
DEPLETED URANIUM (DU) MOBILITY IN THE NATURAL ENVIRONMENT

K. Vala Ragnarsdottir
Department of Earth Sciences, University of Bristol,
Bristol BS8 1RJ, UK
Vala.Ragnarsdottir@bris.ac.uk

ABSTRACT

In 1999 the Balkan's conflict lead NATO war planes to leave 10×10^3 kg of depleted uranium (DU) in the environment of Kosovo and neighbouring states (UNEP, 2001). DU behaves in the same manner in the environment as natural uranium and it can be traced with isotopic analysis due to the fact that DU has the isotopic composition of 0.2% ^{235}U and 99.8% ^{238}U as opposed to natural uranium which has 0.7% ^{235}U and 99.3% ^{238}U . DU is a waste product of the nuclear industry which enrich nuclear fuel by ^{235}U . Large stock piles of DU therefore exist in countries that produce nuclear energy and/or nuclear weapons. The DU is given to the weapons industry for free (or cheap) and has been a popular choice for armour penetrating arsenal due to the high density of uranium (19 g cm^{-3}) and therefore its high penetrating power. Indeed the arsenal used in Kosovo consisted of DU penetrators that were shot from A-10 aeroplanes. They weigh roughly 300 g and have the shape of a fat 9 cm long pencil.

Key words: depleted uranium, ammunition, environment, uranium mobility

URANIUM IN THE ENVIRONMENT

Uranium is ubiquitous in all rocks, soils, rivers and groundwaters on the Earth's surface. Average values for uranium in rocks are about 2-3 mg/kg (mg kg^{-1}) and concentrations vary slightly ($1\text{-}30 \text{ mg kg}^{-1}$) according to rock type. For natural waters uranium is much lower in concentration than in natural rocks and the variations are typically from less than $1 \mu\text{g l}^{-1}$ to roughly $100 \mu\text{g l}^{-1}$.

The results of the United Nations DU Assessment Team's field studies in Kosovo (Nov 2000) demonstrate that the majority of the 10×10^3 kg of depleted uranium penetrators introduced into the Kosovo environment are buried deep in soils and rocks (UNEP, 2001). The most likely harm that the depleted uranium could thus cause to the local population is by dissolution of the penetrators by soil water and transport of the dissolved uranium down to the groundwater table. This uranium could thus enter drinking water wells and be a possible cause of radiation and chemical toxicity. The UNEP study showed that A10

attacks introduced one penetrator into the soil at an interval of 5-6 m. US test range data indicate that for soft soil the penetrators can go as deep as 6-7 m and that they will sometimes shatter. Therefore it can be assumed that each penetrator contaminates a minimum of 1 m³ of rock. The depth to the groundwater table then needs to be taken into account. The UNEP team observed that the shallowest groundwater wells had depths to the groundwater table of 2 m and the deepest one was 35m. Each penetrator thus has the capacity to contaminate 2 m³ to 35 m³ of rock before the groundwater is affected, if it is imagined that a column of 1 m² in area goes down to the groundwater table. The average concentration of uranium in 1 m³ of rock/soil (natural uranium plus one penetrator of 300 g) is 115 ppm (38 fold increase over natural uranium), in 2 m³ of rock is 57 ppm (19 fold increase) and in 35 m³ of rock 3.3 ppm (10% increase).

Uranium metal is unstable in contact with oxygen and water; therefore uranium oxides form on the surface of the penetrators or fragments thereof. In the presence of water these oxides are hydrated. The maximum solubility of oxidised uranium phases (surface layers on penetrators - e.g. schoepite, UO₃·nH₂O) at near-neutral pH as found for the Kosovo waters is about 10 mg l⁻¹. However, there are many processes in nature which can retard the transport of uranium. They include sorption to minerals and organics in the soil, co-precipitation with calcite and reduction (iron-II-bearing minerals, bacteria, organic matter) of the uranium from its hexavalent soluble form to its tetravalent (uraninite, UO₂ - solubility at neutral pH 0.1 µg l⁻¹) insoluble form.

The rocks that comprise the areas UNEP visited were largely limestones. The soil thickness varied, from 4 m in some areas, to only a few cm in others. Most of the wells are less than 10 m in depth and can thus be considered to be in unconfined (or surface) aquifers. Therefore there exists no confining layer that can protect the aquifers from depleted uranium. The climate in Kosovo can be considered humid-continental with precipitation close to 75 cm yr⁻¹. This precipitation value represents the infiltration rate into the surface aquifers.

The penetrators that were retrieved by the UNEP team in Kosovo had clear signs of two alteration phases, one black and the other yellow. Analysis of a penetrator fragment shows that the uranium at the surface consists of U(6+) and U(4+) as determined from reference spectra by Allen et al. (1984). The alteration phases are yellow and black are thus uranium oxides. A French study of depleted uranium metal found in a test site in Southern France (Crançon, 2001) showed that these two phases are UO₂(OH)₂(s) and UO₃·2H₂O (schoepite). The former is likely to be the black alteration phase and the latter the yellow alteration phase. Since the yellow phase is more abundant on the surface, it can be concluded that the black phase (U⁴⁺) is an intermediary step in the alteration from uranium metal (U⁰) to the fully oxidised yellow phase (U⁶⁺).

DU FIELD OBSERVATIONS

At **Djakovica Garrison** a penetrator was found under 5 cm of soil. From studies of the uranium concentrations in soils below this penetrator and the amount of uranium that could be easily "swiped" off the penetrator in the field it can be concluded that 5-10% (15-30g) of the original weight (300 g) of the penetrator has oxidised in 18 months and about two thirds had moved down the soil profile, to the depth of 12.5 cm below the penetrator. This indicates that in soil solutions the rate of schoepite dissolution is about the same as the rate of oxidation of the penetrators. This can be concluded from comparison with laboratory dissolution studies of schoepite (Duro, 1996), which is 32g/300g of schoepite, assuming

that the surface area of the penetrator is 27 cm². If the penetrator shatters, its surface area is increased and the dissolution rate increases accordingly. It is thus likely that all of the penetrators will dissolve totally in less than 15 years. Upon oxidation of the DU metal the soils and rocks will contain elevated concentrations of schoepite. With time the schoepite will dissolve and uranium will move downward through the soil. The distance the uranium will be transported, however, is limited if the penetrator is embedded in organic-rich soil. Once the uranium comes into contact with organic matter and clay minerals (<100 μm) further down the soil profile, the uranium will initially be sorbed to these minerals (Waite et al., 1994) and organic matter (Nash et al., 1981). Due to the presence of divalent iron in the soil minerals (Liger et al., 1999) and bacteria (e.g. Loveley et al. 1991), uranium will be reduced to its insoluble tetravalent form (e.g. Ragnarsdottir and Charlet, 2000).

At **Vranovak** there are apparently 600 kg of depleted uranium embedded in an esker (glacial) ridge that rises about 30 m over the landscape. The minimum depth to the local well water is 2 m. Eskers are generally composed of silty sand and gravel and are thus very permeable. The ridge was covered with soil, and the thickness is about 0.5 m. If the shooting was primarily at the top of the hill then there are about 30 m of sand and gravel for the uranium to pass through before entering the drinking water. Course grained sand and gravel has very low sorption capacity for uranium. Therefore if the DU penetrators were shot deep into the hill (no DU found on the surface). The penetrators are thus lying in rocks with a very low buffering capacity for both uranium reduction and sorption. It is therefore possible that the DU penetrators can dissolve and enter the groundwater. Using laboratory uranium sorption/co-precipitation data for waters that are in equilibrium with calcite (Carroll and Bruno, 1991) it can be calculated that the retardation factor (K_d) for uranium is very low (4-200) for the waters at Vranovak hill. Therefore uranium can be transported with these waters. By assuming a range for hydraulic conductivity in silty sand ($K = 10^{-3}$ m/s to 10^{-7} m/s), that the porosity of the rocks is 0.3 and the hydraulic head 1 m, and that the flow is perpendicular to the length of the hill and using Darcy's law, it can be estimated that it will take the local groundwater 1 day to 27 years (!) to reach the farm-wells along the ridge, if the shooting was aimed at the centre of the ridge (minimum distance to farms, 250 m). The isotopic values for uranium in the local wells show that the depleted uranium has not yet reached the farms. In the UNEP study all of the drinking waters that were analysed in Kosovo had uranium values of 2 μg L⁻¹ and below.

Rznik village is about 500 m from the alleged A10 attack but no evidence of penetrators or radiation was found on the surface. The depth to the closest well is 5m and the soil thickness is about 4 m. The area shows evidence of a typical karst landscape and therefore the bedrock is composed of limestones. The wells sampled in the village (a farm and the school well) have water compositions that are undersaturated with respect to calcite. Iron values of the waters show that the waters may be reduced and therefore it is possible that uranium will precipitate as UO₂ and reduce the mobility of uranium in the water. There exists, however, the possibility that the waters contain some oxygen, allowing uranyl to be transported as carbonate complexes. By assuming a range for hydraulic conductivity in karst limestone ($K = 10^{-2}$ m/s to 10^{-6} m/s), that the porosity of the rocks is 0.4 and the hydraulic head 0.1 m, and that the flow is towards the village and using Darcy's law, it can be estimated that it will take the local groundwater 2 days to 63 years (!) to reach the farms in the village.

Large uncertainties exist for DU mobility due to lack of kinetic and hydrological data. All sites where DU was used need to be monitored and samples taken of private well waters. In

order to evaluate whether populations near an alleged A10 attack are in danger of drinking uranium contaminated waters - waters need to be sampled and filtered and analysed for major elements such as total alkalinity, calcium and iron. An aliquot of the water needs to be acidified on site and analysed for uranium. For monitoring purposes no isotopic analysis is necessary. Another aliquot of water needs to be filtered but not acidified and analysed for Fe and Ca. The alkalinity, pH and Eh need to be analysed in the field. For modeling purposes each site needs to be evaluated with a hydrologist. If the uranium values will rise in the future to concentrations above a limit set by the local authorities, two possibilities remain:

- 1) Boiling of the water prior to drinking, which precipitates uranium with calcium carbonate; or
- 2) apply phosphate to the surface of the soils, precipitating U-phosphate. Uranyl-phosphates and calcium-uranyl phosphates have very low solubility and will retain the uranium in the soils and rocks (Valsami-Jones et al., 1996; Bruno et al., 1998).

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