Nanometer-micrometer sized depleted uranium (DU) particles in the environment

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A B S T R A C T

Depleted uranium (DU) is a waste product from uranium enrichment that has several civilian and military applications. Significant amounts of DU in the form of particles or as fragments have been released into the environment as a consequence of military use of DU munitions, of industrial releases and of aircraft accidents. Thus, the present paper summarizes present knowledge on nanometer-micrometer sized depleted uranium (DU) particles collected in areas contaminated with such particles. Analysis of DU particles released to the environment has shown that uranium can be present in different crystalline structures and in different oxidation states. The weathering rates of DU particles and the subsequent remobilization of uranium species are also strongly connected to the oxidation state and crystalline phases of uranium, influencing the mobility and potential ecosystem transfer. Therefore, as has been observed for radioactive particles released from most nuclear events, the characteristics of DU particles can be linked to the source term and the release scenario as well as to environmental transformation processes. Although the radiation dose and radiotoxicity of DU is less than from natural occurring uranium, the mobility of U from oxidized DU and the associated chemical toxicity could be significantly higher than from natural UO_2. The present paper summarizes present knowledge on depleted uranium particles identified in the environment.

1. Introduction

In typical depleted uranium (DU) materials, the content of ^{235}U and ^{234}U is about 0.2–0.3% of what is found in natural uranium (0.7204% ^{235}U and 0.0054% ^{234}U by mass) (Nucleonica, 2019; USNRC, 2019), causing the activity of DU to be about 60% lower (Bleise et al., 2003). These lower relative isotopic concentrations of ^{235}U and ^{234}U in DU can be attributed to two main processes. Firstly, reprocessing of spent fuel rods with low enrichments of ^{235}U (civil fuel) yields substances that are depleted in ^{235}U and ^{234}U, but is also giving rise to the significant concentrations of ^{236}U often observed in DU materials. Secondly, production of enriched U (elevated concentrations of ^{235}U) from natural U in an enrichment plant also yield DU as a byproduct. Depleted uranium is traditionally treated like waste, but during the years several civilian and military applications have evolved (Betti, 2003; Bleise et al., 2003), which again have given or may potentially give rise to contamination of DU in the environment. Depleted U, as U in general, can be present in different physico-chemical forms (e.g., low molecular mass (LMM)

species, colloids, particles), influencing the mobility and potential transfer in the environment. Low molecular mass (LMM) species (<1 nm or molecular mass about <1 kDa, e.g., ions, molecules, complexes) are assumed to be mobile and bioavailable, high molecular mass (HMM) forms (1 nm - 0.45 μm, i.e,. colloids/nanoparticles, pseudocolloids) are believed to be mobile, while particles (>0.45 μm) are believed to be rather inert (Salbu, 2000). According to IAEA (2011), radioactive particles are defined as localized aggregates of radioactive atoms that give rise to an inhomogeneous distribution of radionuclides significantly different from that of the matrix background, while particles larger than mm are usually referred to as fragments. Consequently, DU particles are also radioactive particles, ranging from submicrons such as nanomaterials (substances of <100 nm in size in more than one dimension, (EC, 2011).

A major fraction of refractory (i.e., non-volatile) radionuclides such as U released from nuclear sources including nuclear weapons tests, accidents with nuclear weapons, reactor accidents, accidental releases from reprocessing installations and military use of DU have been shown

to be associated with radioactive particles (Salbu et al., 2015, 2018). Furthermore, the radioecological and radioanalytical impact of radioactive particles released from nuclear sources has been demonstrated over the years (Kashparov et al., 1999; Salbu et al., 2015). Thus, the objectives of the present work is to provide a summary of present knowledge related to nanometer-micrometer sized depleted uranium (DU) particles in the environment, relevant particle characterization methods, sources and release scenarios as well as transformation processes which influence the mobility of associated U isotopes. A dose assessment estimate of DU particle exposure is also included.

2. Methods for identification, isolation and characterization of DU particles

As for all radioactive particles (IAEA, 2011), a series of analytical tools have been employed for identification, isolation, and characterization of DU particles (Crean et al., 2014; Handley-Sidhu et al., 2008, 2009a, 2009b; Lind et al., 2009; Salbu et al., 2003b, 2005a). Most researchers have utilized either digital autoradiography (Crean et al., 2014; Handley-Sidhu et al., 2009a) or scanning electron microscopes (SEM) combined with energy dispersive x-ray analysis (EDX) to identify DU particles in environmental samples (Lind et al., 2009; Salbu et al., 2003b, 2005a), although visual identification of large yellow DU particles in light microscopes (Buck et al., 2004; Salbu et al., 2005b) and heavy liquid separation (Buck et al., 2004; Lloyd et al., 2009b) have also been used. SEM-EDX or environmental SEM-EDX (ESEM-EDX) also served to characterize particles with respect to surface topography, elemental composition and distribution as well as size distribution. Elemental composition was also determined by bench-top μ-XRF (Crean et al., 2014) and electron probe microanalysis (EPMA) (Buck et al., 2004). Analytical Transmission Electron Microscopy, including Selected Area Diffraction (SAED), provided spatially highly resolved speciation information although authors indicated that beam damage could induce artefacts (Wang et al., 2016b). Salbu and co-workers were the first group to employ a combination of synchrotron radiation (SR) based X-ray microscopic techniques on single depleted uranium (DU) particles (Salbu et al., 2003a, 2005b), as they investigated elemental composition and distribution by means of micro SR based X-ray Fluorescence (μ-SRXRF), oxidation states using micro SR based X-ray Near Edge Spectroscopy (μ-SRXANES) and determining crystallographic forms with micro SR based X-ray Diffraction (μ-SRXRD) in particles from Kosovo and Kuwait collected during IAEA missions. Later, μ-EXAFS has been applied to single particles by Lloyd et el. (2009a). Buck et al. (2004) was also able to identify U minerals in DU particulate material with a conventional X-ray Diffraction (XRD) instrument. Useful speciation information can also be obtained employing μ-RAMAN (Mellini and Riccobono, 2005).

Several mass spectrometric techniques have been employed to characterize environmental DU particles. Isotopic ratios obtained by means of ICP-MS and AMS for confirmation of the DU origin and to demonstrate that DU had been reprocessed were reported by several authors (Danesi et al., 2003; Salbu et al., 2005b), whereas such information was obtained from individually isolates particles using AMS (Salbu et al., 2005b) or using spatially resolved SIMS (Danesi et al., 2003). Gerstmann used TOF-SIMS to obtain speciation information from corroded weapon debris (Gerstmann et al., 2008). Some authors used size fractionation techniques in combination with ICP-OES or ICP-MS to quantify the colloidal fraction (i.e., nanoparticles) of DU in porewaters of contaminated soils (Oliver et al., 2008) and Multi-Collector ICP-MS (MC-ICP-MS) to determine precise $^{235}U/^{238}U$ isotope ratios in the same samples (Oliver et al., 2008). Laser ablation MC-ICP-MS (LA MC-ICP-MS) proved very useful in shedding light on the provenance of a large number of environmental DU particles exhibiting varying isotopic composition (Lloyd et al., 2009b).

In addition to the analytical tools cited for characterization of environmental DU particles, there are a number of potentially powerful methods that so far have been used within radiochemistry, nuclear forensics or on artificial DU samples (Salbu and Lind, 2019). Among these are several promising techniques offering high spatial resolution such as Resonant laser–SNMS (Secondary Neutral Mass Spectrometry) (Franzmann et al., 2018).

3. Existing and potential sources of DU particles in the environment

3.1. Military use

Depleted uranium is used for military purposes in several countries both as ammunition and armor plating (Bleise et al., 2003). Due to the high density, hardness of the metal and pyrophoric properties DU has been extensively applied as armor-piercing ammunition. Several reports have been published on DU contamination associated with the use of large amounts of DU penetrators during war time such as in Kosovo (Danesi et al., 2003b; Danesi et al., 2003a; Salbu et al., 2003a,b), Serbia-Montenegro (McLaughlin et al., 2003), Bosnia and Herzegovina (UNEP, 2003; Wang et al., 2016a), Kuwait (Salbu et al., 2005a,b), Iraq (Gerdes et al., 2004) and in Syria (Oakford, 2019). At all sites, a part of the DU contamination has been identified as DU particles, except in Iraq and Syria where no information on particles appears to be available. Large amounts of DU ammunition have also contaminated military proving grounds and their surroundings (Buck et al., 2004; Cheng et al., 2009; Handley-Sidhu et al., 2008, 2009a, 2009b).

Following the impact of metallic DU penetrators on hard targets such as tanks, DU will disintegrate and a cloud of DU dust would ignite spontaneously (RSC, 2001). Hundreds of thousands of particles have been found in a few milligrams of soils contaminated by such events (Danesi et al., 2003). Based on several studies, the median aerodynamic diameters (AMAD) for particles produced during DU penetrator impact with tank ranged from 0.8 to 7.5 μm (RSC, 2001). Later studies have largely supported that the DU penetrators on impact will disintegrated into particles with size within the respiratory fraction (Cheng et al., 2009; Danesi et al., 2003; Salbu et al., 2003b, 2005b). Thus, resuspension and subsequent inhalation should be a pathway of concern. According to RSC, (2001), UO_2 and U_3O_8 aerosols as well as DU particles are produced upon oxidation of metallic DU at the high temperatures created during impact. However, there are also reports on the presence of metallic U, UC and Fe_2U (Lind et al., 2009), U_4O_9 and U_3O_7 (Chazel et al., 2003), $UO_{2.34}$ (De Nolf et al., 2009) and UO_3 (Chazel et al., 2003) in DU particles produced during DU penetrator impact with tanks.

Depleted U particles with a wider size distribution, ranging from 0.2 to 1500 μm (median 44 μm, n = 43), were attributed to the releases from the DU ammunition storage facility in Al Doha, Kuwait. These particles were also brittle, indicating that mechanical breakdown should contribute to weathering and a shift toward smaller size distributions over time in the arid desert environment of Kuwait. Detailed speciation analyses demonstrated that U was present as schoepite (UO_3·2.25 H_2O), dehydrated schoepite (UO_3·0.75 H_2O) and metaschoepite (UO_3·2.0 H_2O) (Lind et al., 2009), i.e., crystallographic forms of U with relatively high solubility products ranging from $10^{4.70}$-$10^{6.33}$ (Giammar and Hering, 2004). The solubility of schoepite at near neutral pH (~10 mg/l) is ~5 orders of magnitude higher than for UO_2 (~0.1 μg/l) (UNEP, 2001).

Fragments and particles were also formed as unspent DU penetrators deposited in the field corroded over time due to oxidation of the metal (Handley-Sidhu et al., 2010), resulting in the formation of relatively highly soluble and crystalline phases such as schoepite (UO_3·2.25 H_2O), dehydrated schoepite (UO_3·0.75 H_2O) and metaschoepite (UO_3·2.0 H_2O) have been reported (Buck et al., 2004; Lind et al., 2009; Mellini and Riccobono, 2005; Wang et al., 2016a). Less oxidized uranium species such as uraninite (UO_2) have also been reported for corroded penetrators (Mellini and Riccobono, 2005; Salbu et al., 2005b). Wang and co-workers also reported from an environmental study in Bosnia, that the transformation of metaschoepite to less soluble studtite ((UO_2)
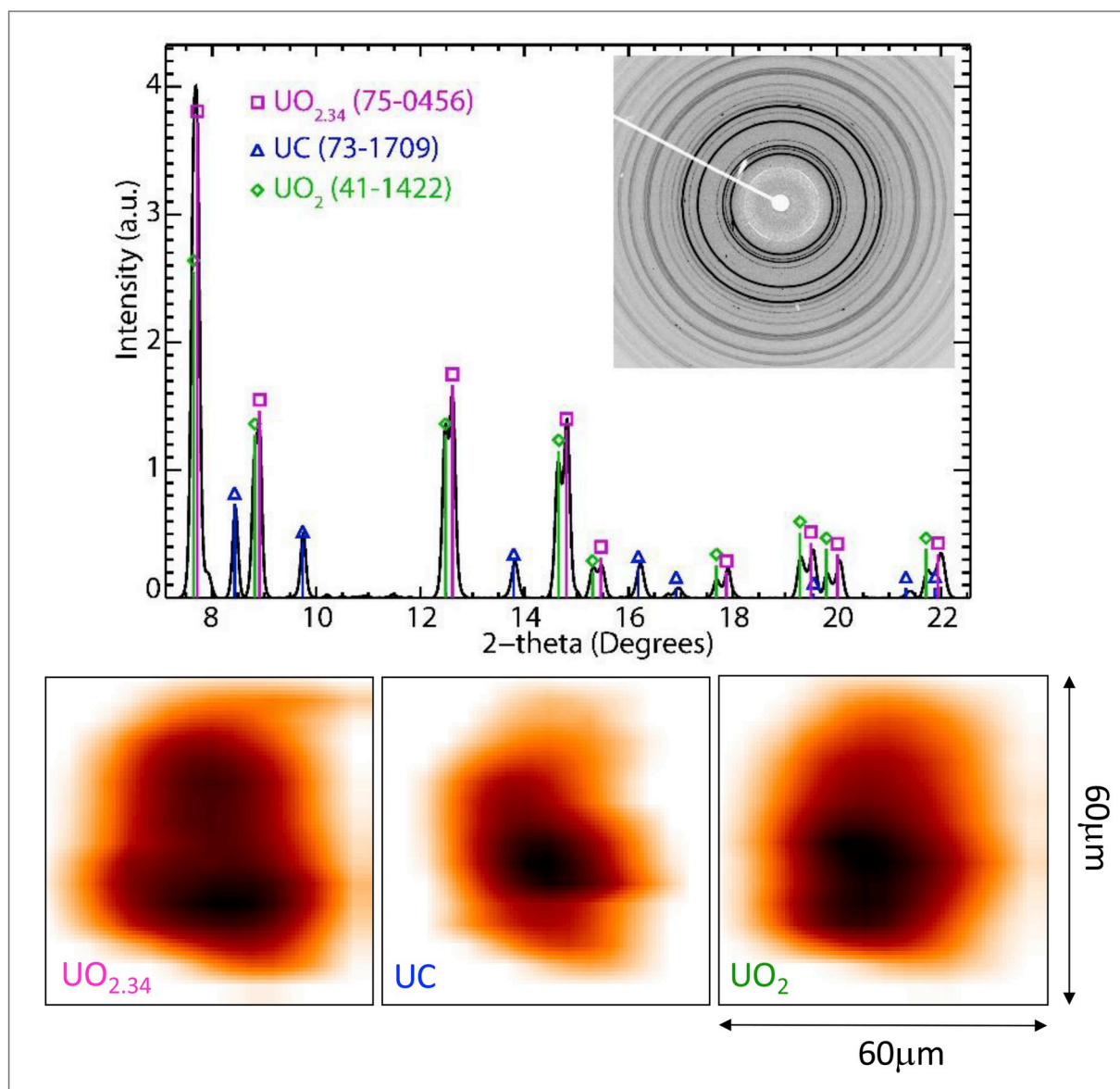
Fig. 1. Two dimensional μ-XRD analysis of a DU particle collected in Kosovo soil contaminated as a result of a DU penetrator impacting a tank. Diffraction patterns from the DU particle and corresponding ICDD PDF-2 database entries (top; modified from (Lind et al., 2009), and phase intensity distribution maps of the 3 detected crystallographic forms (Lind et al., 2019).

$O_2(H_2O)2\cdot2(H_2O)$), and becquerelite $(Ca(UO_2)_6O_4(OH)_6\cdot8(H_2O))$ as a result of the geochemical conditions under which the penetrators corroded (Wang et al., 2016a). The above considerations relate to postconflict contaminated areas but corrosion particles occur as frequently in association with experimental test firing of large amounts of DU alloy penetrators at Solway Firth and Kirkcudbright, UK and Aberdeen, Maryland and Yuma, Arizona proving grounds, USA. However, the literature lacks, with a few exceptions (Buck et al., 2004; Sowder et al., 1999), detailed spatially resolved particle characterization and speciation data, while corrosion rates, DU soil migration and solubility under various environmental conditions have been reported widely (Alvarez et al., 2011; Buck et al., 2004; Handley-Sidhu et al., 2008, 2009a, 2009b, 2009c, 2010; Johnson et al., 2003, 2004). In column experiments with different kinds of soil, Schimmack et al. (2005, 2007) investigated long-term corrosion and leaching of DU penetrators collected in Kosovo. The leaching rates increased much stronger after 3 years than could be expected after 1 year, preventing long-time predictions.

Based on ICP-MS and AMS, the $^{235}U/^{238}U$ atom ratios reported for

individual DU particles were rather constant, at approximately 0.002 (Lloyd et al., 2009b; Salbu et al., 2003b, 2005b; Torok et al., 2004). In contrast, the relative ^{236}U concentrations in DU particles varied depending on the sampling site being 5 to 6 orders of magnitude higher than in natural U (Lloyd et al., 2009b; Salbu et al., 2005b; Torok et al., 2004). The presence of these elevated concentrations of ^{236}U can only originate from the use of DU recycled from spent fuel or relate to the handling of DU with equipment previously contaminated in the course of recycling operations in the enrichment plants.

A major finding using micro analytical techniques was the fact that different crystallographic phases tend to co-exist within individual DU particles (Fig. 1). Many crystallographic phases of U oxides have the same symmetry and their X-ray diffractograms therefore tend to be difficult to differentiate. Thus, high spatial resolution as well as combined XRDP-XRF instrumentation with high angular resolution are key to resolve the complexity of spatial heterogeneity of mixed DU species.

Table 1
Summary of observed characteristics of DU particles collected from contaminated sites.

Source	Release scenario/transformation process	Site	Average U ox. state	Crystallographic structure	References
DU penetrator impact with armoured targets (tanks)	Impact with hard target followed by weathering (~5 y)	Kosovo	+4.0 ± 0.5	UO_2, $UO_{2,34}$, UC, metallic U	(Lind et al., 2009; Salbu et al., 2003b)
	Impact with hard target followed by weathering (~10 y) in arid environment	Kuwait	+4.4 ± 0.5, +4.7 ± 0.5	UO_2, UC, Fe_2U	(Lind et al., 2009; Salbu et al., 2005b)
	Impact with hard target followed by weathering (30 y)	Eskmeal, UK	+4.6;	U_3O_7, U_3O_8	Crean et al. (2014)
	Impact with hard target followed by weathering (30 y) in organic rich soil	Eskmeal, UK	+4.6; +6	$U3O7$, $K(UO_2)(PO_4)\cdot3H_2O$	Crean et al. (2014)
DU ammunition storage fire	Munition explosions and fire followed by weathering (~10 y)	Kuwait	+6	$UO_3\cdot2.25H_2O$, $UO_3\cdot2.0H_2O$, $UO_3\cdot0.8H_2O$	(Lind et al., 2009; Salbu et al., 2005b)
Corroded DU penetrators	Kinetic penetrator missed target, weathering (~7 y) of intact penetrators	Bosnia, Kuwait	+4.6 ± 0.5; +6	$UO_3(H_2O)_2$, $(UO_2)O_2(H_2O)_2\cdot2(H_2O)$, $Ca(UO_2)_6O_4(OH)_6\cdot8(H_2O)$	Wang et al. (2016a)
Industrial release	Incineration of scrap depleted uranium metal, weathering (~25 y)	Colonie, New York	UO_{2+x}		Lloyd et al. (2009a)

3.2. Civilian use

Due to the physical and chemical properties, DU has been used for a number of civilian purposes, representing potential sources of DU particle releases to the environment. The use of DU for counterbalance weights and ballast has been reported to include aircrafts (rudders and flaps) ((De Haag et al., 2000), military aerospace and boat (e.g., keels of sail yachts) industries, as well as oil and gas exploration and production industries (Betti, 2003; Priest, 2001). Also mentioned is counterweights for fork lifts and piling equipment (Russ, 2002) as well as radiation shielding material (e.g., transportable shielded containers for radioactive sources) (Ferrada et al., 2004). A yellow enamel powder used in the manufacture of badges and jewelry contains DU, and up to early 1980s both natural and depleted uranium was widely used within dentistry (Betti, 2003). In scientific laboratories, DU is used as a contrast enhancing reagent for microscopy and as a chemical stressor in ecotoxicological and radioecotoxicological experiments, e.g., (Barillet et al., 2007; Lind et al., 2019; Song et al., 2012). The use of DU nanoparticles as catalysts is emerging (Betti, 2003; Hutchings et al., 1996; Wang et al., 2008), and could be a future source of DU contamination in the environment if industries are not well regulated.

Following accidental events associated with civil sources, DU particles have also been released to the environment. On 4 October 1992, a Boeing 747 cargo plane with 150 kg DU counterweights on-board crashed near Schiphol Airport in the Netherlands, and during the subsequent fire uranium oxide particles were released into the environment (De Haag et al., 2000). However, the characteristics of the particles does not appear to be disclosed in the open literature. In the USA, aerial industrial releases of DU oxide particles occurred in association with production of DU articles, and in this case more details are available. During 1958–1984, National Lead Industries operations involving conversion of DU scrap metal to DU oxides resulted in environmental contamination of a large variety of DU particles at two sites in the USA, namely Fernald, Ohio (Buck et al., 1996) and Colonie, NY (Lloyd et al., 2009a). At Colonie, an estimated 5 tonnes of DU was deposited within 1 km^2 of the factory (Lloyd et al., 2009a, 2009c). From soils and dusts (Lloyd et al., 2009a), collected spherical mixed UO_{2+x} and U_3O_8 microspheres (20–64 μm in diameter), similar to those produced when a penetrator impacts armoured targets.

4. Ecosystem transfer of DU particles

When DU particles are deposited in the environment, soils and sediments can act as sinks and the particles are retained until weathering occurs. Although uptake and retention of DU particles in biota have not been reported in open literature, retention of nanometer – micrometer sized radioactive particles has been observed both in laboratory experiments and in the field (Cagno et al., 2017; Jaeschke et al., 2015; Salbu

et al., 2018). Submicron sized particles (nanoparticles) are believed to be quite mobile, and toxic effects of engineered nanomaterials (substances <100 nm in size in more than one dimension) have been related to the ability of nanoparticles to cross biological barriers (Nowack and Bucheli, 2007). Laboratory experiments in which Atlantic salmon embryos were exposed to DU nanoparticles during fertilization showed that DU particles also could have an indirect effect by delaying the hatching of eggs (H. C. Teien, pers comm). The ecosystem transport of nanoparticles are, however, still generally poorly understood and the knowledge gaps are large (Donia et al., 2019).

The weathering rate of DU particles and the subsequent remobilization of U species depend on particle characteristics such as particle size, crystalline structure and oxidation state, (i.e., source and release dependent) and on environmental conditions such as pH and redox conditions. According to literature (Table 1), a large number of metallic U penetrators has been deposited in sand/soils. Following corrosions processes, the oxidation occurs gradually as zerovalent U metal can be oxidized to U(IV) oxide (UO_2), and further to U(VI) minerals like schoepite and its derivatives such as dehydrated schoepite ($UO_3\cdot0.75$ H_2O) and metaschoepite ($UO_3\cdot2.0$ H_2O) (Lind et al., 2009). The solubility of schoepite at near neutral pH is about 5 orders of magnitude higher than for UO_2 (UNEP, 2001). In addition, further transformation of metaschoepite to less soluble studtite ($(UO_2)O_2(H_2O)2\cdot2(H_2O)$) and becquerelite ($Ca(UO_2)_6O_4(OH)_6\cdot8(H_2O)$) has also been attributed to geochemical conditions under which the penetrators corroded (Wang et al., 2016a).

According to literature (Table 1), DU particles containing UO_2 and U_3O_8 were produced upon impact with hard targets; i.e., oxidation of metallic DU in penetrators due to high temperatures and ignition created during impact. DU particles containing U species such as metallic U, UC, Fe_2U, U_4O_9, U_3O_7, $UO_{2.34}$, and UO_3 have also been reported following the impact of DU penetrators with tanks. Thus, the weathering rate of these particles may vary according to the dominant phases. Due to the impact and the subsequent dispersion, however, these DU particles tend to be smaller (e.g., respiratory sizes) than those produced from corrosion, which also should be reflected in the weathering rates.

According to literature (Table 1), fire in the penetrator storage facility in Kuwait resulted in highly oxidized U such as UO_3 in brittle, large yellow particles that could be subjected to mechanical breakdown, and thereby increase the weathering rates. According to (Lind et al., 2009), U was present in crystallographic phases with relatively high solubility products (i.e., schoepite, dehydrated schoepite, metaschoepite). The particle size distribution was also quite wide, ranging from submicrons to several hundreds of micrometers, that also could influence the weathering rates.

Information on DU particle weathering rates, remobilization and solubility for instance in the intestinal tract of particle associated radionuclides such as DU can be obtained by performing well defined
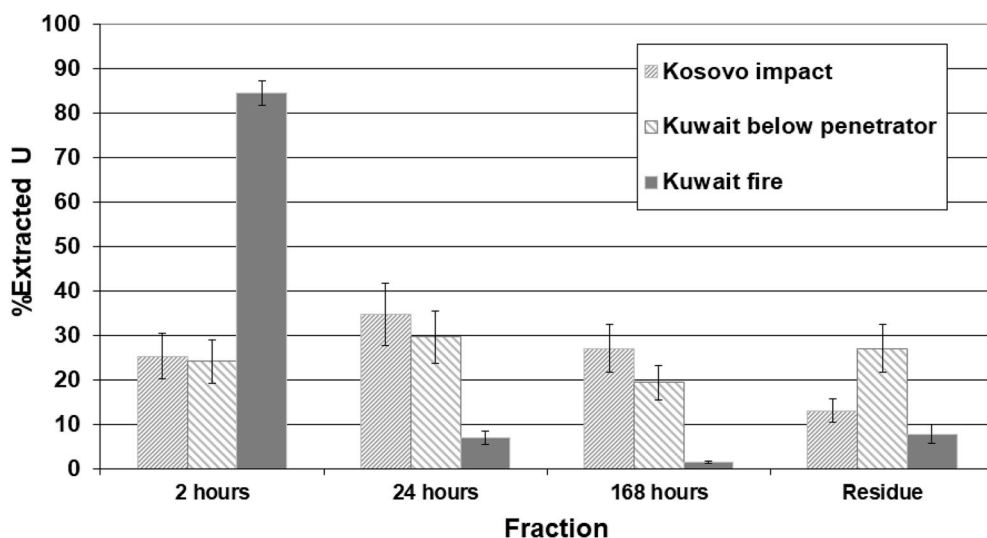
Fig. 2. Relative extracted fraction (%) of U from DU particles as a function of contact time with simulated gastrointestinal fluid (0.16 M HCl) at room temperature. The DU particles were collected at selected sites in Kuwait and Kosovo, and the oxidation state of U depended on the source and release conditions; DU following Kosovo impact (corrosion e.g., U met), DU following Kuwait below penetration weak (slight oxidized e.g., UO2), DU following Kuwait fire (strongly oxidized e.g., schoepite and its derivatives). Modified from Lind et al. (2009).

leaching or extraction experiments. Following the EU COMET-RATE/IAEA-CRP protocols (Salbu et al., 2018), simulated stomach juice (0.16 M HCl) can be utilized for leaching of well characterized single particles as well as of bulk samples under controlled conditions. By performing size fractionation of leachate, particle breakdown products can be quantified. Using advanced micro- and nano-analytical techniques to characterize particles before and after extractions enables quantification of transformation (e.g. decreased size and removal of phases, increased porosity) of particles during exposure in leaching media. Fig. 2 illustrates the usefulness of the leaching protocols, where the relative fractions (%) extracted from soils contaminated with DU particles originating from the ammunition fire incident in Kuwait are compared with those from DU particles originating from corrosion of unspent DU penetrators and from impacted DU ammunition. Particles from the fire incident containing highly oxidized DU were rapidly dissolved in 0.16 M HCl ($84 \pm 3\%$ extracted after 2 h contact time), whereas the fractions leached were much lower for particles originating either from corrosion of unspent DU penetrators or from impacted DU ammunition (20–30% extracted after 2 h). Even though the results are based on a limited number of particles, they indicate that the crystalline structures, the oxidation state of U and subsequently the extractability of DU particles released from similar sources (metallic U-Ti penetrators) will depend on the release scenarios (fire, impact) and to some extent on environmental conditions. Thus, the solid state speciation and consequently the potential mobility and bioavailability of DU particles released during the storage fire and subsequently subjected to weathering in the Kuwaiti desert for ~10 yrs were significantly different from DU particles released during impact ~5 yrs prior to sampling (Lind et al., 2009). Longer term extraction (1 week) showed, however, that most of the DU particles (73–96%) in all investigated samples were dissolved in 0.16 M HCl, indicating that a majority of the DU material at contaminated sites is bioaccessible regardless of release scenario and environmental weathering (Lind et al., 2009).

5. Dose assessment for DU material

Three main pathways for human exposures to DU can be distinguished: inhalation, ingestion and contamination of wounds. Inhalation of dispersed particles may occur either directly after an impact and disintegration of DU ammunition and any accidental release in the atmosphere or the resuspension of previously deposited DU particles. Ingestion may happen from contaminated soils, drinking waters and food stuffs. DU material may enter the human body by wounds either caused by military action or accidental injuries.

Uranium is considered as chemically toxic with the kidneys as main target organ (WHO, 2001, 2011). There are also reports about cytotoxic and clastogenic effects of inhaled DU material to human lung cells (Wise et al., 2007). The World Health Organization (WHO) has established several limits for uptake: as tolerable daily intake (TDI) 60 μg uranium are recommended; the provisional guideline value for drinking water is $30\,\mu g\,l^{-1}$ (WHO, 2011), suggested according to newest epidemiological studies. Long-time studies of uranium leaching rates of corroding DU weapons in soil found huge increases after three years of observation (Schimmack et al., 2005, 2007), emphasizing the need of continuing ground water tests in areas affected by DU material.

In order to perform radiation dose assessment of DU materials, dose coefficients are necessary, which relate the exposure to the resulting organ and effective dose. The International Commission on Radiological Protection (ICRP) has published detailed biokinetic and dosimetric models, which supply these dose coefficients for default conditions for each uranium isotope. First they were provided for workers (ICRP, 1979) and then for the general public (ICRP, 1995a, b) by adapting the general exposure conditions (e.g. aerosol particle size and physiological parameters). The default parameters for both scenarios are discussed in ICRP, (1994a, b, 1996) for inhalation and ingestion. Important material-specific parameters are the particle size of the suspended DU material and its solubility in the lungs and the gastric tract. ICRP emphasized that specific experimental data should be favored over default values for dose assessment where available (Valentin and Fry, 2003). A biokinetic model for radionuclide uptake by contaminated wounds was developed by the National Council on Radiation Protection and Measurements (NCRP) and ICRP (NCRP, 2007). Li et al. (2009) coupled the wound model with the ICRP systemic biokinetic model for uranium to assess the internal dose of DU by a potential route through the wound site.

The instruments for dose assessment are available as detailed above and must be adjusted for the specific DU material. Valentin and Fry (2003) suggested different absorption types according to the speciation of the uranium compounds and gave as an example an inhalation dose coefficient for DU particles of 5 μm size and slow solubility (type S) of 5.6×10^{-6} Sv Bq^{-1}. In the Capstone study (Parkhurst et al., 2004) experimental data on the particle size distribution and *in vitro* solubility were obtained from DU munitions used from the US armed forces during the 1991 Gulf war. Dose coefficients in dependence from the particle size for solubility were reported to range from 40×10^{-6} to 1.0×10^{-6} Sv Bq^{-1} for type S and from 25×10^{-6} to 0.2×10^{-6} Sv Bq^{-1} for type M material, respectively (Guilmette and Parkhurst, 2007). The maxima were in the submicron range. Li et al. (2009) implemented the particle
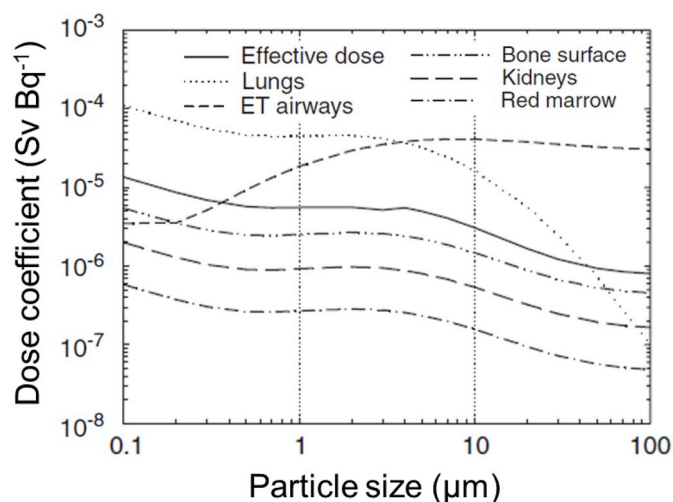
Fig. 3. Inhalation dose coefficient of ^{238}U in dependence on the activity median aerodynamic diameter (AMAD), modified from Li et al. (2009).
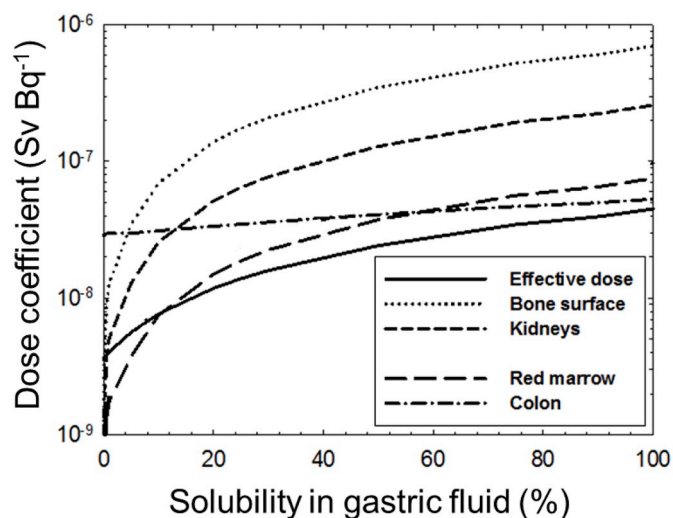

Fig. 4. Ingestion dose coefficient for DU material in dependence of the solubility in the gastric fluid for several organs and the effective dose, modified from Li et al. (2009).

size data of the Capstone study (Parkhurst et al., 2004) and the *in vitro* solubility parameters experimentally determined from ammunition remains of Kosovo origin by Gerstmann et al. (2008) in the ICRP models. The inhalation dose coefficients in dependence of the particle size are given in Fig. 3. The effective dose decreases from 15×10^{-6} Sv Bq^{-1} at 0.1 μm particle size to 0.8×10^{-6} Sv Bq^{-1} at 100 μm. The lungs receive the highest organ dose until a particle size of about 4 μm; the dose to the extrathoracic (ET) region dominates at larger particle sizes.

In regard to the ingestion dose assessment, Valentin and Fry (2003) recommend a gastro-intestinal uptake factor f_1 of 0.02 for unspecified compounds and 0.002 for most tetravalent compounds. Li et al. (2009) calculated the dose coefficient as a function of the solubility of the DU material in the gastric fluid (Fig. 4). The effective dose coefficient increases from 3.6×10^{-9} to 4.8×10^{-8} Sv Bq^{-1}, by a factor of 13.3, as the solubility increasing from 0% to 100% with a value of 2.4×10^{-8} Sv Bq^{-1} at a solubility of 50%. The ingestion dose coefficient of DU materials is about 75% of the natural uranium value.

Studies on American soldiers wounded with DU shrapnel have shown that the DU material slowly solubilizes in the body fluids and that several years after the injury, blood and urine levels are still elevated up

to two orders of magnitude (Hooper et al., 1999). Li et al. (2009) studied wound uptake and retention of DU material in the human body. Uranium retention after entering into the wound depends strongly on the form and solubility of the material. The weak soluble ^{238}U follows the same behavior as injected directly into blood. The other soluble materials, for example, moderate, strong and avid have the similar shape of retention and excretion. Exposure to soluble DU is associated with longer retention times in the body than for exposure to colloidal, particulate or fragments of DU.

Uranium is both a chemical and radioactive toxin, with chemical toxicity dominant at enrichments below about 7–20% (Stannard, 1988; Brodsky, 1996; ATSDR, 2013). As enrichment decreases, so does the radiotoxicity, while chemical toxicity remains constant. Thus, at lower enrichments such as DU (0.2%), the toxic effect is overwhelmingly from chemical and not radiological effects (Kathren and Burklin, 2008).

6. Conclusions

This summary shows that DU particle characteristics are influenced by the source term and the release scenario. Following deposition, transformation processes influencing the DU characteristics can also occur due to geochemical processes in the environment. Information on site-specific particle characteristics obtained by spatially resolved solid state speciation techniques have been linked to extraction kinetics and potential mobility and bioavailability of DU originating from different particle formation processes. Thus, the results from DU particle studies should be of generic value for environmental radioactivity. Future work should benefit from utilizing a combination of advanced solid state speciation techniques and relevant extraction schemes for environmental impact assessments in areas contaminated with DU particles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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