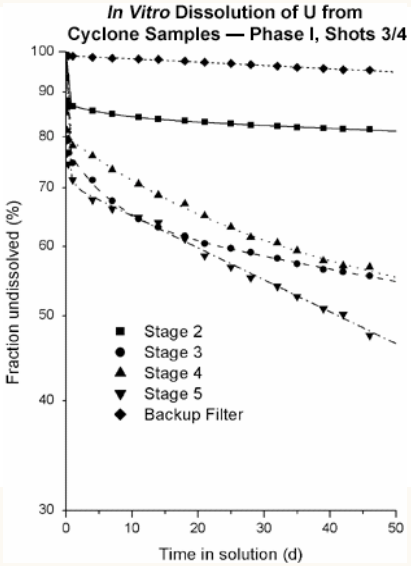
Selected data showing solubility of DU oxide particles illustrating potentially huge variability





US Army Capstone Study, 2005

Experiment	0 days % left	45days % left	1 year % left	10y, 3653d % left	27.4y, 10,000d % left
P1 3/4 BU	100	95.2	72.3	4.3	0.018
U (unsep)	100	96.8	84.9	22.1	1.6
P1 3/4 Stg2	100	56.7	27.4	0.027	4.5E-08
P1 3/4 Stg5	100	48.4	3.3	3.3E-12	2.3E-35
PIII 2I CY-4	100	90.8	89.8	89.8	89.8
PIII 2I CY-5	100	85.6	43.1	15.4	15.4
PIII 2I CY-BU	100	84.4	73.8	19.2	1.42

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Depleted
Uranium
Oversight
Board

The solubility of inhaled DU and its influence on urine excretion

G Etherington
National Radiological Protection Board, Chilton, Didcot, Oxon, OX11 0RQ

1. Introduction

This note briefly discusses the process of absorption of inhaled material from the respiratory tract, and describes how it can be modelled. It then presents some of the available information on absorption of depleted uranium, and describes the effect of variability in absorption on urinary excretion. It is in no way intended to be a comprehensive account; for this, reference should be made to Annexes of the report of the Royal Society Working Group on the Heath Hazards of Depleted Uranium Munitions (RSWGDU) (Royal Society, 2001). Annex A give an account of the current ICRP models used to assess intakes of uranium. In addition, Annexes G and H of the RSWGDU report give summaries of the available information on the absorption characteristics (ie "lung solubility") of particulate DU resulting from penetrator impact and combustion in fires respectively.

2. Absorption from the respiratory tract

Inhaled material is cleared from the respiratory tract by three mechanisms. In regions of the respiratory tract other than the nose, clearance results from a combination of movement of particles towards the gastro-intestinal tract and lymph nodes (*particle transport*), and movement of material from the respiratory tract into the blood and then to body fluids (*absorption*). Material deposited in the nose is cleared by *nose blowing*, particle transport and absorption.

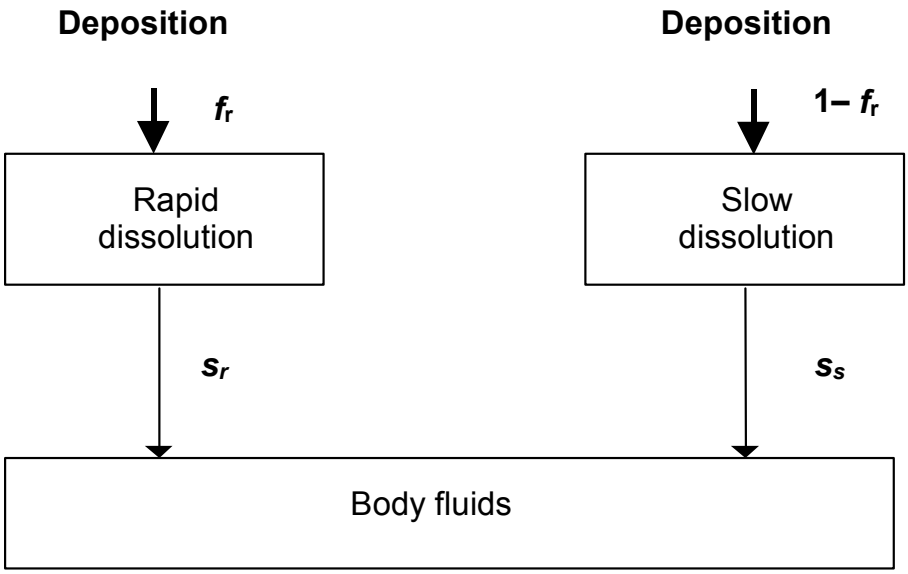
It is generally assumed that :

- all clearance rates are independent of age and sex;
- particle transport rates are the same for all materials;
- absorption into blood, which is material specific, occurs at the same rate in all regions except the front of the nose, where none occurs.

Fractional clearance rates (whether absorption or particle transport) vary with time. However, in order to simplify calculations, most models represent clearance by combinations of compartments that clear at constant rates.

3. Modelling absorption

Absorption to blood is a two-stage process: dissociation of the particles into material that can be absorbed into blood (dissolution); and absorption into blood of soluble material and of material dissociated from particles (uptake). Both stages can be time-dependent. In practice, it is found that dissolution of most materials can be represented by a simple two-compartment model (figure 1). A fixed fraction of deposited material, f_r, is available for rapid dissolution at a rate s_r, while the remaining fraction ($1 - f_r$) dissolves more slowly, at a



rate s_s. Uptake to body fluids of dissolved material can usually be treated as instantaneous. (When this is not the case, the concept of a "bound state" is employed; see Annex A, Royal Society, 2001).

Figure 1. Compartment model describing absorption to blood.

Thus, the absorption behaviour of most materials can be described by making a suitable choice of values for the three absorption parameters, f_r, s_r, and s_s. Some materials are very soluble in the lungs and are absorbed almost instantaneously (eg caesium chloride), and so have an f_r value of 1. Other materials are very insoluble in the lungs (eg plutonium dioxide) and have a very low f_r value (typically 0.001). Three default absorption types have been defined for use when material-specific information is not available, known as Type F ("fast" absorption), Type M ("moderate" absorption) and Type S ("slow" absorption). Absorption parameter values for the three default Types are given in Table 1.

Table 1. Default absorption parameter values for Type F, M, and S materials (ICRP 1994)

Type	F(fast)	M (moderate)	S (slow)

Fraction dissolved rapidly	f_r	1	0.1	0.001
Dissolution rates:				
Rapid (d^{-1})	s_r	100	100	100
Slow (d^{-1})	s_s	-	0.005	0.0001

A rate constant of 100 d^{-1} corresponds to a half time of ~ 10 minutes; a rate constant of 0.0001 d^{-1} corresponds to a half time of ~ 7000 days.

4. Absorption of depleted uranium

A number of studies have been conducted to determine absorption parameter values for uranium oxides produced during the manufacture of nuclear fuel. Results are summarised in Table 2.

Table 2. Summary of absorption parameter values for uranium oxides

	Absorption parameters			
Compound[a]	f_r	s_r (d^{-1})	s_s (d^{-1})	Reference
UO_4	0.87	0.93	0.024	Ansoborlo et al 2001
UO_3	0.75	14	0.02	Bailey et al 1998
UO_3	0.92	1.4	0.0036	Hodgson et al 2000
UO_3	0.71	0.28	0.0011	Ansoborlo et al 2001
U_3O_8	0.044	0.49	0.00035	Hodgson et al 2000
U_3O_8	0.046	2.3	0.0012	Ansoborlo et al 2001
U_3O_8	0.03	2.1	0.00038	Ansoborlo et al 2001
UO_2 – Non-ceramic	0.011	0.95	0.00061	Hodgson et al 2000
UO_2 – Ceramic	0.008	1.3	0.00026	Hodgson et al 2000
UO_2	0.03	1.3	0.0015	Ansoborlo et al 2001
UO_2	0.01	nd	0.00049	Ansoborlo et al 2001
UO_2	0.01	nd	0.00058	Ansoborlo et al 2001

Note. See (Royal Society, 2001) for full references.

It can be seen that the different oxides have a very wide range of absorption characteristics. The chemical form of particulate DU produced as a result of its use in munitions depends on the conditions of formation. Particles formed by impacts are reported to be a mixture of U_3O_8 and UO_2 (but predominantly U_3O_8), while combustion produces an oxide which is almost entirely U_3O_8 (Royal Society, 2001). However, there remains uncertainty as to the absorption behaviour of DU formed as a result of its use in munitions, because of factors such as particle size distribution and the presence of other elements.

Human Respiratory Tract Model (HRTM) (ICRP, 1994) parameter values appropriate for a wide range of possible DU exposure scenarios are discussed in the RSWGDU report (Royal Society, 2001). Central estimates of DU parameter values appropriate for Level II or Level III inhalation of resuspension aerosols (impact or combustion) occurring within a vehicle are shown in Table 3. Also shown are parameter values describing the likely upper and lower limits of absorption. Broadly, the parameter values given in Table 3 for "Low absorption" and "High absorption" are equivalent to the values given in Table 15, Appendix 1 of the RSWGDU report for "Worst-case (radiation)" and "Worst-case (chemical toxicity)", respectively. However, there are some small differences in the data given in the two Tables because in this note we are concerned with predicting the upper and lower limits of urinary excretion per unit intake, whereas Table 15, Appendix 1 of the RSWGDU report is concerned with predicting upper limits on dose per unit intake and chemical toxicity.

Table 3. HRTM model parameters for Level II / III inhalation of resuspension DU aerosols (see text)

Parameter	Central estimate	"Low" absorption	"High" absorption
Rapid dissolution fraction, f_r	0.2	0.005	0.5
Rapid dissolution rate, s_r, d^{-1}	1	0.4	14
Slow dissolution rate, s_s, d^{-1}	0.001	0.0001	0.0015
Subject exercise level	Heavy worker	Heavy worker	Heavy worker
Aerosol activity median aerodynamic diameter, μm	5 (default workplace)	5	1
Aerosol geometric standard deviation	2.5 (default)	2.5	4
Particle density ρ, g cm^{-3}	9	9	11
Gut uptake factor, f_1	0.002	0.002	0.02

5. Urinary excretion of DU

Figure 2 shows daily urinary excretion calculated using the HRTM for the three scenarios described in Table 3. As can be seen, the range spans almost two orders of magnitude at earlier times, but the rates converge at times later than about 500 days.

This figure illustrates the effect on urinary excretion of variability or uncertainty in HRTM model parameters. An additional source of uncertainty in urinary excretion is uncertainties in systemic model parameter values. NRPB is currently planning a study to investigate uncertainties in DU urinary excretion arising from uncertainties and variability in both HRTM and systemic model parameter values.

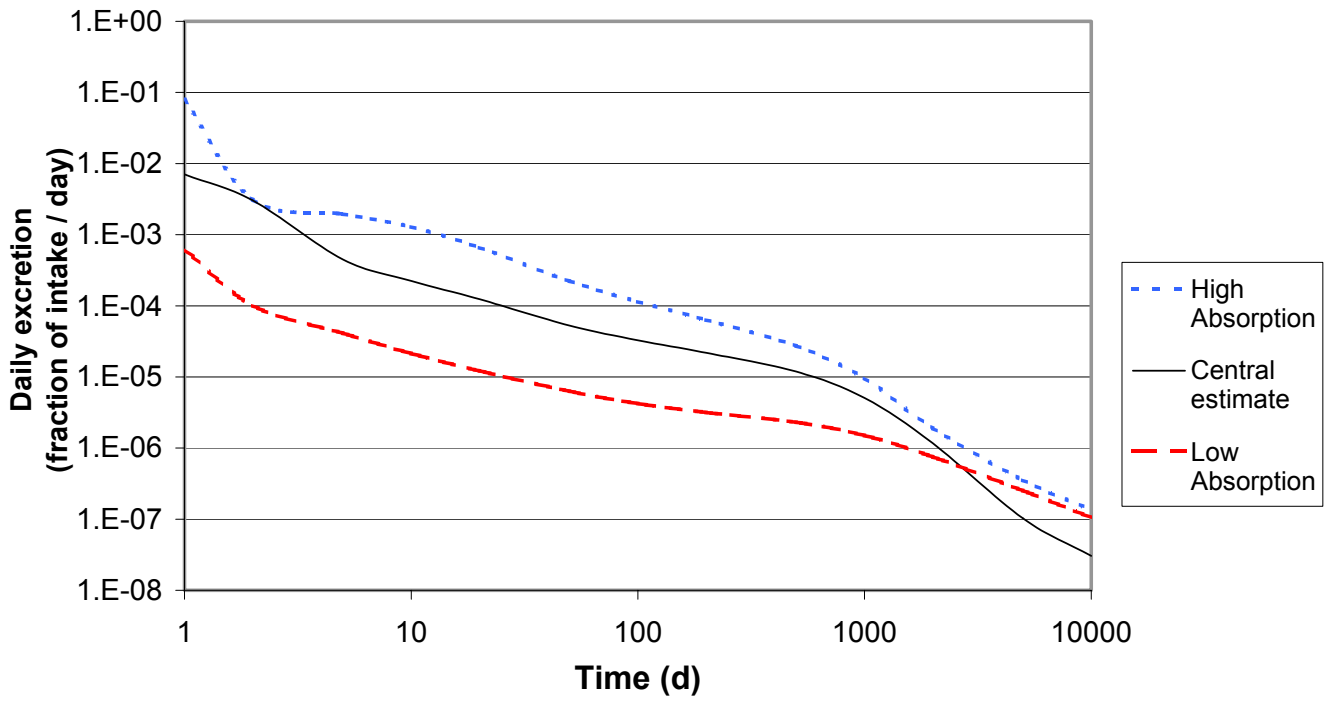


Figure 2. DU urinary excretion rates, calculated using the HRTM using the parameter values given in Table 3.

References

ICRP (1994). Human Respiratory Tract Model for Radiological Protection. ICRP Publication 66, Annals of the ICRP, **24**, No. 1-3. Oxford, Pergamon Press.

Royal Society (2001). The Health Hazards of Depleted Uranium Munitions, Part 1. Policy Document 6/01. London, Royal Society.

Paper

DETERMINATION OF $^{238}U/^{235}U$, $^{236}U/^{238}U$ AND URANIUM CONCENTRATION IN URINE USING SF-ICP-MS AND MC-ICP-MS: AN INTERLABORATORY COMPARISON

Randall R. Parrish,* Matthew F. Thirlwall,† Chris Pickford,‡§ Matthew Horstwood,** Axel Gerdes,**†† James Anderson,‡ and David Coggon‡‡

Abstract—**Accidental exposure to depleted or enriched uranium may occur in a variety of circumstances. There is a need to quantify such exposure, with the possibility that the testing may post-date exposure by months or years. Therefore, it is important to develop a very sensitive test to measure precisely the isotopic composition of uranium in urine at low levels of concentration. The results of an interlaboratory comparison using sector field (SF)-inductively coupled plasma-mass spectrometry (ICP-MS) and multiple collector (MC)-ICP-MS for the measurement of uranium concentration and $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotopic ratios of human urine samples are presented. Three urine samples were verified to contain uranium at 1–5 ng L^{-1} and shown to have natural uranium isotopic composition. Portions of these urine batches were doped with depleted uranium (DU) containing small quantities of ^{236}U, and the solutions were split into 100 mL and 400 mL aliquots that were subsequently measured blind by three laboratories. All methods investigated were able to measure accurately $^{238}U/^{235}U$ with precisions of ~0.5% to ~4%, but only selected MC-ICP-MS methods were capable of consistently analyzing $^{236}U/^{238}U$ to reasonable precision at the ~20 fg L^{-1} level of ^{236}U abundance. Isotope dilution using a ^{233}U tracer demonstrates the ability to measure concentrations to better than ±4% with the MC-ICP-MS method, though sample heterogeneity in urine samples was shown to be problematic in some cases. MC-ICP-MS outperformed SF-ICP-MS methods, as was expected. The MC-ICP-MS methodology described is capable of measuring to ~1% precision the $^{238}U/^{235}U$ of any sample of human urine over the entire range of uranium abundance down to <1 ng L^{-1}, and detecting very small amounts of DU contained therein.**

Health Phys. 90(2):127–138; 2006

Key words: accident analysis; uranium; weapons; radiation, ionizing

INTRODUCTION

Depleted uranium (DU) is a by-product of the manufacture of enriched uranium for use as a fuel in nuclear reactors and in nuclear weapons. It has a $^{238}U/^{235}U$ atomic ratio of up to ~500 as compared with 137.88 for natural uranium, and is ~70% more dense than lead. The latter property along with its hardness has been exploited in various specialized applications in engineering. In addition DU has been used militarily in the armor plating of tanks, and in armor-piercing anti-tank weapons. Such weapons were employed by American and British forces in the 1991 Gulf War, by American forces during operations in Bosnia in 1994–1995 and Kosovo in 1999, and by American forces in the conflict in Iraq that began in 2003.

Because of their effectiveness in combat, DU weapons can reduce battlefield casualties among the forces that use them. At the same time, however, they could pose longer term risks to health and the environment from ionizing radiation (DU is a relatively weak alpha emitter) and through chemical toxicity (WHO 2001; Royal Society 2001). As with any hazardous substance, the health risk will depend on the pathway and extent of exposure. While some soldiers have been exposed to DU as a consequence of shrapnel wounds by fragments of metallic DU, the main DU exposure pathways are inhalation of relatively insoluble oxidized uranium particles formed by combustion when a DU round strikes an armored target, and ingestion of DU-contaminated food and water.

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In Britain, there has been concern among some veterans of the campaigns in the Persian Gulf and Balkans that exposure to DU has impaired their health or significantly increased their risk of cancer and other diseases. In response, the British Government in 2002 undertook to provide a scheme of retrospective testing for veterans who wished to know whether and to what extent they had been exposed to DU, and appointed an independent committee (the Depleted Uranium Oversight Board, DUOB, www.duob.org.uk) to oversee development of the testing program. It was agreed by the DUOB at an early stage that the most practical method of assessing past exposure was likely to be by measurement of uranium isotopes and concentrations in urine, this being a non-invasive procedure.

Inhaled particles of uranium oxide may be retained in the lung and associated lymph nodes, where they undergo slow dissolution in tissue fluids over the course of many years (Royal Society 2001). Soluble uranium species will be excreted by the kidney (adding to the normal low-level excretion of uranium derived from dietary sources), though a small proportion will be incorporated into the crystalline bone structure (Leggett and Pellmar 2003). Because the uranium is depleted, the $^{238}U/^{235}U$ ratio in the urine would be elevated. It should therefore be possible to estimate the daily excretion of DU by measuring the $^{238}U/^{235}U$ ratio and overall rate of uranium excretion in urine, provided the isotopic composition of DU is known.

Detection of DU exposure after an interval of 10 to 15 y is methodologically challenging because the total uranium concentration in urine will commonly be less than 10 ng L^{-1} and the perturbation in isotope ratio may be small. Several laboratories have reported measurements of uranium isotope ratios in the urine of Gulf War veterans (Durakovic et al. 2002; Hooper et al. 1999; Gwiazda et al. 2004). However, the analytical methods used in these studies vary greatly, and the ability to make precise and reproducible measurements at low concentrations of uranium in urine has not been demonstrated. In part, these studies (Gwiadza et al. 2004) involved individuals with retained shrapnel whose uranium levels in urine were relatively high.

To help in the planning of the UK DU testing program, we therefore conducted a study to explore the sensitivity and accuracy with which uranium concentrations and isotope ratios can be measured in urine, comparing results from three laboratories based on different analytical techniques, but all using mass spectrometry more advanced than quadrupole ICP-MS. In addition to the $^{238}U/^{235}U$ ratio, we also attempted to assess the $^{236}U/^{238}U$ ratio, since ^{236}U is generally a contaminant in DU (Royal Society 2001); ^{236}U should not be detectable in uranium from natural sources, except at extremely low levels ($^{236}U/^{238}U \leq 10^{-10}$; Berkovits et al. 2000).

MATERIALS AND METHODS

Overview of experimental design

The study involved three laboratories, the United Kingdom Natural Environment Research Council Isotope Geosciences Laboratory (NIGL), Scientifics Ltd. (Harwell), and the Isotope Geochemistry Laboratory of the Geology Department, Royal Holloway University of London (RHUL). Each of these laboratories prepared a batch of urine that was measured to be homogeneous and of natural isotopic composition, within uncertainty. Each laboratory split each batch of urine into three sub-equal portions; one was left untouched, while the other two were spiked with a specially prepared solution of DU (from metal) to achieve target $^{238}U/^{235}U$ isotope ratios specified by the DUOB. Laboratories were told the target ratios only for their own batches of urine and not for those of the other two laboratories. Each laboratory then prepared three separate 500 mL aliquots of each of these three solutions. These were then transported to a central facility (Department of Earth Sciences, University of Oxford) and were coded. A set of nine samples (one from each batch) was then supplied to each laboratory for analysis of the total uranium concentration and the $^{238}U/^{235}U$ and $^{236}U/^{238}U$ (atomic) isotope ratios with 95% confidence intervals. The NIGL and RHUL laboratories were asked to carry out two sets of analyses on each sample, one using 400 mL and one using 100 mL. It was agreed that Harwell would perform two analyses, each on 50 mL aliquots of the samples, consistent with their standard analysis protocols. The results of these "blind" analyses, and also those from preliminary checks that each laboratory made on the spiking solution and in the preparation of its three urine batches, were forwarded to the last author (DC) for statistical analysis in which the codes were broken and the data collated.

Preparation of spiking and reference solutions

Two uranium reference solutions were specially prepared for this project by NIGL, namely natural uranium metal (CRM112a) whose assay and isotopic composition are well established (U.S. DOE 2002), and DU metal supplied by Goodfellow Industries (Cambridge, UK). An appropriate quantity of each was obtained, cleaned in ultrapure water and HNO_3 and dried in clean air conditions. Metals were precisely weighed, dissolved in ultrapure HNO_3 and brought up to a specifically known mass, allowing a calculation of the gravimetric concentration of U in the solution, taking into account the

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purity of the assay, if known (i.e., for CRM112a). Dilution was intended to result in a target concentration of 500 pg g^{-1} for the diluted DU solution, termed DU-D, and 10 ng g^{-1} for the natural U solution, termed NU-C. A high purity ^{233}U tracer (from National Physical Laboratory, Teddington, UK) was provided to NIGL by RHUL and its isotopic composition measured and its concentration re-determined by isotope dilution using the CRM112a solution as a reference. To calibrate the concentration and the purity of the assay of the Goodfellow DU solution, admixtures of the ^{233}U tracer and the DU solution were measured by mass spectrometry.

Methods of laboratory analysis

Harwell Scientifics: Sector Field (SF)-ICP-MS. Using standard procedures at the Harwell laboratory, the 500 mL samples were treated as a source of two duplicate, 50-mL samples. The remaining ~400 mL of solution was saved.

After addition of a ^{233}U spike, a phosphate precipitation step in non-acidified urine was carried out, centrifuged, and followed by two washing steps. The phosphate precipitate was then dissolved in nitric acid and deionized water and diluted back to the original volume (50 mL) ready for analysis. Semiconductor grade nitric acid and deionized water were used.

Table 1 lists the instrumental and chemical processing parameters for each of the three laboratories involved in this study. At Harwell, each sample was analyzed using a SF-ICP-MS operated with an ultrasonic nebulizer using a single-collector ion counting detector system, with rapid mass scanning. The concentration of uranium was calculated from the relative response of ^{233}U to ^{238}U, and compared to the response of ^{233}U spiked natural uranium standard with each batch of samples. Typical limits of detection in urine "as analyzed" for ^{235}U and ^{236}U were 0.1 pg L^{-1}. The limit of detection for ^{238}U was typically 5 pg L^{-1}. The total reagent blank was estimated as 5 pg or less for the 50 mL of urine used for analysis.

All isotope composition measurements were normalized relative to the measured $^{238}U/^{235}U$ of a natural uranium reference material (uranium metal EC101 from IRMM, Geel, Belgium), a procedure that also corrects for mass bias (typically 1–2% for the $^{238}U/^{235}U$ ratio), to achieve the natural isotope ratio for $^{238}U/^{235}U$ of 137.9 on standards.

Uncertainties in isotope composition measurement and uranium concentration were estimated from the long-term reproducibility of uranium measurements in synthetic and other urine solutions rather than from individual measurements, and may in low concentration samples be underestimated.

RHUL: Collision cell multicollector (MC)-ICP-MS. Uranium isotopic analysis of urine at RHUL was accomplished by evaporation and ashing of the supplied urine sample followed by chemical separation of uranium using Eichrom TRU resin (Eichrom Europe, Bruz, France). Reagents used were high purity sub-boiling

Table 1. Summary of instrument and chemical procedures parameters.

Laboratory	Harwell	RHUL	NIGL
Instrument	Plasma Trace2 SF-ICP-MS	Micromass Isoprobe MC-ICP-MS Collision cell	VG Elemental P54 MC-ICP-MS Double focusing
Nebulizer	CETAC ultrasonic	ESI PFA50	ESI PFA50
Spray chamber	CETAC desolvating membrane	Aridus desolvating spray chamber	Aridus desolvating spray chamber
Scan mode	E scan	Both magnet static and magnet mass switching	Magnet mass switching
Sensitivity for U	5,000,000 cs^{-1} ppb^{-1}	7,500,000 cs^{-1} ppb^{-1}	3,000,000 cs^{-1} ppb^{-1}
Sample uptake	1 mL min^{-1}	50 μL min^{-1}	50 μL min^{-1}
Number of scans	5 replicates × 10 sweeps	10–15	30
Dwell time per mass			
^{238}U	400 ms	Simultaneous to 235 and 236	12 s, simultaneous to 233, 235, & 236
^{235}U	2,000 ms	10 s	12 s, simultaneous to 238
^{236}U	2,000 ms	10 s	7 s, simultaneous to 233, 238
^{233}U	400 ms	Simultaneous to 235 and 236	12 s, simultaneous to 238
Mass resolution	300	400	400
Detector(s)	Ion counting electron multiplier	Ion counting Daly photomultiplier and multiple Faraday cups	Ion counting Daly photomultiplier and multiple Faraday cups

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distilled acids, prepared mainly in-house. Uranium solutions were analyzed on a single focusing MC-ICP-MS with Ar-gas collision cell, with instrumental parameters shown in Table 1.

For each 500-mL urine sample, ~400 mL and ~100 mL urine aliquots were prepared. The ~100 mL aliquot was the second aliquot taken from the sample bottle, and included a rinse of the sample bottle in concentrated HNO_3, which dissolved black particulate residues adhering to the bottle walls. This allowed investigation as to whether significant uranium was held in these particulate residues. Urine aliquots and ^{233}U spiked samples were weighed into quartz-glass beakers and evaporated. Preliminary ashing of urine samples and quartz-glass blanks was carried out on a ceramic hotplate in a fume cupboard at up to 500 °C. Final ashing to a white residue was initially carried out in a furnace at 450 °C for 8–12 h, but samples prepared later were instead treated to 2–3 repeat hotplate ashings interspersed by evaporation with 10–15 mL HNO_3, which appeared to be sufficient to destroy all organic material. Uranium was separated from the resultant solution using two passes through Eichrom TRU resin in disposable polypropylene ion exchange columns, collected into Teflon beakers. Uranium chemical recovery was >70% for samples ashed in the furnace but sometimes as low as 10% for samples ashed on the hotplate. Eluted uranium was converted to nitrate and dissolved in 2% HNO_3 for analysis. Isotopic measurements were made using both static multicollector with mixed ion counting and Faraday detectors, and in magnet switching multiple collection mode. Corrections were made to measured uranium intensities using similar methods to Seth et al. (2003), including a memory correction based on analysis of the 2% HNO_3 used to dissolve the samples.

The limit of detection on a Faraday cup is 83 fg g^{-1} of any uranium isotope in solution (determined by the noise on the Faraday amplifier), and for the Daly ion counting system 1.0 fg g^{-1} in solution, determined by the noise on the 10–50 counts s^{-1} organic memory observed at most high masses (Seth et al. 2003). Uncertainties in the reported isotope ratios were the result of propagating the counting statistics of peak and background measurements together with estimates of uncertainties in the mass bias and Daly gain correction. Errors in concentrations additionally included an estimate of weighing uncertainty. No attempt was made to correct for blank, or to incorporate blank correction uncertainty into the overall uncertainties because of low chemical recoveries. As a result, some of the uncertainties reported may be slightly to somewhat underestimated.

NIGL: Double-focusing multicollector (MC)-ICP-MS. The 400-mL and 100-mL aliquots of samples were acidified and spiked with a ^{233}U tracer. Reagents were purified in-house and supplemented by commercial reagents (Romil Ltd, Cambridge, UK). For 400-mL samples, uranium was co-precipitated with calcium phosphate whereas for 100 mL samples the total urine sample was evaporated to dryness. Dried residues were ashed using concentrated HNO_3 and 30% H_2O_2 on a hotplate with temperatures up to ~170 °C, until nearly white in color. The remaining U-bearing salts were dissolved in 3M HNO_3 and, using Eichrom UTEVA resin, were separated and purified by ion exchange chromatography, and converted to 2% HNO_3 for mass spectrometry. The recovery of uranium from this procedure was mainly 80–100%. Multiple blanks on the two procedures showed a total range from 13–59 pg, and the blank corrections applied to the data were 16 ± 5 pg for co-precipitation and 42 ± 13 pg for evaporation.

Mass spectrometry utilized a double focusing MC-ICP-MS equipped with multiple Faraday cups and an axial ion counting Daly photomultiplier detector set behind the Faraday cup array beyond a 30 cm electrostatic analyzer (ESA), in magnet switching multiple detector mode. 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 ^{236}U and ^{235}U in the ion counting system with other peaks measured in Faraday cups.

Uncertainties for final ratios were propagated by quadratic weighted additions of all relevant sources of uncertainty, including uncertainty in the blank. The limits of detection in the measured solutions were estimated as 0.2 ppt for ^{238}U, 0.01 ppt for ^{235}U, and 0.002 ppt for ^{236}U, these being constrained by blank corrections and detector noise.

Predicted values of spiked samples

In attempting to spike solutions to reach the specified "target" values, the three laboratories used their measured urine batch concentrations and the concentration and isotopic composition of the DU-D solution. The best estimate of the composition and concentration of the spiked urines can be calculated using the most precise measurements for the unspiked concentrations of each three unspiked urines and the mass of DU-D added to each. These calculations are outlined in the Appendix, and the predicted values are listed in relevant tables. Harwell did not report predicted values.

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RESULTS

Table 2 reports the measurements on the DU-D solution used for spiking the urine batches, with a range from ~460–670 ppt. Harwell only provided limited data on these reference solutions. The differences in measured concentrations of aliquots of DU-D solutions were unexpected. Harwell values are lower than NIGL by an amount similar to other comparable concentration measurements and suggest a bias, further mentioned below. The higher value at RHUL appears to result from either unintended evaporation or heterogeneity in the DU-D solution; its concentration was carefully measured using other standards prior to spiking so that analyses on urine samples are directly comparable.

Table 3 reports the measured concentrations of uranium for the three unspiked batches of urine, with the pre-distribution values being a mean of 2 or 3 measurements. Uranium concentrations reported by RHUL are systematically higher in the 100 mL aliquots compared with the 400 mL aliquots, sometimes by a factor of >2. This is true also for RHUL data for the spiked urine samples discussed later. Our preferred explanation is that higher uranium contents in the 100 mL fractions are due to the dissolution of the particulate organic material in the HNO_3 rinse of the bottle that was incorporated into the 100 mL fraction. If so, the true uranium concentration of the urine sample may be calculated from the total uranium mass in both fractions divided by the total mass of urine: this is reported as "total conc." in Tables 3 and 5. This total uranium content agrees to within ~3% or better with the predicted uranium contents of the spiked samples, and with NIGL measurements that in themselves agree to within ~3% (e.g., samples F and H). This suggests that in some samples a significant fraction of uranium was incorporated into particulate organics that adhered to the sample container walls. The values from Harwell on 50 mL urine aliquots are internally consistent but on average about 10% lower than the other two laboratories, a similar discrepancy as that measured for the uranium concentration of the DU-D solution relative to that at NIGL (Table 2), possibly the result of a systematic bias at Harwell or other unknown factors.

Table 3. Uranium concentration in unspiked urine samples.[ab]

Solution	NIGL (pg g^{-1})	Harwell (pg g^{-1})	RHUL (pg g^{-1})
A			
– pre-distribution	1.57 (24–42%)	—	—
– 400 mL	1.51 (92%)	1.4	1.52 (11%)
– 100 mL	1.42 (88%)	1.3	1.74 (27%)
			total conc. = 1.57
F			
– pre-distribution	—	1.1	—
– 400 mL	1.33 (58%)	1.2	0.99 (6%)
– 100 mL	1.31 (65%)	1.2	2.16 (13%)
			total conc. = 1.26
X			
– pre-distribution	—	—	5.10 (66%) $n = 1$
– 400 mL	5.11 (100%)	4.8	5.08 (89%)
– 100 mL	4.96 (94%)	4.5	5.33 (10%)
			total conc. = 5.14

[a] Batch mean concentrations (excluding the one unsatisfactory measurement) were: A, 1.49 pg g^{-1}; F, 1.18 pg g^{-1}; X, 5.01 pg g^{-1}. % values in brackets for RHUL and NIGL data represent % uranium recovery from the column procedure; Harwell recoveries not provided. Harwell measurements were made on 50 mL aliquots of urine instead of 100 mL or 400 mL. Densities of urine were assumed to be 1.0.

[b] NB 100 mL analyses at RHUL included a rinse of remaining solid residue in the bottle with sub-boiled HNO_3: dissolution of this residue best explains the higher concentrations in the 100 mL fractions. "Total conc" = total pg uranium determined in both fractions divided by total mass of the two fractions.

Table 2. Analysis of spiking solution (DU-D) and CRM112a (NU-C).[a]

Parameter	NIGL	Harwell	RHUL
DU-D spiking solution			
Uranium concentration (pg g^{-1})	502 ± 0.046% ($n = 3$)	462 (uncertainties not provided)	661.82 ± 0.4% ($n = 2$) ^{233}U
			670.3 ± 0.4% ($n = 1$) ^{236}U
$^{238}U/^{235}U$ atomic ratio	286.39 ± 0.132% ($n = 6$)	291.6 ± 3.0%	286.76 ± 0.047% ($n = 2$) DS
			286.76 ± 0.16% ($n = 6$) F,ext
			288.8 ± 0.6% ($n = 2$) D,ext
$^{236}U/^{238}U$ atomic ratio	0.0001771 ± 0.46% ($n = 6$)	Not analyzed	0.000176 ± 2.6% ($n = 1$) D
			0.000177 ± 8% ($n = 4$) F
$^{234}U/^{238}U$ atomic ratio	0.0000232 ± 0.64% ($n = 6$)	Not analyzed	0.0000231 ± 2% ($n = 3$) D
CRM112a solution NU-C			
Uranium concentration (pg g^{-1})	9924 (gravimetric)	Not analyzed	10110 ± 0.4% ($n = 1$) ^{233}U
$^{238}U/^{235}U$ atomic ratio	137.95 ± 0.24% ($n = 6$)	Not analyzed	138.08 ± 0.16% ($n = 1$) F,ext
$^{236}U/^{238}U$ atomic ratio	$<4 \times 10^{-8}$	Not analyzed	<0.00000008 ($n = 10$) D
			<0.000008 ($n = 1$) F
$^{234}U/^{238}U$ atomic ratio	0.0000532 ± 3.0% ($n = 3$)	Not analyzed	Not analyzed

[a] The figures in parentheses are the number of analyses. Uncertainties on Royal Holloway data are observed 2 sd of the population for >1 analysis, or propagated 2 se of a single analysis, whichever is worst. D and F signify minor isotope measurement on the Daly electron multiplier or Faraday cup, respectively, DS signifies mass bias correction using a ^{233}U-^{236}U double spike, ext signifies external mass bias correction using bracketing standards. Concentrations were determined either using a ^{233}U or a ^{236}U spike as indicated.

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There was no indication that the blind measurements made after the urine samples had been distributed differed systematically from those made before distribution (in spite of several weeks storage), or that the 400 mL samples provided markedly more reliable measurements than the 100 mL samples (apart from the RHUL caveat above).

Table 4 and Fig. 1 report measured $^{238}U/^{235}U$ atomic ratios in the unspiked batches of urine. Excluding one poor measurement, values ranged from 134.5 to 140.4, with a weighted mean of 137.85 ± 0.34 [2 standard error (SE) weighted mean, $n = 20$], consistent with the natural uranium value. Six analyses fell outside of the natural value within the errors reported, suggesting that uncertainties may have been somewhat underestimated by all laboratories.

Table 5 shows the uranium concentrations measured in spiked samples of urine. Taking the total concentration as measured by pooling the two RHUL measurements, RHUL and NIGL values agree within ~4%, but Harwell values are 9.3 ± 3.3% lower than the mean of NIGL and RHUL measurements. The systematically slightly higher total concentrations measured at RHUL are broadly consistent with the 1.9% higher concentration reported at RHUL for NU-C (Table 2) combined with the fact that RHUL data are not blank-corrected. The differences in concentration between the 100 mL and 400 mL aliquots at RHUL suggest that it may not be easy to reproduce routinely the concentration of uranium in urine by measurement of single aliquots. Agreement to ~2–3% for uranium in urine may be the best reproducibility that can be routinely achieved.

Table 6 presents the measured $^{238}U/^{235}U$ atomic ratios in spiked urine samples. For batch C (spiked with DU-D at NIGL), the predicted ratio and all of the measured ratios, including that obtained before samples were coded and distributed, were higher than the target, a result of adding too much DU-D spike on the basis of a lower quality measurement of unspiked urine uranium concentration. Otherwise, ratios were very close to the target and the "predicted" values. All but one of the NIGL and RHUL results are within ~1% of the batch means for these two laboratories combined, though it is clear that some of the measurements lie outside of agreement at the 95% confidence level, suggesting again a modest underestimation of uncertainty in some analyses. Harwell results showed a wider scatter, with results for a single batch of urine varying by up to 2.5% from the laboratory mean for that batch. When compared with the batch means for NIGL and RHUL combined, 9 of the 14 measurements made by Harwell differed by more than 1%, and six by more than 2%, with the best agreement for those urines having highest uranium concentration (Y, Z).

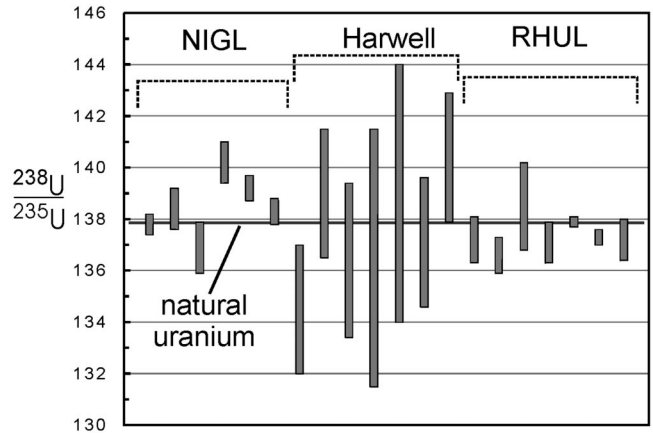

Fig. 1. $^{238}U/^{235}U$ of unspiked samples measured in this study with reported 95% uncertainties. The analyses of the three separate laboratories are identified. The value for natural uranium is indicated as the horizontal line.

Table 4. $^{238}U/^{235}U$ atomic ratio in unspiked urine samples.[a]

Solution	NIGL	Harwell	RHUL
A			
– pre-distribution	137.8 ± 0.4 ($n = 3$)	—	—
– 400 mL	138.4 ± 0.8	134.5 ± 2.5	137.2 ± 0.9
– 100 mL	136.8 ± 1.0	139.0 ± 2.5	136.6 ± 0.7
F			
– pre-distribution	—	136.4 ± 3.0	—
– 400 mL	140.2 ± 0.8	136.5 ± 5.0	138.5 ± 1.7
– 100 mL	[130.9][b]	139.0 ± 5.0	137.1 ± 0.8
X			
– pre-distribution	—	—	137.9 ± 0.2 ($n = 1$)
– 400 mL	139.2 ± 0.5	137.1 ± 2.5	137.3 ± 0.3
– 100 mL	138.3 ± 0.5	140.4 ± 2.5	137.2 ± 0.8
Mean ± 2 sd	138.5 ± 2.3	137.6 ± 4.0	137.4 ± 1.2

[a] Uncertainties are the 95% confidence intervals reported by each laboratory and are propagated 2 se for single analyses. Pre-distribution values are 2 se for 2 or 3 measurements.
[b] Measurement recognized to be unsatisfactory at the time it was made, excluded from the mean value.

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Table 5. Uranium concentration in spiked urine samples.[a]

Solution	Predicted[b]	NIGL (pg g^{-1})	Harwell (pg g^{-1})	RHUL (pg g^{-1})
B				
– pre-distribution	1.67	1.61 (n = 3, 43–64%)	—	—
– 400 mL		1.63 (100%)	1.4	1.59 (17%)
– 100 mL		1.49 (100%)	1.4	1.73 (34%)
				total conc. = 1.62
C				
– pre-distribution	1.92	1.93 (52–78%)	—	—
– 400 mL		1.83 (100%)	1.6	1.96 (16%)
– 100 mL		1.76 (83%)	1.7	2.10 (59%)
				total conc. = 1.99
G				
– pre-distribution	N/A	—	1.3	—
– 400 mL		1.27 (72%)	1.2	1.22 (4%)
– 100 mL		1.23 (55%)	1.2	1.60 (10%)
				total conc. = 1.31
H				
– pre-distribution	N/A	—	2.2	—
– 400 mL		2.14 (100%)	2.1	1.85 (12%)
– 100 mL		2.14 (100%)	2.1	3.18 (11%)
				total conc. = 2.17
Y				
– pre-distribution	5.555	—	—	5.65 ± 0.03 (n = 3, 44–90%)
– 400 mL		5.25 (3%)	5.0	5.58 (120%)
– 100 mL		5.38 (100%)	4.9	5.68 (18%)
				total conc. = 5.60
Z				
– pre-distribution	6.032	—	—	6.10 ± 0.02 (n = 2, 57–85%)
– 400 mL		5.93 (100%)	5.4	6.04 (114%)
– 100 mL		5.81 (78%)	5.5	6.23 (7%)
				total conc. = 6.09

[a] Percent values in brackets for RHUL and NIGL data represent % uranium recovery from the procedure. NB 100 mL analyses at RH included a rinse of remaining solid residue in the bottle with sub-boiled HNO_3: dissolution of this residue is the probable cause of the higher concentrations in the 100 mL fractions (see text). "Total conc" in RHUL data = total pg uranium determined in both fractions divided by total mass of the two fractions.
[b] Predicted based on masses of unspiked urine and DU-D used and their concentrations using pre-distribution figures.

Table 6. $^{238}U/^{235}U$ atomic ratio in spiked urine samples.[a]

Solution	Predicted[b]	NIGL	Harwell	RHUL
B (target ratio 140)	141.5			
– pre-distribution		141.1 ± 1.2 (n = 3)	—	—
– 400 mL		140.6 ± 0.5	147.3 ± 2.5	140.1 ± 0.7
– 100 mL		139.1 ± 0.6	144.7 ± 2.5	139.0 ± 0.7
C (target ratio 146)	151.0			
– pre-distribution		154.2 ± 2.1 (n = 3)	—	—
– 400 mL		151.4 ± 0.9	157.9 ± 2.5	154.2 ± 0.6
– 100 mL		151.7 ± 2.4	154.0 ± 2.5	153.8 ± 0.5
G (target ratio 142)	not provided			
– pre-distribution		—	141.9 ± 0.8	—
– 400 mL		139.9 ± 0.8	138.8 ± 5.0	139.8 ± 1.3
– 100 mL		139.4 ± 1.1	144.7 ± 5.0	138.5 ± 1.1
H (target ratio 180)	not provided			
– pre-distribution		—	178.2 ± 2.0	—
– 400 mL		180.6 ± 1.2	171.4 ± 2.5	179.6 ± 1.2
– 100 mL		182.3 ± 7.1	172.0 ± 2.5	174.2 ± 1.7
Y (target ratio 144)	144.0			
– pre-distribution		—	—	143.8 ± 0.2 (n = 3)
– 400 mL		[140.1][c]	145.6 ± 2.5	144.4 ± 0.3
– 100 mL		145.0 ± 0.6	144.1 ± 2.5	143.6 ± 0.6
Z (target ratio 150)	150.0			
– pre-distribution		—	—	150.3 ± 0.2 (n = 2)
– 400 mL		151.2 ± 0.5	153.3 ± 2.5	149.5 ± 0.3
– 100 mL		151.7 ± 1.0	150.9 ± 2.5	149.7 ± 0.6

[a] Uncertainties quoted are propagated 2 se for single analyses, or 2 sd for replicate analyses if worse.
[b] Predicted based on masses of unspiked urine and DU-D used.
[c] Measurement recognized to be unsatisfactory at the time it was made.

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Table 7. Comparison of observed and predicted uranium concentrations in spiked urine samples.

	NIGL (pg g^{-1})			Harwell (pg g^{-1})			RHUL (pg g^{-1})		
Solution	Observed[a]	Predicted[b]	Difference %[c]	Observed[a]	Predicted[b]	Difference %[c]	Observed[a]	Predicted[b]	Difference %[c]
B	1.55	1.53	1	1.40	1.67	19	1.62	1.52	7
C	1.80	1.80	0	1.65	1.92	16	1.99	1.86	7
G	1.24	1.21	2	1.20	1.25	4	1.31	1.20	9
H	2.14	2.19	2	2.10	1.90	11	2.17	2.13	2
Y	5.32	5.53	4	4.95	5.51	11	5.60	5.45	3
Z	5.87	6.04	3	5.45	6.10	12	6.09	5.89	3

[a] Mean of blinded measurements on batch excluding those recognized to be unsatisfactory at the time they were made; for RHUL these are the combined total conc. values listed in Table 5.
[b] Predicted from the mean estimate by the laboratory for the isotope ratio of the batch, the mean estimate from all laboratories combined for the uranium concentration in the unspiked urine from which the batch was derived, and values of 502 pg g^{-1} and 286.6 for the uranium concentration and isotope ratio of the spiking solution (see text).
[c] Difference between observed and expected expressed as a percentage of predicted.

Table 8. $^{236}U/^{238}U$ ratio in unspiked and spiked urine samples.

Solution	Predicted[a]	NIGL ($\times 10^{-6}$)[b]	Harwell ($\times 10^{-6}$)	RHUL ($\times 10^{-6}$)
A	0.00			
– pre-distribution		2.5 ± 0.7	—	—
– 400 mL		1.1 ± 0.2	<5	[41 ± 3][c]
– 100 mL		<0.5	<5	[49 ± 5][c]
B	9.2			
– pre-distribution		11 ± 1	—	—
– 400 mL		8.7 ± 0.6	<5	[198 ± 6][c]
– 100 mL		10 ± 1	<5	[1425 ± 10][c]
C	31.7			
– pre-distribution		36 ± 6	—	—
– 400 mL		33 ± 1	23	[42 ± 2][c]
– 100 mL		35 ± 2	25	[364 ± 5][c]
F	0.00			
– pre-distribution		—	<5	—
– 400 mL		1.3 ± 0.2	<5	[15 ± 9][c]
– 100 mL		<0.5	<5	[154 ± 8][c]
G				
– pre-distribution		—	<5	—
– 400 mL		0.4 ± 0.3	<5	[50 ± 7][c]
– 100 mL		<0.5	[37][c]	[307 ± 14][c]
H				
– pre-distribution		—	53	—
– 400 mL		77 ± 3	73	[609 ± 12][c]
– 100 mL		82 ± 2	69	[3762 ± 31][c]
X	0.00			
– pre-distribution		—	—	0.3 ± 0.8
– 400 mL		<0.1	<5	0.2 ± 0.1
– 100 mL		<0.5	<5	[279 ± 11][c]
Y	14.6			
– pre-distribution		—	—	14.8 ± 0.5 $n = 1$
– 400 mL		—	15	14.3 ± 0.2
– 100 mL		13 ± 1	5	[110 ± 3][c]
Z	27.6			
– pre-distribution		—	—	28.3 ± 0.5 $n = 2$
– 400 mL		26 ± 1	28	26.6 ± 0.4
– 100 mL		28 ± 1	49	[410 ± 9][c]

[a] Predicted based on masses of unspiked urine and DU-D used.
[b] No subtraction for blank count rate has been made on 236 mass at NIGL.
[c] Measurement recognized to be unsatisfactory at the time it was made. Uncertainties quoted are propagated 2 se for single analyses, or 2 sd for replicate analyses if worse. Uncertainties for Harwell data were not provided.

Table 7 compares the mean uranium concentrations for spiked urine with the predicted concentrations. The observed and predicted concentrations for NIGL agreed to within 4% (mean 1.8%), at Harwell the agreement was between 4% and 19% (mean 12%), while at RHUL the level of agreement was 2–9% (mean 6%). The systematically higher values at RHUL are largely a function of the higher uranium content of the DU-D solution used at RHUL than the 502 ng L^{-1} assumed in Table 7.

Table 8 shows measured $^{236}U/^{238}U$ ratio in unspiked

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and spiked samples in comparison with predicted values. With few exceptions Harwell was unable to measure accurately or precisely the $^{236}U/^{238}U$ ratio. The best data derives from NIGL and selected RHUL analyses.

For RHUL, in spite of some low ^{238}U signal intensities in the blind analyses, ^{236}U intensities were well in excess of the 10 to 16 counts s^{-1} background at this mass, and often greater than ^{236}U intensities in DU-spiked samples pre-distribution. Although cross-contamination from previous ^{236}U spiked samples is a possibility, it is more likely that the poor chemical recovery and inadequate ashing have led to residual sample organic moleculars at mass 236 well in excess of background plus uranium counts. This is a potential source of additional uncertainty that could lead to inaccuracy at very low count rates.

A comparison with the predicted values clearly demonstrates that it is possible to accurately measure $^{236}U/^{238}U$ ratios at low count rates, as portrayed in Fig. 2. In this plot any admixture of two isotopically distinct uranium reservoirs will fall on a straight line with end points at the two end member compositions.

DISCUSSION

In this study the three participating laboratories agreed well in their measurement of urinary $^{238}U/^{235}U$ ratios, although reported uncertainties appear modestly underestimated. The MC-ICP-MS techniques are predictably more precise than the SF-ICP-MS method.

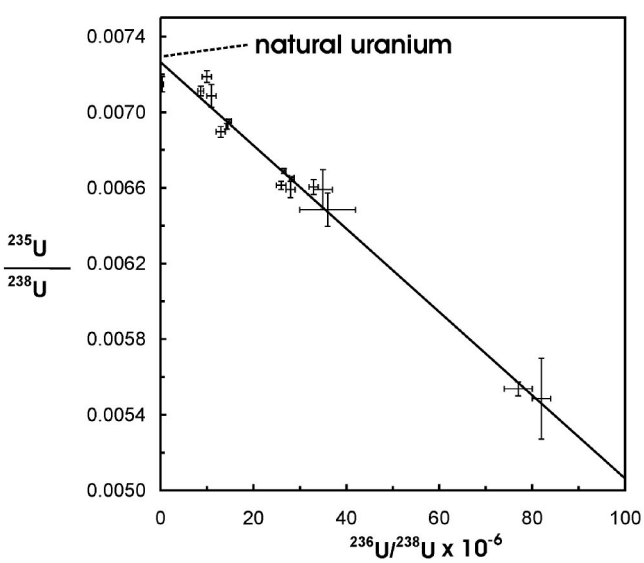

Fig. 2. Measured $^{236}U/^{238}U$ vs. $^{235}U/^{238}U$ in urine samples. Only data for which a laboratory achieved satisfactory measurement of both ratios and reported uncertainties, with the $^{236}U/^{238}U$ ratio above the limit of detection, are shown. The plotted data consist of 15 analyses from NIGL and 5 from RHUL, and while uncertainty estimates provided by the laboratories appear to be underestimated, the scatter about the theoretical mixing line demonstrates accuracy. The value of natural uranium corresponds to the Y-intercept of the mixing line.

Measurements at RHUL for uranium concentration suggest that U-containing particulates may adhere to walls of containers, consistent with the difference in uranium concentration of the 400-mL v. 100-mL aliquots. The implication is that with some chemical procedures, single measurements of an aliquot of urine may not faithfully reflect the uranium concentration of the sample. It is clear that the use of isotope dilution provides a means of more accurate and precise concentration measurements, and when high precision is needed, it is recommended that it be used.

When all of the concentration measurements are summarized (Table 7), the NIGL and RHUL data show good consistency and no apparent bias, whereas Harwell measurements suggest a 9.6 ± 1.4% bias on the low side. This could be a result of miscalibration of either a tracer or reference solution prior to or during the course of this study, or some other unrecognized methodological difference. The results from the 100-mL urine samples did not appear to be markedly less reliable than those from the 400-mL samples, though it is clear that mass spectrometric precision is enhanced with larger ion intensities.

The data suggest that all three of the analytical methods employed in this study are capable of measuring $^{238}U/^{235}U$ ratios to within ±4% in urine with a total uranium concentration as low as 1–5 ng L^{-1}, and most of the time to within ±2.5%. Moreover, with the multicollector techniques used by NIGL and RHUL, accuracy better than 1.5% (95% confidence) can be achieved with total uranium concentrations as low as 1 ng L^{-1}, and with as little as 100 mL of urine being processed, provided that uranium pre-concentration is utilized with low analytical blanks. This study shows that with appropriate techniques it is possible to identify the presence of DU in urine when the measured $^{238}U/^{235}U$ is as low as 141, a threshold that may decrease with further improvements in measurement. These procedures therefore permit an accurate and precise determination of the $^{238}U/^{235}U$ in urine for essentially the entire range of uranium concentrations in human urine.

Measurements of uranium concentration tended to be less reliable than measurements of $^{238}U/^{235}U$ ratio. The results presented in Tables 3 and 5 suggest that it is possible to measure consistently concentrations to ±4% or better using isotope dilution with a ^{233}U tracer. These levels of reproducibility are substantially lower than those that would be expected using the same techniques on aqueous samples, probably because of inherent particulates in urine.

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Our attempts to measure $^{236}U/^{238}U$ were generally successful with MC-ICP-MS methods. The highest sensitivity for ^{236}U measurement is obtained using uranium pre-concentration and MC-ICP-MS. Accurate and consistent results are demonstrated by the excellent inverse correlation between $^{236}U/^{238}U$ and $^{235}U/^{238}U$ as shown in Fig. 2, where the data fit the predicted mixing line between the DU-D spike and natural uranium. The collision cell MC-ICP-MS at RHUL encountered problems with organic interferences on mass 236 with some analyses, and the SF-ICP-MS method had insufficient sensitivity in their smaller urine aliquots. While the $^{236}U/^{238}U$ may not be as useful as the $^{238}U/^{235}U$ ratio when assessing historical exposures to DU, it may provide a useful check against rogue results, and may allow detection of DU sources of variable isotopic composition. It could also be helpful where there was suspicion that an individual had been exposed to enriched as well as depleted uranium.

This contribution is the first to present consistent measurements of $^{236}U/^{238}U$ and $^{238}U/^{235}U$ in human urine samples. The only other published study we are aware of is that of Durakovic et al. (2002), which while presenting $^{236}U/^{238}U$ data in addition to $^{238}U/^{235}U$ data, lacked replicates, had a number of samples with substantial ^{236}U but with natural $^{238}U/^{235}U$ signatures, and had no analysis of DU metal shrapnel to assess comparable accuracy of these urine measurements.

Over the years the threshold for detection of uranium and other transuranic elements in urine has declined markedly (Epov et al. 2005; Schaumlöffel et al. 2005), and the ability to make precise and accurate determinations of the isotopic composition of uranium in urine has steadily improved (Krystek and Ritsema 2002; Westphal et al. 2004). Currently, quadrupole ICP-MS is the most common method, but accurate isotopic measurements are only possible with uranium concentrations exceeding 20 ng L^{-1} and even then the precision is ~10% or worse (Hooper et al. 1999; Becker et al. 2002; Ejnik et al. 2000). The use of uranium chemical separation and thermal ionization mass spectrometry may be capable of increased sensitivity but the only relevant recent study is that of Durakovic et al. (2002), and while it presented measurements of urine containing variable proportions of DU, many analyses were unsuccessful and it lacked replicates and rigorous assessment of uncertainties. More recently, SF-ICP-MS methods like those used by the Harwell laboratory in this study are increasingly being used and have better performance, particularly when uranium separation is used (Krystek and Ritsema 2002; Gwiadza et al. 2004; Pappas et al. 2003; Treŝl et al. 2004). Indeed, the Harwell data of this study compares favorably with these other SF-ICP-MS cited studies, even with its lack of uranium chemical separation.

A recent intercomparison of quadrupole ICP-MS, SF-ICP-MS, thermal ionization mass spectrometry (TIMS), and induced neutron activation analysis (INAA) was conducted by the Canadian government (D'Agostino et al. 2002) using a methodology not dissimilar to this study, but with synthetic urine having total uranium concentrations ranging from 25–770 ng L^{-1}, 5–700 times those presented in this paper. The Canadian study showed that both ICP-MS methods (quadrupole ICP-MS and SF-ICP-MS) were able to measure accurately both concentrations and isotopic ratios at these relatively high concentrations of uranium. However, the TIMS method reported inaccurate concentration and isotopic values in a number of samples, with significant underestimation of internal uncertainties. The European Commission is currently conducting interlaboratory tests on uranium isotopes in simulated urine with ~100 ng of contained uranium as part of its Nuclear Signatures Interlaboratory Measurement Evaluation Program (www.irmm.jrc.be/imep/nusimep.html), but it has yet to undertake a study using human urine with "normal" uranium concentrations (<10 ng L^{-1}). On the basis of this study, such a study on low-concentration urine is feasible but will be challenging for many instrumental methodologies.

CONCLUSION

There is as yet no published account of the use of chemical separation of uranium from urine combined with MC-ICP-MS instruments. The data presented in this study show clearly that MC-ICP-MS methods are superior to all of these other methods in that they reproduce concentrations reliably to better than ±5%, $^{238}U/^{235}U$ to better than ±1.5%, and in the case of the NIGL procedure, successful measurement of the low abundance ^{236}U isotope with accurate $^{236}U/^{238}U$. Very significantly, this has been accomplished on samples containing between 0.16–2.4 ng uranium extracted from urine with 1.6–6.0 ng L^{-1} uranium. These results show that with chemical separation combined with MC-ICP-MS techniques, high precision measurement of uranium is feasible with any sample of human urine, even in the low-uranium abundance end of the concentration spectrum.

Relevance to determination of DU exposure

It has been estimated that inhalation of 10 mg of DU together with an ingested dose of 5 mg would lead to an excess lifetime risk of fatal cancer less than 3 per 100,000 (Royal Society 2001). Using biokinetic models (i.e., WHO 2001; Royal Society 2001) and estimates of solubility of uranium oxide and other specific parameters, an inhaled dose of 10 mg of DU might be expected

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to cause additional urinary excretion of uranium (above background levels) of >0.3 ng per day 10–15 years after inhalation. Against a background excretion of natural uranium of 10 ng per day, and assuming a $^{238}U/^{235}U$ ratio of 350 for DU, this would produce a $^{238}U/^{235}U$ ratio in urine of approximately 144. Our study suggests that the analytical techniques used by NIGL, RHUL, and to a lesser degree of confidence Harwell, are all sufficiently sensitive to detect a perturbation of the isotope ratio at this level, and as such can be applied to the testing of individuals to assess past DU exposure.

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APPENDIX

Derivation of expected uranium concentrations in spiked urine samples

Define variables as follows:

C_U = total uranium concentration of unspiked urine;
C_D = total uranium concentration of spiking solution (= 502 ng L^{-1});
C_S = total uranium concentration of spiked urine;
R_U = $^{238}U/^{235}U$ isotope ratio of unspiked urine (= 137.9);
R_D = $^{238}U/^{235}U$ isotope ratio of spiking solution (= 286.6);
R_S = $^{238}U/^{235}U$ isotope ratio of spiked urine; and
V = volume of spiking solution per liter of unspiked urine.

$$C_S = \frac{C_U + VC_D}{1 + V} \tag{A1}$$

and to a close approximation

$$R_S = \frac{C_U + VC_D}{C_U/R_U + VC_D/R_D} = \frac{R_U R_D (C_U + VC_D)}{R_D C_U + VR_U C_D}$$

$$\rightarrow R_S R_D C_U + VR_S R_U C_D = R_U R_D C_U + VR_U R_D C_D$$

$$\rightarrow V = \frac{(R_U R_D - R_S R_D) C_U}{(R_S R_U - R_U R_D) C_D}.$$

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Thus, substituting for V in (A1)

$$C_S = \frac{\left[C_U + \frac{(R_U R_D - R_S R_D) C_U}{(R_S R_U - R_U R_D)} \right]}{\left[1 + \frac{(R_U R_D - R_S R_D) C_U}{(R_S R_U - R_U R_D) C_D} \right]}$$

$$= \frac{C_U C_D (R_S R_U - R_U R_D + R_U R_D - R_S R_D)}{(R_S R_U C_D - R_U R_D C_D + R_U R_D C_U - R_S R_D C_U)}$$

$$= \frac{C_U C_D R_S (R_U - R_D)}{(R_S R_U C_D - R_U R_D C_D + R_U R_D C_U - R_S R_D C_U)}.$$

■■

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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 ^{235}U isotope relative to natural uranium; EU, enriched uranium, enriched in the ^{235}U 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 Industies, 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

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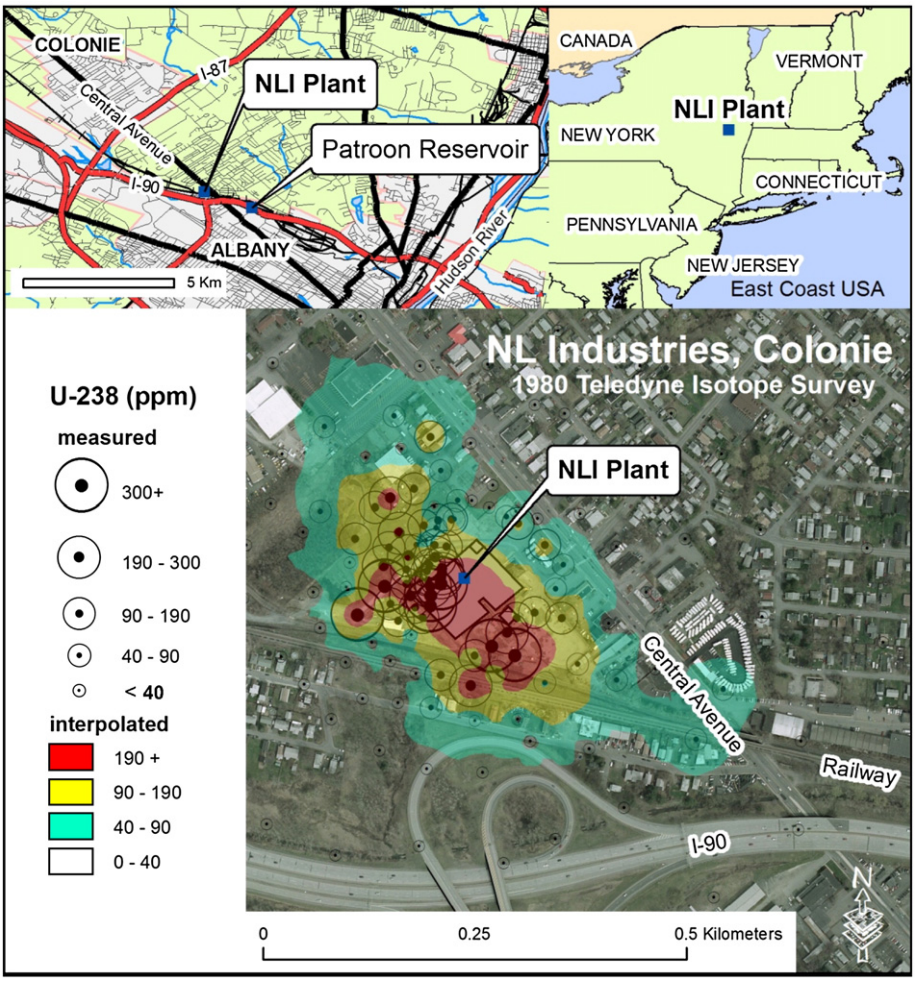

Fig. 1 – Map of the Colonie New York area (in Albany County) showing location, and detailed pattern within the city of the uranium pollution plume from the NLI plant, superimposed upon an aerial view of Colonie. The data used are from the Jeter and Eagleson (1980) study. The figure also uses mapping 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 ≥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

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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 kg of ^{238}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}U/^{235}U isotope signatures using ThermoElemental Excell quadrupole ICP-MS at the British Geological Survey. All data

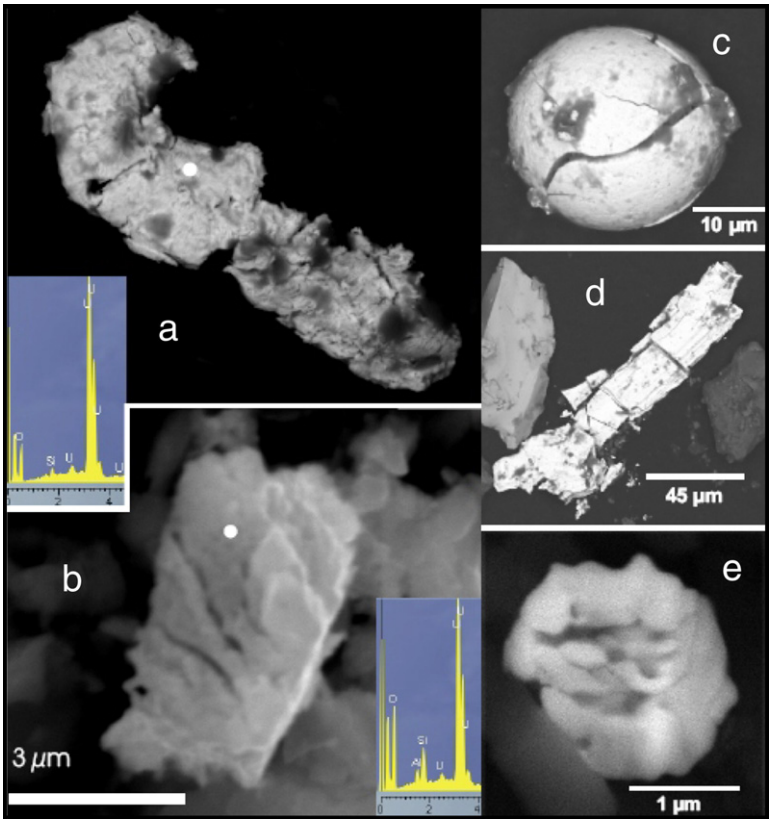

Fig. 2 – Scanning electron photomicrographs of uranium oxide particles from dust samples from residential locations within 400 m of the NLI site illustrating the variety and sizes observed; a,b: energy dispersive X-ray spectrometry (scale in keV) has identified only U, O, and minor Si in the particles (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.

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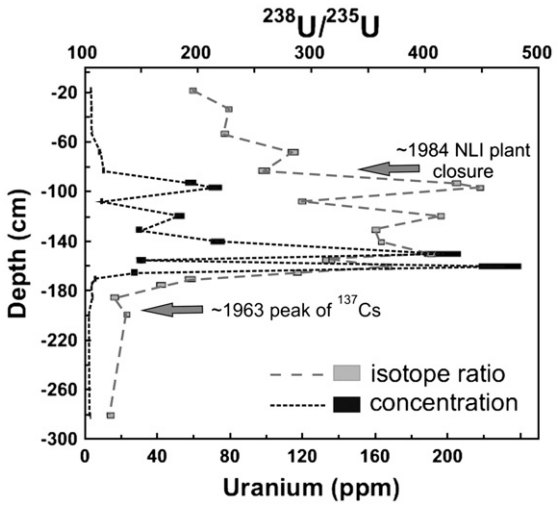

Fig. 3 – Plot of depth (cm) against both U concentration (ppm) and $^{238}U/^{235}U$ of the lake sediments. The peak of ^{137}Cs is shown as a time line approximately 1963, and the rapid decline of U concentration at ~ 90 cm is inferred to coincide with the closure of the plant in ~ 1984. The dip in 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 $Ca(NO_3)_2$ and $NH_4(PO_4)\cdot 4H_20$ 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	$^{238}U/^{235}U$	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

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Purified uranium extracted from urine and dissolved in ~1 ml of 2% high purity HNO_3 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 ^{234}U, ^{235}U and ^{236}U in the ion counting system with other peaks measured in Faraday cups. The measurement of ^{235}U 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 $^{238}U/^{235}U$ 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)	$^{234}U/^{238}U$	2 SD%	$^{235}U/^{238}U$	2 SD%	$^{236}U/^{238}U$	2 SD%	$^{238}U/^{235}U$	2 SD%
Drinking water samples of selected residents										
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
NLI plant workers										
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
Residents and other worker										
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
Internal standard (urine)										
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.

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5. Results

5.1. Nature of primary aerosols

By subjecting accumulated dry household dusts (with up to ~300 μg g^{-1}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 <1–40 μm diameter. These cross both the respirable particle size range (<10 μm) and the 'hand to mouth' contact ingestible size range (<250 μm). 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 $^{238}U/^{235}U$ 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 $^{238}U/^{235}U$, $^{235}U/^{238}U$, $^{234}U/^{238}U$, and $^{236}U/^{238}U$ being 137.88, 0.0072527, 0.00003–0.0002, and $<10^{-10}$, respectively, with only the $^{234}U/^{238}U$ having any natural variability. Enriched uranium has $^{238}U/^{235}U$ 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 $^{238}U/^{235}U$ is 139.0 or larger, we are confident the sample is DU-positive, this assessment being based upon approximately 400 urininary uranium measurements of DU-negative samples as part of a related large study (DUOB, 2007). Similarly, when $^{236}U/^{238}U$ 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 $^{238}U/^{235}U$ 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 $^{238}U/^{235}U$ 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 64–122 ng L^{-1}, much higher than the range of residents' urine (0.9–5.4 ng L^{-1}, summarised below), which is a finding consistent with uranium contamination as the dominant contribution to

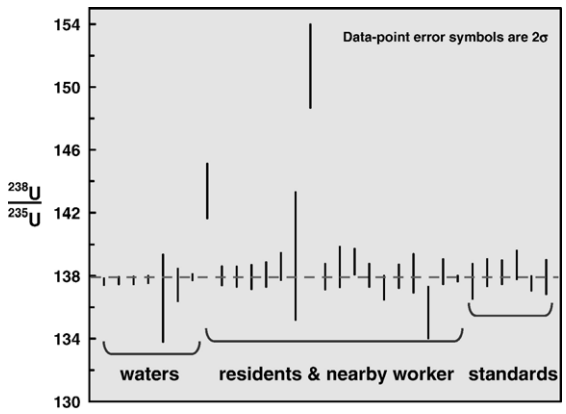

Fig. 4 – Plot of $^{238}U/^{235}U$ of drinking water and resident urine samples and 'standard urine samples' measured in this study, omitting those from factory workers that are off the scale of the diagram (see Table 2). The 'standards' refer to repeat measurements of an internal urine sample known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

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

The values of $^{236}U/^{238}U$ for four of the five workers range from 2.5–3.3 × 10^{-5} and are close to the measured composition of DU penetrators as shown by analyses of DU shrapnel ($^{238}U/^{235}U$ and $^{236}U/^{238}U$ of DU of ~500 and 2.5–3.0 × 10^{-5}, respectively, McLaughlin et al., 2003; Trueman et al., 2004). On the $^{236}U/^{238}U$ vs. $^{235}U/^{238}U$ 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 $^{238}U/^{235}U$ 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 $^{238}U/^{235}U$ 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

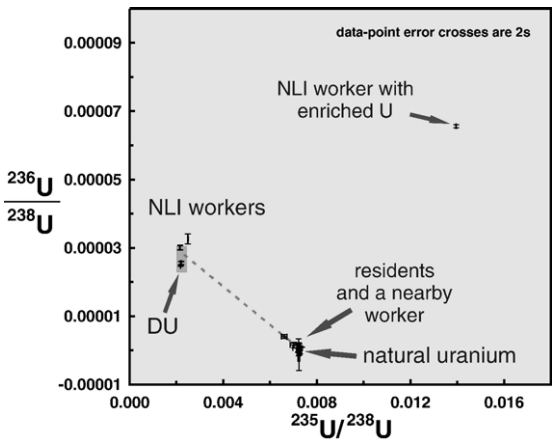

Fig. 5 – Plot of $^{235}U/^{238}U$ vs. $^{236}U/^{238}U$ of tested individuals. The end member composition of DU and the mixing line between natural uranium and DU is shown. Any mixture of two distinct compositions will define a straight line on this plot. Natural uranium contains no ^{236}U and plots 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 $^{236}U/^{238}U$ of 1.5–4.0 × 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 0.02–0.05 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 ~1–12% 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

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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 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

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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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Precise and accurate isotopic analysis of microscopic uranium-oxide grains using LA-MC-ICP-MS†

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Uranium isotope (^{235}U, ^{236}U, ^{238}U) ratios were determined for microscopic uranium-oxide grains using laser-ablation multi-collector inductively-coupled-plasma mass-spectrometry (LA-MC-ICP-MS). The grains were retrieved from contaminated soil and dust samples. The analytical technique utilised is rapid, requires minimal sample preparation, and is well suited for nuclear forensic applications. Precision and accuracy were assessed by replicate analyses of natural uraninite grains: relative uncertainty for ^{235}U/^{238}U is 0.2% (2σ), and the mean is in agreement with the natural ratio. A total of 115 uranium-oxide grains were analysed from environmental samples (soils and dusts); all of these were depleted uranium (DU) from a factory that produced uranium articles. Knowledge of the range of isotope ratios from particles of this controversial contaminant has proven useful when interpreting isotope ratios from bulk samples. Variation of the measured isotope signatures reveals details of the history of uranium processing and emissions.

1. Introduction

Case-study

National Lead Industries (NLI) operated a plant in Colonie (NY, USA), from 1958–1984. The plant processed uranium metals (depleted uranium and some enriched uranium); manufacturing kinetic energy penetrators (munitions), counterweights and radiation shielding from depleted uranium (DU). Scrap metal was combusted in a furnace prior to disposal as uranium-oxide, and this resulted in emissions of uranium-oxide particulate to the environment (at times *via* an unfiltered chimney).[1] Contamination of the suburban environment surrounding NLI by depleted uranium is evident in air filters, surface soils, reservoir sediments, and the urine of former employees and some residents.[2–7]

It is desirable to know the isotope ratios of the contaminant uranium when assessing bulk samples that comprise both background natural uranium and anthropogenic uranium. Furthermore it is possible that the uranium feedstock(s) used at NLI varied in isotopic composition. DU particulates from air filters collected 15.6 km NNW of NLI in 1979 had variable isotopic composition.[2]

We hypothesise that bulk soil and dust samples aggregate particulates over several decades, and that individual primary uranium-oxide grains from these samples each record the isotopic composition emitted from NLI during a short interval of time.

The bulk environmental samples of interest are contaminated soils (silica-rich medium to fine grained mineral sands with organic matter) and wind-blown dusts, typically comprising up to 500 mg kg^{-1} anthropogenic uranium, as microscopic uranium-oxide particulate in a matrix of natural mineral grains (that comprise trace natural uranium, less than 2.2 mg kg^{-1}). The aim of this study is to analyse the isotopic composition(s) of a population of anthropogenic uranium-oxide grains on an individual particle basis.

Depleted uranium (DU)

DU is the by-product of nuclear enrichment, and is depleted in the fissile isotope ^{235}U, typically (2–3) × 10^{-3} ^{235}U/^{238}U.[8] The atom ratio, ^{235}U/^{238}U (or n^{235}U/n^{238}U), of natural uranium has a traditional consensus value 7.253 × 10^{-3} (1/137.88),[9,10] recently recommended as 7.257 × 10^{-3}.[11–13] However, there is evidence of natural isotopic fractionation c. ± 0.009 × 10^{-3} of this value,[14] and one known example (Oklo, Gabon) of sustained natural fission resulting in ^{235}U depletion.[15,16]

A useful fingerprint of anthropogenic contamination is the presence of ^{236}U, which naturally occurs at negligible abundances (in the order of ×10^{-11}–×10^{-10} ^{236}U/^{238}U[17,18]). In contrast, DU is typically contaminated by up to 3 × 10^{-5} ^{236}U/^{238}U from reprocessed uranium.[8] ‡

Fig. 1 shows a range of ^{236}U/^{238}U and ^{235}U/^{238}U ratios that have been reported in the literature for DU penetrators. There are

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‡ The source of ^{236}U contamination is from reprocessed uranium (neutron capture on ^{235}U in nuclear power or production reactors). Reprocessed uranium can comprise up to 0.5% ^{236}U,[26] typically 0.4–0.6% ^{236}U,[45] which when enriched would produce by-product DU in the order of a part per thousand ^{236}U, with ^{236}U concentrated in the enriched uranium. For DU with 3 × 10^{-5} ^{236}U, the source of ^{236}U is either cross-contamination *via* enrichment-plant machinery, or blending of virgin uranium with reprocessed uranium, on the order of a percent reprocessed uranium. Presumably the level of contamination depends on the nuclear enrichment facilities' history of handling reprocessed uranium. Civilian uranium reprocessing in the USA ceased in 1977,[45] therefore the abundance of ^{236}U in recently produced DU is likely to be lower.

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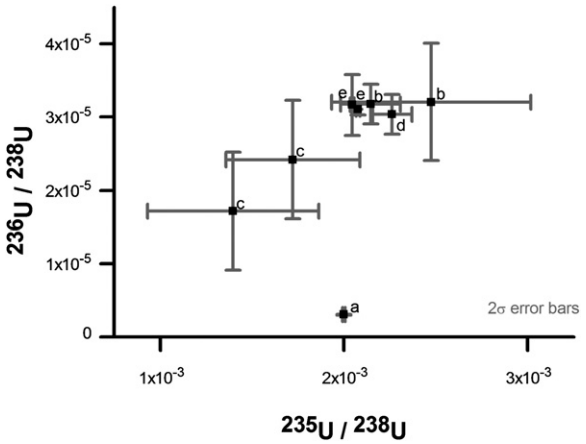

Fig. 1 Isotope ratios of DU penetrators reported in the literature. Measured by gamma-ray spectrometry: a) Trueman *et al.* (uncertainties from counting statistics only);[19] alpha spectrometry: b) McLaughlin *et al.*,[20] c) Pöllänen *et al.*,[21] d) Jia *et al.*;[22] ICP-MS: e) Desideri.[23]

ranges for both these ratios, but the data are scarce and it is not clear if this reflects a continuously variable range, or discrete batches of DU with distinct isotope signatures. Furthermore, it is possible that the isotopic compositions of other DU articles are not represented by these data.

Depleted uranium is also depleted in ^{234}U; literature values for DU munitions range (0.64–1.1) $\times$ 10^{-5} ^{234}U/^{238}U.[19–23] However, the abundance of this isotope is variable in nature (in the order of 10^{-4}–10^{-5} ^{234}U/^{238}U) due to alpha recoil effects, and ^{234}U/^{238}U is not a reliable measure of low-level anthropogenic contamination.[24,25]

Analytical methods

Radiometric methods of uranium isotopic analysis include alpha and gamma-ray spectrometry. Due to the long half-lives of the uranium isotopes, long counting times (days) are required for precise determination of the minor isotopes. Furthermore, alpha spectrometry requires laborious chemical separation of the analyte from its matrix.

The high-precision analysis of actinide bearing particles by a combination of fission track analysis and thermal ionisation mass spectrometry (FT- TIMS) was described by Dietz,[2] and is the traditional, but laborious method in nuclear forensics.[26] Fission-track analysis is first used to locate actinide-bearing particles for analysis by TIMS. It is also possible to estimate ^{235}U/^{238}U ratios directly by fission-track analysis.[27] Fission-track analysis is time consuming and requires access to neutron irradiation facilities. Digital autoradiography[28] or environmental scanning electron microscopy (SEM) are alternatives for particle location. A disadvantage of TIMS is the requirement for careful chemical separation of the analyte, which may be imperfect and result in poor ionisation and hence precision (risky with only a 'one-shot' analysis per particle).

Inductively-coupled-plasma mass-spectrometry (ICP-MS) offers faster analyses when compared to TIMS, and achieves good precision with multi-collector instruments (MC-ICP-MS). However, as for TIMS, particles of interest need to be manipulated and dissolved prior to analysis, and ideally the analyte is chemically separated from its matrix to avoid isobaric interferences. Hydride formation is also an issue when introducing solution samples, *e.g.* ^{235}U^{1}H on ^{236}U, but this can be minimised by the use of a desolvating nebuliser.

Secondary ion mass spectrometry (SIMS) has been used in the nuclear forensics context for the precise analysis of uranium and plutonium isotope ratios directly from particulates.[29–31] SIMS offers excellent spatial resolution, enabling particle location and sub-sampling.[32]

More recently laser ablation ICP-MS (LA-ICP-MS) has been used,[33–35] a method that also requires only minimal sample preparation. Varga[36] applied LA- sector-field single-collector ICP-MS (LA-SF-SC-ICP-MS) to non-environmental microscopic grains, demonstrating good agreement with solution SF-SC-ICP-MS, obtaining relative uncertainties (2σ) of c. 5% for ^{235}U/^{238}U.

Multi-collector (MC-) ICP-MS offers superior isotope ratio measurement precision to ICP-MS and SF-SC-ICP-MS, as the isotope signals are measured simultaneously and generally with higher sensitivity. This is especially important for laser ablation, which produces a variable and transient signal. Boulyga and Prohaska[37] used a lengthy screening procedure to identify six micro-samples from Chernobyl contaminated soils, for analysis by LA-MC-ICP-MS, obtaining relative uncertainties (2σ) of 2–3% for ^{235}U/^{238}U.

The major advantage of both SIMS and LA-ICP-MS is that particles of interest can be selectively sampled directly from solid materials, requiring only minimal sample preparation. However, in practice particles of interest may be very scarce in environmental samples. It is therefore desirable to concentrate these particles prior to analysis, and essential to locate them within the sample mount. The sampling volumes for both techniques are small, enabling replicate analyses of particles, or analysis by other methods.

The NERC Isotope Geosciences Laboratory (NIGL) are experienced users of LA-MC-ICP-MS for U-Pb dating of zircons (trace uranium decay series) from geological samples. We have 'borrowed' these sample preparation and analytical techniques for this novel application. To the best of our knowledge, this paper demonstrates for the first time, the application of high precision isotope ratio LA-MC-ICP-MS analysis to a large population of individual uranium-oxide grains from environmental samples.

2. Experimental

Sample preparation

Samples. A dust and a surface soil sample were collected from residential properties within 200 m of the former NLI site. Aliquots of these materials were analysed by scanning electron microscopy with an energy dispersive X-ray analyser (SEM-EDX: Hitachi S-3600N with Oxford Instruments Inca x-sight), revealing discrete uranium-oxide particles. Bulk uranium concentration and isotopic composition were estimated by quadrupole ICP-MS (VG Elemental PQ ExCell with Cetac Technologies Aridus II desolvating nebuliser) after total dissolution: for the soil 90 $\pm$ 9 mg kg^{-1} uranium, (2.1 $\pm$ 0.1) $\times$ 10^{-3} ^{235}U/^{238}U (2s); and for the dust 385 $\pm$ 33 mg kg^{-1} uranium, (2.2 $\pm$

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Table 1 Methodology for concentrating uranium-oxide grains from soil and dust sample, and fractions removed

process	criteria	fraction removed
dry	60 °C	moisture
sieve	<250 μm	coarse grains
hand-magnet	magnetic	magnetite, iron
dense-liquid (di-iodomethane)	ρ > 3.3 g cm^{-3}	silica and silicates, fine particulate
isodynamic magnetic separation (Frantz LB-1)	0.1–1A	iron-oxides, some zircons
sieve	40 μm	coarse and fine fractions

0.1) × 10^{-3} ^{235}U/^{238}U. These isotope ratios confirm that the vast majority of the uranium in these samples is from anthropogenic DU contamination.

Pre-concentration. The uranium-oxide particulates were concentrated from the bulk samples using the protocol summarized in Table 1. Dense-liquid (di-iodomethane, ρ 3.3 g cm^{-3}) was used to separate low-density silicates from the bulk samples, recovering dense grains including uranium-oxides (ρ 10.96 g cm^{-3}) greater than about 20 μm diameter.

Grain mounts. Aliquots of the concentrates were mounted in epoxy resin, ensuring separation of grains, and then ground and polished to reveal cross sections (alternatively, they could be adhered whole to the surface of a suitable mount). The mounts were scanned using SEM-EDX to map the uraniferous grains, see Fig. 2. Sample preparation and the grain mapping are moderately time consuming. However, the methodology does produce robust grain mounts with a good density of uraniferous grains, which can be quickly located using the laser ablation system's optical microscope.

Solutions. Solutions were prepared from uraniferous grains from these and two other soil dust samples collected from the vicinity of NLI, for comparison with the laser ablation dataset. Spherical grains that appeared metallic or glassy (anthropogenic in appearance) under an optical microscope were picked from the concentrates (under ethanol) using fine tweezers, and then transferred to a low-tack adhesive (*Glue Dots Repo* ™), as shown in Fig. 3. These mounts were scanned using SEM-EDX, but fewer than 1 in 40 proved to be uraniferous (the others were mostly lead, tin or lead glass).

SEM-EDX analyses show the uraniferous grains were typically comprised of only uranium and oxygen (elemental LLD c.

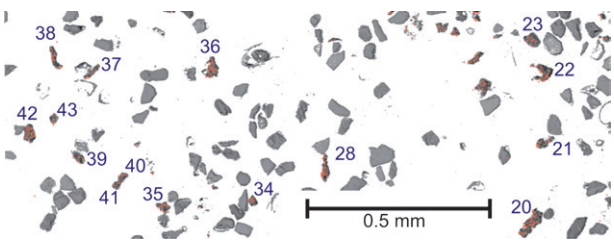

Fig. 2 SEM image of a grain mount surface, overlain by uranium EDX map (highlighting uraniferous grains). Uraniferous grain dimensions for this mount range 12 to 82 μm, mean 36 μm.

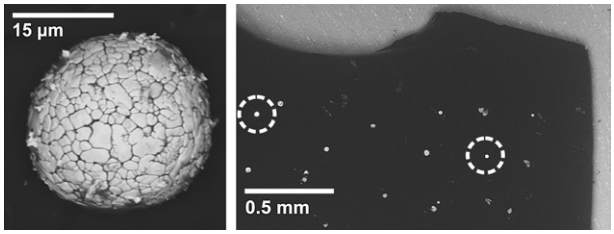

Fig. 3 SEM (uncoated sample, 20 Pa pressure, back scattered electron) image of a typical uranium-oxide sphere, picked from dust concentrate (left). SEM image of a temporary mount, particles with identifiable U Mα X-ray peaks from EDX analysis circled (right).

1%), for this reason, it was not considered necessary to chemically separate the uranium from these solutions. Subsequent analysis of similar grains shows that they are typically polycrystalline UO_2 (unpublished data), and they often include cavities.

Twenty-four uranium-oxide grains were successfully transferred by tweezers into individual pre-leached micro-centrifuge tubes, and then dissolved in ultrapure double-distilled concentrated nitric acid (within a class 100 clean room, typical digest blanks <100 fg U). This method of sample preparation is by comparison with the previous, relatively time-consuming.

Analysis

Mass spectrometry. Analysis was made using a double-focussing MC-ICP-MS instrument (VG Elemental Axiom), coupled with a desolvating nebuliser (Cetac Technologies Aridus) to reduce hydride interference from solutions. Following peak centring, low abundance ^{236}U was measured on a secondary electron multiplier, ^{235}U and ^{238}U on Faraday cups. Abundance sensitivity and mass bias were quantified at the start and end of each analytical run, using a natural uranium solution (U950a).

Solutions. The solutions were diluted in ultrapure 2% HNO_3 $_{(aq)}$ to approximately 25 ng g^{-1} uranium. The sample analyses were bracketed by analyses of a solution of enriched uranium standard reference material U010 that includes ^{236}U (New Brunswick Laboratory).

Laser ablation of grain mounts. The grain mounts were sampled by laser-ablation (New Wave Research LUV266x), using a c. 25 × 14 μm spot, 1 Hz repetition rate at a fluence of c. 68 mJ cm^{-2} (sufficient to give a stable signal within detector range). The output from the desolvating nebuliser provided the carrier-gas flow (c. 1 l min^{-1} Ar_2) for the ablation cell, and was used for the introduction of solution reference materials U950a and U010 at the start and end of each analytical run.

For each analysis, two baselines were measured at half-mass units (217.5 and 216.5), well away from the masses of interest, to record a good instrument baseline. The laser shutter was opened and the ^{238}U signal monitored until approximately stable, prior to acquisition of 30 one-second integrations. These data were output as the mean and standard error of the mean, after rejection (10%, 2σ). The large volume (c. 30 cm^3) of the ablation cell attenuates the pulses of sample from the ablation, and thereby

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minimises the effects of the detector response delays between Faraday cups and electron multiplier. The ^{238}U signal was then monitored for approximately 30 seconds, to allow the passing of 'spikes' from previously ablated material and the return to baseline values, before the next analysis was started.

The ablation protocol used produced irregular conical pits, approximate dimensions 25 × 14 × 1 μm in uranium-oxide sample grains (measured using SEM and Caminex Enterprises Alicona infinite focus microscope). The sampling volume is roughly equivalent to a 9 μm diameter uranium oxide sphere, or 4 ng uranium.

Ablation of the resin gave negligible ^{238}U detector responses (c. 3×10^{-5} V using a 10^{11} ohm resistor, *c.f.* 1.6 V from typical samples). Sample grains were bracketed by analyses of natural uraninite grains for quality control. Of the 115 sample grains, 68 were analysed in replicate (up to 21 repeats from a single grain).

Data processing. Corrections were made to the data using U950a as a primary reference material: abundance sensitivity (^{238}U on ^{236}U, c. 1.2×10^{-6}); hydride for solutions ($^{238}U^{1}H/^{238}U$ c. 4×10^{-6}, resulting in $^{235}U^{1}H/^{238}U$ on $^{236}U/^{238}U < 1 \times 10^{-8}$); followed by external correction for $^{235}U/^{238}U$ instrumental response effects[38] (approximated by an exponential mass-bias function[39]). A secondary reference material, U010, was used to correct for bias between the ion counter and Faraday cups. Estimates of uncertainty were propagated from the analytical standard error of the mean (σ_m) and the relative standard deviations of the corrected primary and secondary reference materials.

3. Results

Quality control

Natural uraninite grains were ablated 155 times throughout the four analytical runs for quality control. The data are presented in Fig. 4 (with 8 outliers removed). Following mid-session calibration, the data in the fourth analytical run drift from a significant low bias. Nine of the uraninite data have been used to bracket the remaining sample and quality control data for that interval (as a tertiary reference material). These self-corrected data are highlighted in Fig. 4, and are excluded from the following quality control statistics.

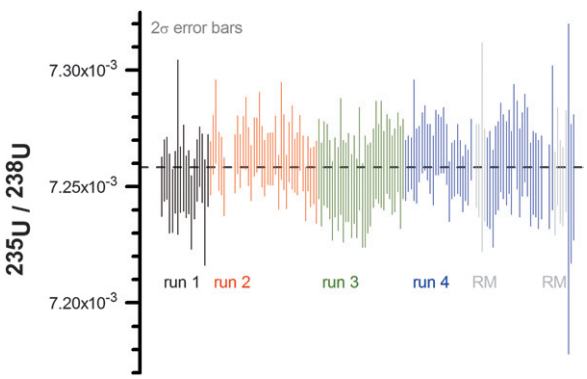

Fig. 4 $^{235}U/^{238}U$ ratios for natural uraninite grains by LA-MC-ICP-MS, from four analytical runs. Nine of the data have been used as reference materials (RM) to correct an observed bias in the second half of run 4.

The remaining data (n = 138) are normally distributed about an arithmetic mean $^{235}U/^{238}U$ $(7.259 \pm 0.002) \times 10^{-3}$ ($2\sigma_m$). The relative precision for these data is 0.22% (2σ). The mean is within uncertainty of the recently recommended value,[12] within the range of natural variability,[14] or slightly biased when compared to the traditional consensus.[9]

The mean square weighted deviation (MSWD) for these QC data was 1.2, demonstrating that the propagated uncertainty had probably been slightly underestimated.[40] Therefore, the uncertainties for $^{235}U/^{238}U$ have been expanded by 0.1%.

A sample grain (of unknown composition), analysed in replicate during one analytical run (2 outliers excluded, n = 21) has an MSWD of 1.6 for $^{235}U/^{238}U$; demonstrating that the expanded uncertainties are reasonable. For $^{236}U/^{238}U$, an MSWD of 2.6 suggests the uncertainties were underestimated; therefore, they have been expanded by 2%.

The relative expanded uncertainties (2σ) for the sample grain data-points, range from 0.2–1.8% for $^{235}U/^{238}U$, 2.3–4.0% for $^{236}U/^{238}U$, with medians of 0.4 and 2.7% respectively. Compared to the uraninite grains, the sample grains have lower $^{235}U/^{238}U$, and their ablation is more variable and hence signal, resulting in slightly poorer precisions.

Data

The analytical data for the laser ablation of uranium-oxide grains are presented in Fig. 5A, alongside those from analyses of solutions. The solution data show a similar spread of isotopic compositions to the laser ablation data. All these data are expressed as atom ratios.

Fig. 5B shows the data for soils and dusts, and the spread of isotopic compositions from these samples are similar. Particle-solution exchange in the wet soil environment does not explain the spread of data.

4. Discussion

Case-study interpretation

The data confirm the hypothesis that the individual particles of uranium-oxide record a variety of anthropogenic isotopic compositions, which are averaged in bulk soil and dust samples.

All of the uranium-oxide grains analysed are from DU, with $^{235}U/^{238}U$ less than 2.4×10^{-3}. Enriched uranium grains were not observed; these may be very scarce as comparatively little enriched uranium was handled by NLI, and it may have been recycled because of its value. Enriched uranium was evident in one former employee's urine,[6] implying dispersal of some of this material within the plant and possibly further afield.

NLI reduced uranium tetrafluoride (UF_4, greensalt) feedstock during the 1960s and '70s,[1]§ these may have been from discrete batches with distinct isotope signatures, or an evolving series of isotopic compositions. A number of processes at NLI could also have mixed these isotopic compositions: feedstock storage,

§ It is not clear where the DU feedstock for NLI was sourced. A DoE press release[46] identifies 11 US sites that handled reprocessed uranium, including 3 gaseous diffusion enrichment plants (Oak Ridge, TN; Puducah, KY; Portsmouth, OH) and 1 uranium hexafluoride reduction facility (Fernald, OH). If Fernald produced the UF_4 for NLI, it seems likely that the UF_6 was supplied from neighbouring Portsmouth.

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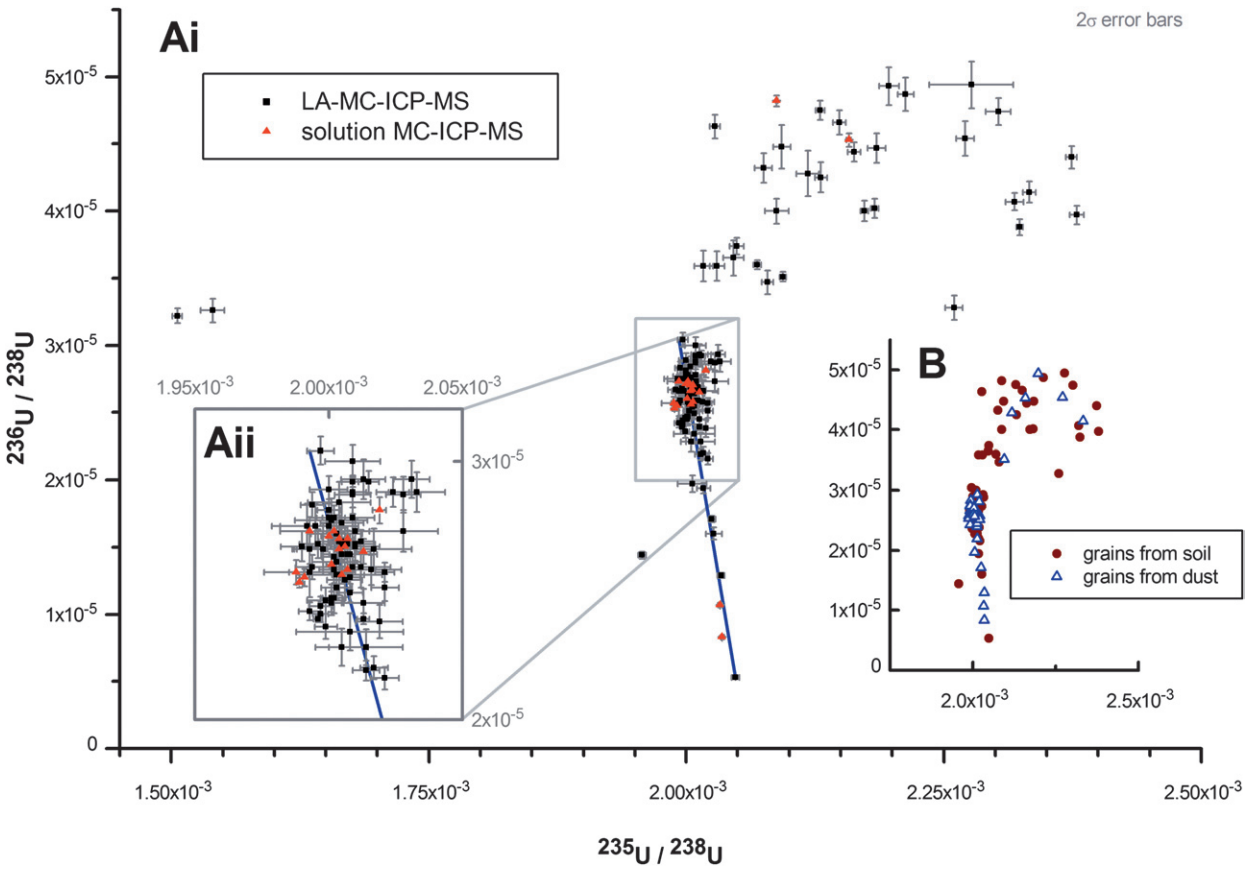

Fig. 5 **Ai** Isotopic compositions from LA- and solution MC-ICP-MS of individual grains. A mixing line passes through the data up to 3×10^{-5} $^{236}U/^{238}U$ (**Aii** expansion of clustered region showing some deviation of, and scatter away from a simple mixing line). **B** Comparison between analyses of grains from soil and dust samples, showing similar distributions of isotopic compositions.

reduction to uranium metal (derby), castings, machining, shop-floor debris, scrap storage, and finally chip burning (conversion) in the furnace releasing uranium-oxide particulates to the environment.

There is a large spread in ^{236}U abundance, with a reasonably well defined mixing-line from (5–31) $\times 10^{-6}$ $^{236}U/^{238}U$. These data range from (2.05–1.99) $\times 10^{-3}$ $^{235}U/^{238}U$ with increasing $^{236}U/^{238}U$. The data cluster around 2.7×10^{-5} $^{236}U/^{238}U$, 2.0×10^{-3} $^{235}U/^{238}U$. We interpret these ratios to follow either a mixing line between two isotopically discrete batches, or an evolving series of compositions. The former hypothesis seems less likely, as there does not appear to be a second cluster.

There is a scatter of ratios up to 5×10^{-5} $^{236}U/^{238}U$, and up to 2.4×10^{-3} $^{235}U/^{238}U$. These ratios are explained by inhomogeneous mixing (possibly in the NLI conversion furnace) of a continuation of the previous trend with a third component of slightly less depleted uranium. This hypothesised process also appears to affect some of the grains from the clustered region (Figure Aii), drawing them away from the mixing line.

Two grains have distinct isotope signatures with (1.5–1.6) $\times 10^{-3}$ $^{235}U/^{238}U$, and (3.2–3.3) $\times 10^{-5}$ $^{236}U/^{238}U$. The scarcity of these grains suggests that this was a small batch, or that little was released due to improvements in stack filtration.

The isotope signatures revealed by this study are not constrained with respect to age, except for four particles collected by air filters in April and May 1979 and analysed by FT-TIMS[2] (Fig. 6). These ratios fit into the scattered region of our dataset, and support the continuation of the trend of increasing ^{236}U to at least 6×10^{-5} $^{236}U/^{238}U$. These are most likely to have been from emissions at that time. However, the scrap metal may have accumulated for several months before conversion. The isotopic compositions of the uranium materials processed by NLI appear to have been more variable during this period.

It was reported that in 1980, 150 drums of waste uranium had accumulated over several months, and nearly 2 tonnes were converted to oxide in March and April of that year, with the release of only 7.5 g of uranium, thanks to operation of, and improvements to a filtration system, following enforcement action.[41] Extensive uranium contamination of soils is evident by 1980,[3] estimated in the order of 5 tonnes uranium deposited on soils within 1 km^2.[6] The vast majority of the contamination from NLI pre-dates 1980, therefore the sample grains analysed in this study probably also pre-date 1980. Based on the number of grains loosely tied to 1979 (c. 20%), a significant portion of the contamination appears to have been emitted during that period.

We speculate that the feedstock received by NLI evolved through a series of compositions, from 2.05×10^{-3} $^{235}U/^{238}U$ with minor ^{236}U contamination ($<5 \times 10^{-6}$ $^{236}U/^{238}U$), to 1.99×10^{-3} $^{235}U/^{238}U$ with 3×10^{-5} $^{236}U/^{238}U$. Subsequently, and by 1979, the primary NLI feedstock evolved to at least 6×10^{-5} $^{236}U/^{238}U$, but

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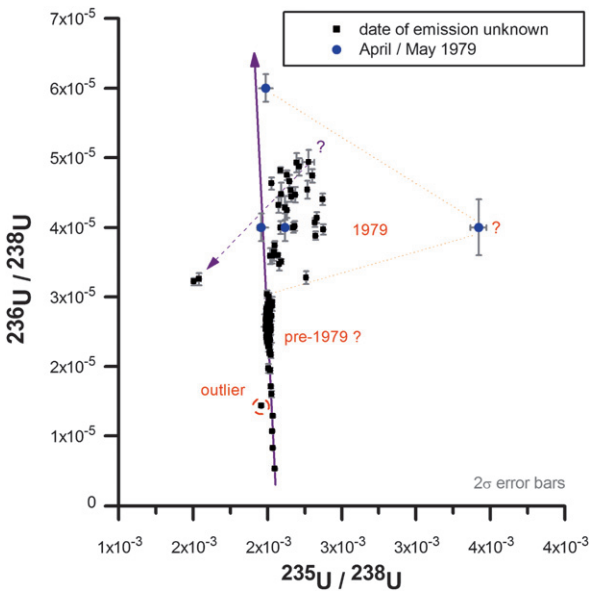

Fig. 6 Speculative explanation of the isotope ratios measured for this case-study. The solid arrow shows the primary NLI feedstock evolving with increasing ^{236}U contamination. A possible secondary feedstock follows the dashed arrow with increasing ^{235}U depletion at the gaseous diffusion plant, leading to the most depleted grains. A scatter of isotopic compositions within the dotted triangular region can be explained by inhomogeneous mixing with 'less depleted' uranium batch(es). The timing is loosely tied by four particles collected by air filters in April and May 1979.[2] A larger dataset could resolve these details.

during that time 'less depleted' uranium was also used. Continued depletion at the gaseous diffusion plant of uranium comprising 2×10^{-3} ^{235}U/^{238}U, 4×10^{-5} ^{236}U/^{238}U could result in the isotope ratios of the most depleted uranium-oxide grains analysed. These interpretations are summarised in Fig. 6.

A chronology for these data could be established using ^{230}Th/^{234}U, ^{231}Pa/^{235}U or possibly ^{232}Th/^{236}U dating of particles. The measurements would be technically challenging; with daughter radionuclides in the sub-femtogram range per grain (and are dependent on initial uranium separation). Uranium dating by ^{230}Th/^{234}U using ICP-MS has been successfully demonstrated by Varga and Surányi,[42] but improvements in sensitivity would be required for the dating of individual grains.

The spread of ^{235}U/^{238}U isotope ratios revealed by this study is matched by those in Fig. 1, but we are able to resolve more information from this large and precise dataset. Some of these DU grains comprise more ^{236}U than previously reported.

These data show that at least some of the DU processed at NLI had low levels of ^{236}U. Therefore, ^{236}U cannot be used as a defining fingerprint of DU contamination if, as for quadrupole ICP-MS, the lower limit of detection of the analytical technique approaches these ratios.

Analytical methodology

Laser ablation allows for the rapid collection of data, when compared to TIMS or solution ICP-MS. A typical sample grain analysis took less than two minutes, and the instrumental productivity (including set-up, reference materials, and particle location), was around 16 minutes per sample grain. Modern MC-ICP-MS systems offer faster set-up times, which could further improve productivity.

Pre-concentration of particles of interest using dense liquid separation was quick and effective, and allows for efficient analysis by laser ablation (or SIMS). However, the methodology does bias the sample by excluding particulates and grains smaller than approximately 20 μm. Smaller grains could be recovered using heavy-liquids with centrifugation,[43] froth-floatation,[44] or inertial separation. Alternatively raw samples may be analysed, but requiring more time searching for the grains of interest and exchanging sample mounts. It is not necessary to embed and polish the particles; they could be adhered to a mount with a clean adhesive, or sampled directly from a swipe sample.

The volume of sample consumed per analysis is small when compared to the volume of the grains of interest, and allows for replicate analyses. The sampling area is similar to the extent of the grains presented on the mount surface. Smaller particles can be analysed, when sufficiently separated from each other, as the uranium content of the resin is indistinguishable from detector noise. However, there is potential for minor additional ^{235}U^{1}H formation with hydrogen liberated from the epoxy resin. Clean mounting material would be necessary for fine particulates, for example carbon planchets. Modern laser systems can also achieve better spatial resolution.

An observed bias in the quality control data for part of one analytical run was corrected by using some of these data as a tertiary standard. There are variations in the uraninite data, and the uncertainties were slightly underestimated, both of which can also be explained by changes in instrument bias between external corrections. This demonstrates the need for more frequent monitoring, preferably by laser ablation of a solid reference material that includes ^{236}U (*e.g.* New Brunswick Laboratory U005-A). These minor issues were not significant to our interpretations of the sample data.

Accuracy was demonstrated by repeat analyses of natural uraninite grains; the mean value agrees with the 'natural ratio'. Relative precision over four analytical runs of 0.2% (2σ) for ^{235}U/^{238}U is better or at least comparable to the current methodologies used for nuclear forensic applications. Relative uncertainties (2σ) for the sample grains ranged between 0.2–1.8% for ^{235}U/^{238}U, and 2.3–4.0% for ^{236}U/^{238}U. The precision of this method was more than adequate to resolve differences in the isotopic composition of microscopic grains of DU-oxide.

The precision of LA-MC-ICP-MS compares favourably with LA-SF-SC-ICP-MS,[36] and is similar for SIMS analyses of particles from environmental samples.[29,31] It is hard to judge from the literature that achieved by FT-TIMS, although TIMS may offer better analytical precision. However, our method allows the acquisition of large datasets that may be more representative of the samples, the precision is fit-for-purpose, and appears to be a significant way forward for nuclear forensics. For this case-study, a larger dataset could resolve further details regarding the history of uranium processing at NLI (perhaps twice as large, and including sample from other locations for representativity).

5. Conclusions

We have demonstrated the use of LA-MC-ICP-MS to rapidly analyse a large population of microscopic uranium-oxide grains

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for an environmental case-study. It is clear from these and other data that the isotopic compositions of depleted uranium are variable, especially with respect to ^{236}U.

The accuracy and precision analysing $^{235}U/^{238}U$ for natural uranium was excellent. Typical relative uncertainties (2σ) of 0.4% for $^{235}U/^{238}U$ and 2.7% for $^{236}U/^{238}U$, are well-suited to nuclear forensic applications, and are an improvement over single-collector (quadrupole or sector-field) LA-ICP-MS. LA-MC-ICP-MS offers several advantages to nuclear forensics, including fast analysis time, minimal sample preparation, and partial ablation of the sample.

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In memoriam Leonard A. Dietz: an inspiration to this study as a pioneer of early TIMS and electron multiplier technologies. He highlighted the contamination of the environment by NLI in 1979, and latterly campaigned against DU munitions.

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