Science of the Total Environment 408 (2009) 397–407

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

The distribution of depleted uranium contamination in Colonie, NY, USA

N.S. Lloyd [a,*], S.R.N. Chenery [b], R.R. Parrish [a,c]

[a] Department of Geology, University of Leicester, University Road, Leicester, LE1 7RH, UK
[b] British Geological Survey, Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG, UK
[c] NERC Isotope Geosciences Laboratory, Kingsley Dunham Centre, Keyworth, Nottingham, NG12 5GG, UK

ARTICLE INFO

Article history:
Received 3 July 2009
Received in revised form 11 September 2009
Accepted 14 September 2009
Available online 23 October 2009

Keywords:
Depleted uranium
DU
Particulate
Isotope ratio
ICP-MS
Soils

ABSTRACT

Uranium oxide particles were dispersed into the environment from a factory in Colonie (NY, USA) by prevailing winds during the 1960s and '70s. Uranium concentrations and isotope ratios from bulk soil samples have been accurately measured using inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) without the need for analyte separation chemistry. The natural range of uranium concentrations in the Colonie soils has been estimated as 0.7–2.1 µg g^{-1}, with a weighted geometric mean of 1.05 µg g^{-1}; the contaminated soil samples comprise uranium up to 500 ± 40 µg g^{-1}. A plot of $^{236}U/^{238}U$ against $^{235}U/^{238}U$ isotope ratios describes a mixing line between natural uranium and depleted uranium (DU) in bulk soil samples; scatter from this line can be accounted for by heterogeneity in the DU particulate. The end-member of DU compositions aggregated in these bulk samples comprises $(2.05 \pm 0.06) \times 10^{-3}$ $^{235}U/^{238}U$, $(3.2 \pm 0.1) \times 10^{-5}$ $^{236}U/^{238}U$, and $(7.1 \pm 0.3) \times 10^{-6}$ $^{234}U/^{238}U$. The analytical method is sensitive to as little as 50 ng g^{-1} DU mixed with the natural uranium occurring in these soils. The contamination footprint has been mapped northward from site, and at least one third of the uranium in a soil sample from the surface 5 cm, collected 5.1 km NNW of the site, is DU. The distribution of contamination within the surface soil horizon follows a trend of exponential decrease with depth, which can be approximated by a simple diffusion model. Bioturbation by earthworms can account for dispersal of contaminant from the soil surface, in the form of primary uranium oxide particulates, and uranyl species that are adsorbed to organic matter. Considering this distribution, the total mass of uranium contamination emitted from the factory is estimated to be c. 4.8 tonnes.

1. Introduction

The by-product of uranium enrichment, where the fissile isotope ^{235}U is artificially concentrated for use as nuclear fuel or weapons, is depleted uranium (DU). In contrast to natural uranium, DU typically comprises $(2–3) \times 10^{-3}$ $^{235}U/^{238}U$, is also depleted in ^{234}U, and is contaminated by anthropogenic ^{236}U from reprocessed uranium (Bleise et al., 2003). Worldwide nuclear programmes have amassed c. 1.2 million tonnes of DU, most of which is stored as UF_6 (NEA and IAEA, 2001). Applications for depleted uranium metal include ballast, munitions and radiation shielding. The use of armour piercing DU munitions (kinetic energy penetrators) in the Gulf and Balkans conflicts, and recently the Iraq invasion has been highly controversial, because they disperse a radioactive and toxic material into the environment. However, DU exposure is unlikely to present a significant health risk (e.g. Priest, 2001).

The Royal Society (2001, 2002) reports focus on the health risks from inhalation of DU particulates. The reports recommended that the environmental behaviour of alloys and particles of DU, should be compared to natural uranium minerals, and information should be obtained on their bioavailability.

Several recent studies have investigated the environmental behaviour of DU metals, which corrode in oxidising environments to form soluble uranyl species (e.g. Buck et al., 2004; Fomina et al., 2008; Handley-Sidhu et al., 2009; Schimmack et al., 2005). The DU particulates released from munitions impacting armour are characterised in Krupka et al. (2009) and other papers in Health Physics 96 (3) resulting from the Capstone Aerosols study (Parkhurst et al., 2004). These and the particulates from the combustion of DU metals are introduced to the environment in a range of oxidation states: UO_2–UO_{2+x}–U_3O_8–UO_3. UO_3 and uranyl species are thermodynamically favoured, but bulk oxidation to these more soluble oxides is limited by slow kinetics and surface passivation (McEachern and Taylor, 1998). This appears to be the case for the persistence of low solubility UO_{2+x} (hyperstoichiometric UO_2) and U_3O_8 particles in soils (Lloyd et al., 2009a). Radiogenic lead reduces the mobility of uranium from natural uraninite (e.g. Finch and Ewing, 1992), which otherwise is a logical analogue. Studies by Oliver et al. (e.g. 2008) have recently made environmental observations on the distribution of contamination from DU munitions test firing. A number of other studies have

---

* Corresponding author. Tel.: +44 115 936 3100.
E-mail address: nsl3@alumni.leicester.ac.uk (N.S. Lloyd).

0048-9697/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2009.09.024

characterised individual particles from environmental samples contaminated by the combustion of uranium metals and DU munitions (e.g. Lind et al., 2009; Salbu et al., 2005; Török et al., 2004).

The aim of this environmental case-study is to identify the processes that affect the distribution and bioavailability of uranium from DU particulate contamination. The field site offers an accessible and large contamination footprint, with the absence of confounding contamination from DU metal fragments, and more than 25 years of environmental processing. It is therefore an attractive analogue for battlefield contamination, and potentially for epidemiological studies related to DU particulate inhalation exposure.

Natural uranium comprises three isotopes: ^{238}U, ^{235}U and ^{234}U, all of which are unstable with long half-lives. The conventional value for ^{235}U/^{238}U (atom ratio, n^{235}U/n^{238}U) is 7.253×10^{-3} (Steiger and Jäger, 1977), recently recommended as 7.257×10^{-3} (De Laeter et al., 2003), with slight (‰) natural fractionation about this value (Weyer et al., 2008). With the exception of the Oklo natural reactors (Neuilly et al., 1972) deviation of ^{235}U/^{238}U implies anthropogenic contamination. Subtle, but geographically widespread ^{235}U/^{238}U deviations, caused by contamination from nuclear weapons use and from nuclear accidents, have been reported by Warneke et al. (2002). Uranium in secular equilibrium has a ^{234}U/^{238}U ratio of 5.5×10^{-5} (Richter et al., 1999), but there are significant natural deviations from this ratio (e.g. Fleischer, 2008). The abundance of ^{236}U in natural uranium is negligible (e.g. Berkovits et al., 2000).

The distribution of uranium within the Earth is discussed in Plant and Saunders (1996), the continental crust comprises an average 2.7 μg g^{-1} (Taylor, 1964), hosted in resistate igneous accessory minerals including thorite, monzanite and zircon, and occasionally concentrated in ore minerals including uraninite and pitchblende (impure uranium oxides), and coffinite (a hydrated uranium silicate). The natural background concentration is variable in environmental samples, typically low μg g^{-1} and ng g^{-1} levels.

As discussed previously, natural environmental samples comprise variable trace quantities of uranium, but anthropogenic contamination can be determined from ^{235}U/^{238}U. Analytical methods for determining uranium in environmental samples were reviewed in Wolf (1999), the precisions of radiometric techniques are often limited by the low activities of the uranium isotopes. Mass spectrometry techniques can achieve good precisions, especially for isotope ratios. Isotope dilution thermal ionisation mass spectrometry (ID-TIMS) offers the best precision, but is costly and requires laborious sample preparation. Taylor et al. (1998) obtained relative uncertainties of 0.2% ($k=2$) for ^{235}U/^{238}U from soil samples using single-spike ID-TIMS.

The performance of four inductively coupled plasma mass spectrometers (ICP-MS, multi and single collector sector field, and quadrupole) in combinations with several nebulisers (ultrasonic and desolvating), measuring ^{236}U/^{238}U, are compared in Boulyga et al. (2002). The multicollector ICP-MS (MC-ICP-MS) achieved excellent precision; and the desolvating nebuliser reduced hydride interference by up to two orders of magnitude. Quadrupole ICP-MS (ICP-QMS) instruments offer lower costs with generally good precision. As for most ICP techniques, sample dissolution is required. Analyte separation chemistry is often preferred (e.g. Zheng and Yamada, 2006), but it is desirable to avoid this costly step. Other than hydride, there appears to be little potential for polyatomic interferences on the uranium isotopes (Lariviere et al., 2006). Ehrlich et al. (2004) found analyte separation to be unnecessary for ^{234}U/^{238}U measurements from manganese nodules, although deposition of dissolved solids on the sampler and skimmer cones could be an issue. However, Gwiazda et al. (2004) and Shen et al. (2002) experienced background interferences on m/z 235 when working at very low uranium concentrations; the latter study attributed this to organic-rich samples and the interference was removed by separation chemistry.

A significant objective of this case-study is to define the present distribution of DU contamination. ICP-QMS was used for the determination of uranium isotope ratios from trace concentrations in contaminated soil samples. Adequate precision was realised using a desolvating nebuliser, and without the need for analyte separation chemistry. There is heterogeneity in the isotopic composition of DU contaminant (Lloyd et al., 2009b) and the effect of this variability on the isotopic compositions of bulk environmental samples is explored in this paper. The dataset demonstrates the clarity for resolving DU contamination that precise ^{235}U/^{238}U ratios offer.

2. The Colonie case-study

2.1. Site history

National Lead Industries (NLI) operated a factory in Colonie (NY, USA), from 1958 to 1984. The factory reduced UF$_4$ to metal, and machined depleted uranium articles including kinetic energy penetrators, counterweights and radiation shielding (ATSDR, 2004). The storage of scrap uranium metal is hazardous, because this material is pyrophoric when it is finely divided (Wilkinson, 1962). Therefore, this waste was converted to uranium oxides in a furnace, which resulted in emissions of uranium oxide aerosols to the atmosphere. This was not contemporary best practice. National Lead was also responsible for uranium contamination surrounding the Fernald site in Ohio (Buck et al., 1996).

The history of permits for the NLI site is documented in a draft report by the New York State Department of Health (1979). In 1968, it was noted that the converter stack operated without filtration, and immediately south of the site ^{238}U soil concentrations of 163 μg g^{-1} were reported, Department of Labour permitted nearly 600 μg g^{-1} on site at that time. In 1973 NLI were permitted to discharge a total of 3.9 kg of uranium from 23 stacks. In 1975 the site was limited to handling natural and depleted uranium, prior to that licences were also held for enriched uranium and thorium. In 1977, when production increased, an electrostatic precipitator was added to the conversion furnace (chip-burner), although this was reportedly bypassed on occasion.

In May 1979 routine analyses of air filters, sampled at locations 40.8 and 15.7 km NNW of the NLI site, revealed contamination by micrometer diameter DU particles (Dietz, 1980). A survey conducted later that year revealed extensive depleted uranium contamination of soils surrounding the site (Jeter and Eagleson, 1980). The legal proceedings that led to the closure of NLI for excessive emissions of uranium to the environment are detailed in Romano (1982).

In 1984, US Department of Energy took over responsibility for the site, and since 1997 the U.S. Army Corps of Engineers has been responsible for the environmental remediation of the site under the Formerly Utilized Site Remedial Action Programme (USACE, 2009). The remediation threshold used for soils is 35 pCi g^{-1} from ^{238}U (USACE, 2002), equivalent to 104 μg g^{-1}, highly conservative when compared to 190 pCi g^{-1} derived by Dunning (1996). Remediation of the site and limited remediation of surrounding properties, involving removal and disposal of contaminated soils, is reported to have cost US$ 190 million (Dlouhy, 2009).

Contamination is evident in reservoir sediments at a site downstream of NLI (Arnason and Fletcher, 2003; Arnason et al., 2008; Lo et al., 2006). Depleted uranium has been detected in the urine of former employees (with enriched uranium from one individual) and from some residents (Parrish et al., 2008).

Examination of contaminated soils and dusts reveals primary uranium oxide particles in the size range 0.5–150 μm, including mixed UO$_{2+x}$ and U$_3$O$_8$ spheres with diameters 20–64 μm, and rarely secondary uranium precipitates (Lloyd et al., 2009a). These spheres and other specific particle morphologies are directly comparable to those from munitions. Laser ablation (LA-) MC-ICP-MS reveals a spread of depleted uranium isotope ratios from individual particles, attributed to variations in the NLI feedstocks (Lloyd et al., 2009b).