

1 Introduction

WHO commissions reviews and undertakes health risk assessments associated with exposure to potentially hazardous physical, chemical and biological agents in the home, work place and environment. This monograph on the chemical and radiological hazards associated with exposure to depleted uranium is one such assessment.

The purpose of this monograph is to provide generic information on any risks to health from depleted uranium from all avenues of exposure to the body and from any activity where human exposure could likely occur. Such activities include those involved with fabrication and use of DU products in industrial, commercial and military settings.

While this monograph is primarily on DU, reference is also made to the health effects and behaviour of uranium, since uranium acts on body organs and tissues in the same way as DU and the results and conclusions from uranium studies are considered to be broadly applicable to DU. However, in the case of effects due to ionizing radiation, DU is less radioactive than uranium.

This review is structured as broadly indicated in Figure 1.1, with individual chapters focussing on the identification of environmental and man-made sources of uranium and DU, exposure pathways and scenarios, likely chemical and radiological hazards and where data is available commenting on exposure-response relationships.

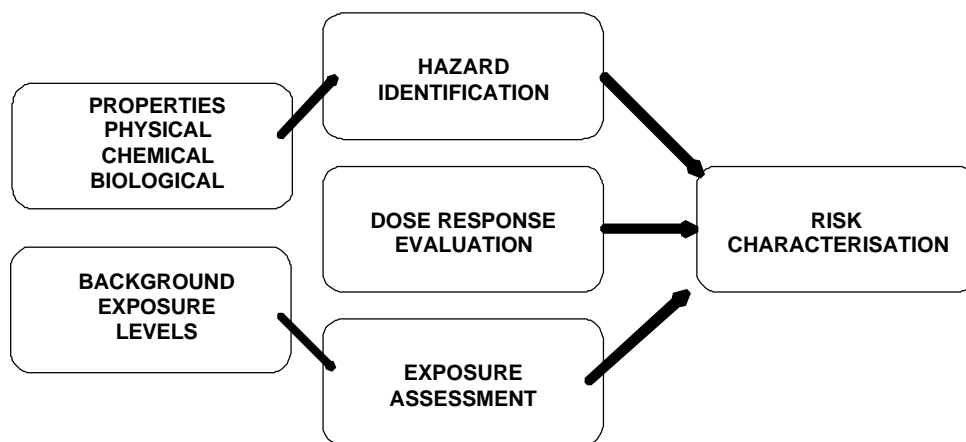


Figure 1.1 Schematic diagram, depicting areas covered by this monograph.

It is expected that the monograph could be used as a reference for health risk assessments in any application where DU is used and human exposure or contact could result. Information is provided that should also be applicable to exposure of people during or following military conflict. Details are provided on the characteristics of uranium and DU, historical and current applications, behaviour in the environment, factors that influence human exposure, how it acts on the body, chemical and radiological toxicity, health and medical monitoring, protective measures and public health standards.

Gaps in knowledge have been identified that require further research which will improve future health risk assessments. Scientists world wide are encouraged to take up the challenge to undertake this research in order that a more complete picture of the health effects of DU will result.

Readers who will benefit most from this monograph are:

- scientists involved in the assessment of health risks and environmental protection.
- clinicians needing to assess situations where people may be exposed excessively to DU and may be considering medical monitoring or follow-up.
- national authorities developing programmes to deal with human exposure and environmental contamination following conflicts where DU weapons were used.

A glossary of key terms and units is provided.

2 Properties of uranium and depleted uranium

2.1 Uranium

Uranium is a silver-white, lustrous, dense, natural and commonly occurring weakly radioactive element. It is ubiquitous throughout the natural environment, being found in varying but small amounts in rocks, soils, water, air, plants, animals and in all human beings.

Elemental uranium has an atomic number of 92 and an atomic weight of 238.0289 g/mol and is a member of the actinide series of the periodic table. Metallic uranium has a high density of 19 g/cm³, slightly less than tungsten but significantly greater than lead with a density of 11.3 g/cm³. The metal tarnishes in air and is ductile, malleable and capable of being highly polished.

Natural uranium contains three radioactive isotopes (or radio-isotopes) ²³⁴U, ²³⁵U and ²³⁸U. The percentage of each radio-isotope by weight is about 0.0054% ²³⁴U, 0.72% ²³⁵U and 99.27% ²³⁸U. About 48.9% of the radioactivity is associated with ²³⁴U, 2.2% with ²³⁵U and 48.9% with ²³⁸U. The half-lives (time for the radioactivity to decay to half its original value) of the uranium radio-isotopes are very long, 244 000 years for ²³⁴U, 710 million years for ²³⁵U and 4500 million years for ²³⁸U. The longer the half-life the less radioactive is a given mass of material. Uranium decays into many other radio-isotopes, called progeny, until it finally ends up as stable (nonradioactive) isotopes of lead. Due to its long radioactive half-life in comparison to the age of the solar system, uranium is considered to be a naturally occurring primordial radio-element.

When finely divided in air, uranium metal is combustible and ignites readily, a property known as pyrophoricity which is also typical of other metals such as aluminium (Al) and iron (Fe). Thus when used in military armour or projectiles, or when present in an air crash or fire in which significant heat is generated, uranium may form fine dust containing a mixture of uranium oxides.

All isotopes of uranium undergo the same chemical reactions in nature and possess almost identical physical characteristics, such as melting point, boiling point and volatility. The radioactive properties (half-life, specific activity, decay mode etc.) of all uranium isotopes are however different.

In their pure form, natural uranium, enriched uranium and DU vary only according to their isotopic composition and are therefore almost chemically identical, undergoing identical chemical reactions in the environment and exerting the same chemical, biochemical and biological effects on the human body. Where small differences in chemical behaviour exist these will be due to the small mass difference between various uranium isotopes.

Uranium compounds These differ substantially in their chemical and physiological properties and in the toxicological effects they exert. For example, compounds such as uranium trioxide (UO₃), uranyl chloride, uranyl nitrate and uranyl ethanoate are relatively soluble, whereas uranium dioxide (UO₂) and triuranium octaoxide (U₃O₈) are considered to be relatively insoluble. Many publications have been devoted to the aqueous chemistry, mineralogy and properties of uranium, and numerous reviews are available (e.g. Burns and Finch, 1999; ATSDR, 1999, DeVivo et al., 1984).

Units Units of concentration used to describe the abundance of uranium are diverse, and often complicate, rather than facilitate a comparison of data from differing sources. The concentrations of individual isotopes of uranium are generally recorded as the radiochemical activity present in a unit volume of a substance, e.g. picocuries per litre (pCi/l) or becquerels per litre (Bq/l), picocuries per kilogram (pCi/kg) or becquerels per kilogram (Bq/kg). The use of picocuries is still common in the literature even though this has been superseded by the becquerel as the SI unit for radioactivity. One Bq is defined as one nuclear transformation per second. One Bq is equal to approximately 27 pCi.

It is equally common practice to measure and report natural uranium content or concentration in mass units (i.e. $\mu\text{g/l}$, $\mu\text{g/kg}$ or moles/kg). These units are used throughout this work for consistency. Concentrations of uranium may also be quoted in terms of molar concentrations, 1 μmole of uranium being equivalent to 0.000 238 g of ^{238}U and correspondingly 1 μg of ^{238}U = 0.0042 μmole .

Radio-isotope properties In most situations the natural uranium isotopes occur with the relative mass abundances given in Table 2.1. However, in some circumstances such as in the natural nuclear reactor at Oklo in Gabon (e.g. Burns and Finch, 1999) and in natural waters (e.g. Ivanovich and Harmon, 1982), soils and atmospheric dusts (US EPA, 1994), these ratios may be influenced by natural nuclear and chemical processes that have led to the enrichment or depletion of ^{235}U and/or ^{234}U relative to ^{238}U . It is therefore important when using isotopic ratios to forensically identify exposure to DU that the potential for changes in natural isotopic ratios are taken into account.

Table 2.1 Relative mass abundances and isotopic ratios for natural uranium isotopes (Steiger and Jager, 1977; Kaye and Laby, 1993).

Isotope	Abundance
^{238}U -	99.2745%
^{235}U -	0.7200%
^{234}U -	0.0054%
$^{235}\text{U}/^{238}\text{U}$	0.00725
$^{234}\text{U}/^{238}\text{U}$ *	0.0000554

* Range from 0.000 05 to 0.0004 in atmospheric dusts (US EPA, 1994) and 0.000 03 to 0.0014 in natural waters (Ivanovich and Harmon, 1982).

In nature, uranium occurs in conjunction with its radioactive decay products (Tables 2.2 and 2.3). However, when purified for chemical or nuclear purposes, uranium is generally separated from its decay products and is therefore less radioactive than original impure ore containing a similar weight of uranium.

Table 2.2 ^{238}U decay series (Kaye and Laby, 1993).

Isotope	Half-life	Principal decay mode
^{238}U	4.5×10^9 y	alpha
^{234}Th	24 d	beta
$^{234}\text{Pa}^{\text{m}}$	1.17m	beta
^{234}Pa	6.8 h	beta
^{234}U	2.4×10^5 y	alpha
^{230}Th	7.3×10^3 y	alpha
^{226}Ra	1.6×10^3 y	alpha
^{222}Rn	3.8 d	alpha
^{218}Po	3.1 m	alpha
^{218}At	2 s	alpha
^{214}Pb	27 m	beta
^{214}Bi	20 m	beta
^{214}Po	160 μs	alpha
^{210}Tl	1.3 m	beta
^{210}Pb	22 y	beta
^{210}Bi	5.0 d	beta
^{210}Po	138 d	alpha
^{206}Tl	4.2 m	beta
^{206}Pb	Stable	—

Table 2.3 ^{235}U decay series (Kaye and Laby, 1993).

Isotope	Half-life	Principal decay mode
^{235}U	7.0×10^8 y	alpha
^{231}Th	26 h	beta
^{231}Pa	3.3×10^4 y	alpha
^{227}Ac	22 y	beta
^{227}Th	19 d	alpha
^{223}Fr	21.8 m	alpha
^{223}Ra	11.4 d	alpha
^{219}Rn	4.0 s	alpha
^{215}Po	1.8 ms	alpha
^{215}At	1×10^{-4} s	alpha
^{211}Pb	36.1 m	beta
^{211}Bi	2.2 m	alpha
^{211}Po	0.5 s	alpha
^{207}Tl	4.8 m	beta
^{207}Pb	Stable	—

2.2 Depleted uranium

DU, as a by-product of uranium enrichment (see Annex 1) required for the nuclear industry, has only been available since about 1940. As such it can only contain very low levels of many of the naturally occurring radioactive decay products of uranium listed in Tables 2.2 and 2.3.

Uranium is classed as DU when the abundances of ^{235}U and ^{234}U are reduced relative to ^{238}U . Depleted uranium typically has around 0.3% to 0.2% ^{235}U by mass, although the Nuclear Regulatory Commission in the US defines DU as uranium in which the percentage of ^{235}U is less than 0.711% (NRC, 2000). Consequently, DU has a marginally higher percentage of ^{238}U (99.8%) than naturally occurring uranium (99.3%). The isotopic composition of DU typically used by the US Department of Defence as quoted in CHPPM (2000) is $^{234}\text{U} = 0.0006\%$, $^{235}\text{U} = 0.2\%$, $^{236}\text{U} = 0.0003\%$ and $^{238}\text{U} = 99.8\%$.

Some preparations of DU may also contain transuranic elements and fission products (e.g. Rich, 1988; CHPPM, 2000). This occurs because the same enrichment plants are used for both natural uranium and for reprocessing spent uranium nuclear fuel rods. The latter can cause contamination of the enrichment plant with reactor-made isotopes that will subsequently contaminate the DU from natural uranium enrichment. Such DU may consequently be very slightly more radioactive than DU derived from mined uranium ore. Typical trace isotopes identified as being present in DU used in munitions and armour manufacture include ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{241}Am , ^{237}Np and ^{99}Tc . These impurities typically add less than 1% to the dose from DU and are therefore inconsequential from a radiological or chemical toxicity standpoint (CHPPM, 2000). This has been verified from a radiological standpoint based on available data regarding the concentrations of these isotopes in DU stocks from the USA (see Annex 2).

A recent survey of DU in Kosovo by the United National Environment Programme provided an analysis of penetrators found in conflict areas (UNEP, 2001). The activity concentration of transuranic elements in these penetrators indicated that there was up to 12 Bq/kg of plutonium isotopes and for ^{236}U the activity was up to 61 kBq/kg. This compared to an activity concentration of 12 700 kBq/kg for ^{238}U .

^{238}U has a longer half-life than either ^{235}U or ^{234}U and it is present in a much greater abundance in natural and DU than ^{235}U or ^{234}U . The number of alpha particles produced per year in one milligram of natural uranium from the decay of ^{238}U , ^{235}U and ^{234}U may be calculated to be 3.9×10^{11} , 1.7×10^{10} and 3.9×10^{11} , respectively.

Specific activities and data related to isotopes commonly found in DU are given in Table 2.4.

As well as decay through the emission of alpha particles, atoms of ^{238}U may also decay through spontaneous fission, an energetic process that releases approximately 40 times more energy per nuclear decay. The spontaneous fission half-life for ^{238}U is estimated to be 8.5×10^{17} years (De Carvalho et al., 1982) which, although much longer than its alpha decay half-life, results in approximately two atoms of ^{238}U in every milligram of uranium decaying by this process each year. Similarly rates of spontaneous fission from other natural and anthropogenic (human produced) isotopes of actinides associated with DU are low compared to the rates of other decay modes (e.g. alpha).

DU has a specific activity of 14.8 Bq/mg which is approximately 60% that of natural uranium (25.4 Bq/mg) due to the partial removal of ^{234}U . In practice, not all ^{234}U is removed in the separation process and the exact concentration remaining in DU depends on separation plant characteristics and required yields.

Following chemical separation of uranium, radioactive progeny (or ‘daughter products’) are produced by the radioactive decay of uranium ‘ingrow’ (for an extensive discussion of radioactive ingrowth, radioactive equilibrium, secular equilibrium, radioactive decay series and their effect on isotopic composition the reader is referred to Faure, 1986). During the first year, the activity of immediate progeny (the beta decaying isotopes ^{234}Th , $^{234\text{m}}\text{Pa}$ and ^{231}Th) reach secular equilibrium. Following this initial ingrowth period the activity of isotopes remains approximately constant for over 1 000 years (Figure 2.2a and 2.2b), although ^{231}Pa (^{235}U decay chain) will begin to ingrow during this period (Figure 2.2b)

Table 2.4 Specific activities of uranium and other radionuclides associated with DU (Lederer et al., 1978; Kaye and Laby, 1993).

Radionuclide (Decay Modes)	Half-life (million years)	λ (per second)	Atomic weight (MW)	Specific activity as Bq/mg
Natural U	-	-	-	25.4
^{238}U (α) + (sf_{rare})	4470	4.91×10^{-18}	238	12.4
^{236}U (α)	23.42	9.38×10^{-16}	236	2390
^{235}U (α and γ)	704	3.12×10^{-17}	235	80
^{234}U (α)	0.245	8.96×10^{-14}	234	2.31×10^5
^{232}U (α)	0.000072	3.05×10^{-10}	232	7.92×10^8
^{231}Pa (α and γ)	3.28×10^{-2}	6.70×10^{-13}	231	1.75×10^6
$^{234}\text{Pa}^{\text{m}}$ (β)	2.29×10^{-12}	9.59×10^{-3}	234	2.47×10^{16}
^{231}Th (β and γ)	2.91×10^{-9}	7.54×10^{-6}	231	1.97×10^{13}
^{234}Th (β and γ)	6.06×10^{-8}	3.33×10^{-7}	234	8.57×10^{11}

sf_{rare} indicates decay through spontaneous fission with a half-life much greater than that of other major decay modes.

Note: ^{236}U does not occur naturally although it may be present in DU derived from the nuclear industry.

The short half-lives, chemical nature and decay mode of many of the decay products of ^{238}U and ^{235}U significantly increase the radiological hazard of natural uranium mineralisation and uranium ore. These radioactive progeny are removed during the preliminary stages of uranium ore purification, making the processed chemically pure uranium significantly less radiologically toxic than equivalent amounts of the original ore.

On a weight-by-weight basis the reduced proportion of ^{235}U and ^{234}U , and the absence of radioactive progeny such as radium in DU, means that DU poses less of a radiological hazard than either pure processed uranium or naturally occurring uranium ores, respectively. Figures 2.2a and 2.2b show the ingrowth of ^{235}U and ^{238}U progeny,

and consequent increase in total activity over time in freshly prepared DU. One result is a marked increase in beta and gamma radiation levels as times passes, although the level of alpha decay continues to be the principal concern in respect of internal dose estimation.

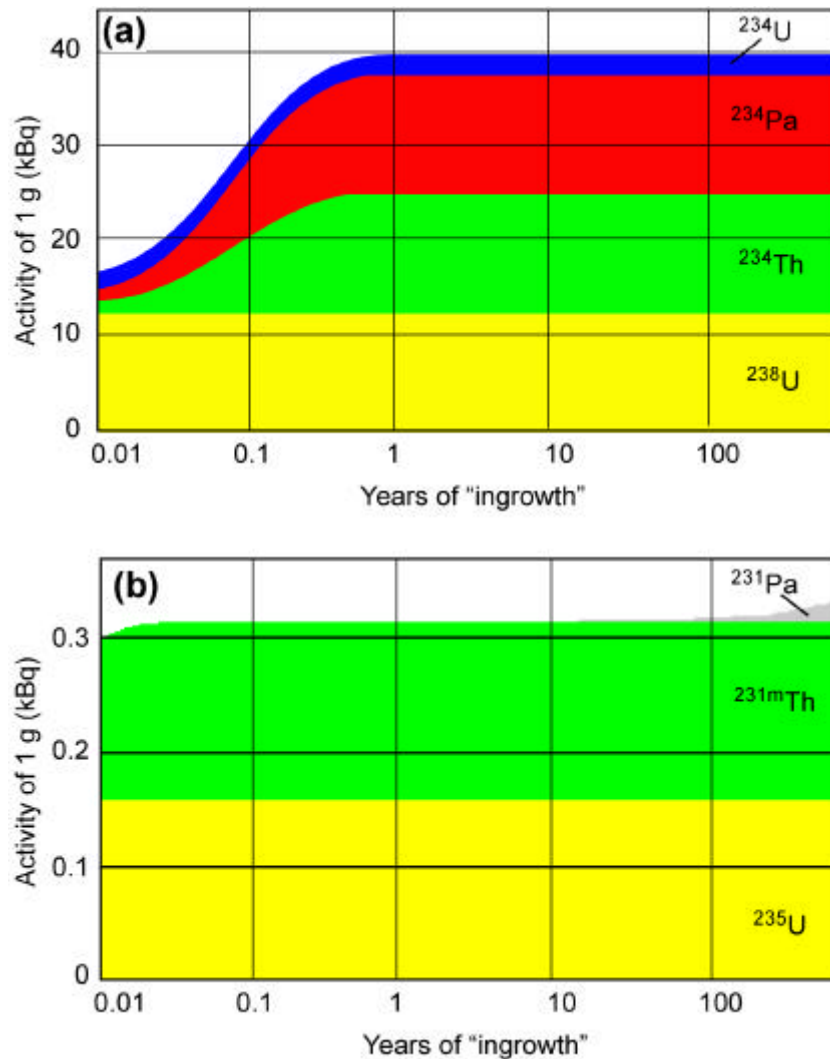


Figure 2.2a ^{238}U decay and **Figure 2.2b** ^{235}U decay. Variation in activity (kBq/g) of uranium and uranium decay products for the first 1000 years following chemical separation of a sample of DU containing 0.2% ^{235}U and a typical amount of ^{234}U . Note the numerical dominance in activity due to the ^{238}U decay series and the beginning ‘ingrowth’ of ^{231}Pa (^{235}U decay series) after approximately 500 years.

2.3 Summary

Natural uranium consists of three different isotopes: by mass the composition is ^{234}U (0.0054%), ^{235}U (0.72%) and ^{238}U (99.2746%). It is present to some extent in all environmental materials (e.g. soils, surface waters, groundwaters, foodstuffs, air, etc.).

Uranium is classed as depleted uranium (DU) when the abundance of its isotopes ^{235}U and ^{234}U are reduced relative to ^{238}U . Depleted uranium has typically about 60% of the radioactivity found in natural uranium with only an infinitesimal change in mass.

Both uranium and DU and their immediate decay products (e.g. ^{234}Th , $^{234\text{m}}\text{Pa}$ and ^{231}Th) emit alpha and beta particles with a very small amount of gamma radiation. Alpha and

beta radiations are not very penetrating and are easily absorbed in the air and the skin. The half-life of DU, or the time for the radiation dose to decay to half its original value is many millions of years.

Natural uranium and DU are considered to be weakly radioactive. In the event that DU is produced by enrichment of spent reactor fuel rods, the additional radio-isotopes in the DU increase the overall radiation dose of the DU by less than 1%. This additional radiation dose is considered to produce no additional radiological consequence.

3 Uranium in the environment

Uranium occurs in rocks, sea and fresh water and in the human body (see Table 3.1). Uranium (U) is a naturally occurring element with an average abundance in the Earth's crust of about 2 mg per kg (range 0.1 to 20 mg per kg). It is more abundant than silver or gold. For example Alloway, (1995) has quoted an average concentration and range in typical crustal rocks of 2.5 mg/kg and 0.05 mg/kg to 5 mg/kg, respectively, although higher concentrations commonly exist in some mineralized environments.

Table 3.1 Concentrations of uranium in various environmental systems and materials (Kaye and Laby, 1993).

Physical Entity	Abundance (mg/kg)
Crustal rocks	1.800*
Sea water	0.0033
Stream water	0.00004
Human	0.001

* Note different value from that quoted by Alloway (1995) emphasising the variability of such gross compositional estimates, which is also the case for many other elements in crustal rocks.

During natural geological processes such as the partial melting and fractional crystallisation of the Earth's mantle, uranium becomes preferentially concentrated in the liquid phase and consequently becomes incorporated into the more silica-rich products. Because of this, igneous rocks such as granites are typically enhanced in uranium compared with rocks of basaltic or ultramafic composition. Uranium released into the terrestrial environment from the weathering of igneous rocks has also become redistributed and concentrated over geological time into many sedimentary rocks such as siltstones and mudstones. In these rocks it is commonly associated with organic matter and phosphates (particularly in marine environments due to the relatively high concentration of uranium in seawater). Further enrichment due to geochemical processes leads to the formation of primary and secondary ores (i.e. 0.1% to 5 % U; 1000 to 50 000 mg/kg) and an elevated abundance in certain geological materials such as phosphorite (i.e. 0.01% to 1% U; 100 to 10 000 mg/kg). Uranium is also present at relatively high concentrations in sea water and has a wide abundance in natural waters, often being more abundant in groundwater than surface water due to contact with underlying rock structures and weathering of surface rocks.

Uranium mineralisation occurs in many parts of the world (see Annex 3) and in a variety of mineral deposits (Plant et al., 1999; De Vivo et al., 1984). Relatively high-grade ores found in Canada and West Africa contain percentage levels of uranium in the form of pitchblende (uranium dioxide) and uraninite (mixed $\text{UO}_2 \cdot \text{U}_3\text{O}_8$). Low-grade sources such as uranium-bearing phosphorites, lignites, and shales are widespread but contain less than 0.01% U. However, the concentration of uranium in such low-grade sources still often exceeds the concentrations observed in granites by up to two orders of magnitude. Similarly uranium may also be found in association with other metalliferous and non-metalliferous mineralisation. Examples of this include

phosphates and other commercial sources of phosphorus such as some deposits of clays, guano, sedimentary molybdenum deposits and coal. In nature, uranium forms chemical compounds in three ionic states, U^{4+} , U^{5+} and U^{6+} , although U^{6+} exists only under oxidising conditions.

Table 3.2 Concentration of uranium in rocks (De Vivo et al., 1984).

Rock Type	Uranium Concentration (mg/kg)
Basalts (tholeiitic and plateau, andesitic and alkali)	0.1-1.0
Carbonate rocks (of North America and the Russian platform)	2
Tertiary rocks (of the Texas Gulf Coast)	2-4
North American and Russian platform (average)	3.7
Granites (of USA, Russia and France)	2-15
Alkaline intrusives (Russia)	3-20

This chapter discusses the abundance and spatial variability of uranium in the environment. In the context of studies of DU, such data are also essential in order to compare exposure due to natural baseline concentrations of uranium with that due to anthropogenically introduced DU.

Without the presence of uranium, Earth would be a rather different planet as heat produced by the radioactive decay of uranium is partly responsible, in addition to other naturally occurring radionuclides such as ^{232}Th and ^{40}K , for keeping the Earth's core and mantle hot enough for convective flow to occur (Plant et al., 1999). Similarly, it is also important to realize that uranium may become depleted (or enriched) in some of its isotopes due to purely naturally occurring processes such as chemical weathering.

When considering radiation toxicity of DU in a given area, it is also important to know the levels of radioactivity existing in the environment prior to the DU being deposited. In this context, radioactivity due to previous man-made events such as the Chernobyl reactor accident and weapons testing need to be taken into account to determine the true background levels.

3.1 Air

Reported background levels of uranium in air vary widely. For example, WHO (1998b) quotes values in ambient air from 0.02 ng/m^3 to 0.076 ng/m^3 , while in the USA, the NCRP quotes a background concentration of 0.30 ng/m^3 (NCRP, 1975) and the US EPA a range of 0.15 to 0.40 ng/m^3 in 51 urban and rural areas across the USA (US EPA, 1986). During these surveys it has also been established that $^{234}\text{U}/^{238}\text{U}$ ratios vary widely in dust samples (range 0.00005 to 0.00040 as mass abundance or 1 to 7 as an activity ratio, indicating the presence of excess ^{234}U). It was considered that this enrichment was due to natural processes such as alpha recoil (e.g. Faure, 1986) and that atmospheric levels of uranium were principally derived from suspension of soils

(ATSDR, 1999). This observation is also consistent with such dusts containing absorbed weathered uranium, as alpha recoil would lead to depletion of primary uranium phases in soils, due to the preferential leaching of ^{234}U . Bou-Rabee (1995) measured uranium concentrations and isotopic ratios in 8 air samples collected following the Gulf-War (sampled in 1993–1994). The observed concentrations varied between 0.22 and 0.42 ng/m^3 with $^{235}\text{U}/^{238}\text{U}$ ratios ranging between 0.005 and 0.007.

When undertaking local measurements of DU in air, it is essential to take into account the levels of natural uranium in that air, especially in dusty environments. Also, it may be necessary in some cases to take into consideration the short and long range transport of natural and anthropogenically produced atmospheric particulates. Particularly as the transport of other airborne particulates has been observed to occur over large distances (UN, 1991).

In addition to other carcinogens, tobacco smoke contains significant quantities of uranium and ^{210}Po . Smoking two packs of cigarettes produces in the region of 50 ng of uranium in a form that may subsequently be inhaled (WHO, 1998b). Elevated levels of uranium in air (e.g. 3 ng/m^3) have also been found down wind of coal fired power stations associated with their discharges (NCRP, 1975).

Many of the data relating to uranium concentrations in air come from the mining of uranium and from industries such as the fertilizer industry in which uranium rich dusts may be produced. These data have not been collated in this chapter because these levels represent extremes of conditions unlikely to be replicated outside the mining and chemical industries.

Concentrations of various dusts in uranium mining have progressively decreased over the years complicating the use of such data in epidemiological studies. For example, potential dust exposure in the underground mines of Wismut Ltd during the late 1940s and early 1950s were estimated (Bauer, 1997) to be in the order of 33.7 mg/m^3 (total weight of airborne particulates). However, the same author noted that exposure to dust was reduced to less than 3% of this level after the adoption, of water rather than air flush, drilling in the 1960s.

Levels of uranium in air surrounding nuclear facilities in which uranium is handled in the preparation and fabrication of fuel assemblies are commonly sampled to monitor discharge released from such sites. Data from measurements in the United Kingdom indicate annual atmospheric discharges from such sites to be in the range of less than 0.005 to 130 kg (MAFF, 1999). Similar releases are documented elsewhere. For example, it has been estimated that airborne releases of uranium at one U.S. Department of Energy facility amounted to 310 000 kg between 1951 and 1988 (equivalent to a rate of approximately 8000 kg per annum). This produced an estimated offsite inventory of 2130–6140 kg of excess uranium in the top 5 cm of soil in the vicinity of the facility (Meyer et al. 1996).

Other data from the USA and Canada have also shown elevated uranium levels in and around milling and processing facilities, measured values ranging from 3 to 200 ng/m^3 at distances of up to 2 km from site boundaries (ATSDR, 1990; 1999).

3.2 Water

Uranium is always present in surface water and groundwater. There is an extremely wide range of concentrations from below $0.01\text{ }\mu\text{g/l}$ to in excess of $1500\text{ }\mu\text{g/l}$ water. Its

natural abundance in water is variable and reflects the concentration of uranium in surrounding rocks and soils through and/or over which water may pass (e.g. see Figure 3.1), and the mobility of various forms of uranium in the prevailing aqueous environment (Figure 3.2). Concentrations of uranium in rainfall are low and variable (e.g. range 0.018 to 0.17 $\mu\text{g/l}$ for the USA during March–May 1993; ASTDR, 1999)

Various anthropogenic activities involving the processing or use of materials rich in uranium may modify the natural abundance of uranium in water. These activities include the use of phosphate fertilizers, various mining activities (uranium, silver, and other mineral mines) and the industrial processing of uranium for the manufacture of nuclear fuel and other products, including DU for various uses. Although the isotopic ratio of ^{235}U to ^{238}U generally remains constant in waters some fractionation occurs in the relative isotopic abundance of ^{234}U compared to ^{238}U and ^{235}U due to disequilibrium phenomena. Additionally, variations in ^{235}U to ^{238}U ratios have been measured in the vicinity of Oklo, Gabon in a natural uranium deposit which has been shown to have reached nuclear criticality approximately 2000 million years ago as a result of natural processes (e.g. Burns and Finch, 1999).

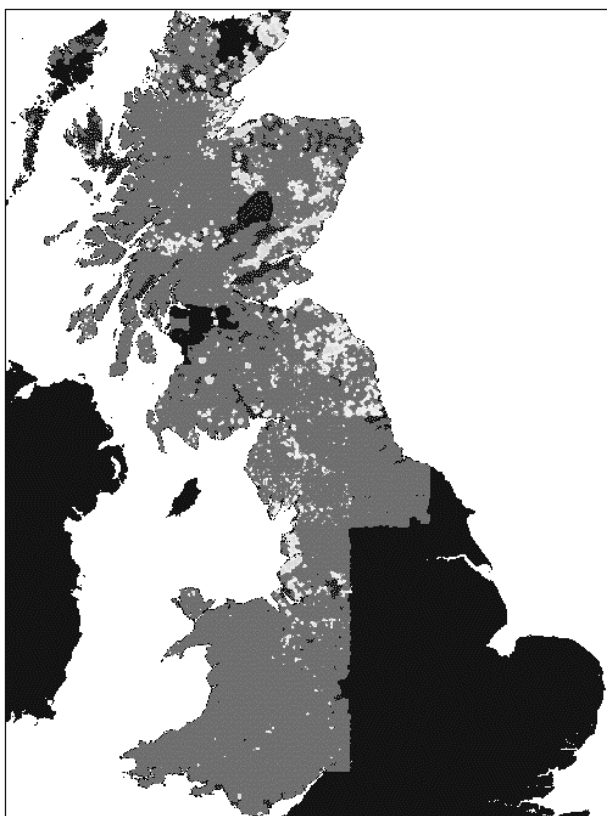


Figure 3.1 Map showing areas (in light grey) of the United Kingdom in which the measured concentration of uranium in surface stream waters exceeds 2 $\mu\text{g/l}$. The total number of samples in the sampled area (dark grey) exceeds 100 000. The mean uranium concentration in these surface waters has been determined to be 0.65 $\mu\text{g/l}$ with a maximum observed concentration of 233 $\mu\text{g/l}$. The spatial distribution of elevated concentrations of uranium in stream water were observed to reflect areas of high uranium mobility rather than the abundance of uranium in bedrock, and also to reflect areas of anthropogenic input such as nuclear facilities handling the purification and production of fissile uranium (British Geological Survey, 1992; 1997). This figure has been compiled from data collected during the Geochemical Baseline Survey of the Environment (G-BASE), British Geological Survey.

Uranium acetates, sulphates, carbonates, chlorides and nitrates readily dissolve in water and their chemical form in typical groundwaters and surface waters is generally dominated by the presence of carbonate species, although sulphate and phosphate may also form important species in other circumstances (e.g. Bernhard et al., 1998; Smith et al., 2000). These carbonate complexes may be either negatively charged or neutral and, as such, are highly mobile in most soils despite the presence of cation exchangers such as clays (Abdelouas et al., 1998; Duff and Amrhein, 1996; Elless and Lee, 1998). This makes uranium particularly mobile in soils and infiltrating groundwater in arid and semi-arid regions, such as those typified by Mediterranean environments. Under weakly acidic conditions typical of soils and infiltrating groundwaters found in wetter climates, the chemical speciation of uranium may become dominated by the formation of stable complexes with soil organic matter. This commonly results in the retention and accumulation of uranium in peat deposits, although in situations where a significant proportion of the organic matter is in the dissolved form this may assist in the dissolution and mobilisation of soil-bound uranium (Ebbs et al., 1998; Benes et al., 1998). In addition to transport in the dissolved phase, labile uranium may also be redistributed from soils and sediments into watercourses and surface water reservoirs as, or sorbed onto, particulate matter during storms and other modes of physical erosion (Batson et al., 1996; Zielinski et al., 1997; Porcelli et al., 1997).

Drinking water: Many studies have been undertaken on the concentrations of uranium in drinking water. These have included surveys of treated water, surface water, groundwater and bottled water. However, significant improvements in the precision and accuracy of analytical methods used to determine uranium content over the past twenty years raises doubts as to the reliability of some of the data collected prior to the 1980s. A summary of typical studies and surveys performed prior to 1980 on the concentration and isotopic signature of uranium in water is given in Ivanovich and Harmon, (1982). A selection of data from studies performed since 1980 are given in Annex 3

From this selection of studies and those quoted elsewhere (i.e. WHO, 1998a, 1998b) it can be concluded that the concentration of uranium determined in drinking water covers a very wide range. It is generally affected not only by the presence of significant concentrations of uranium in the local geological or surface environment, but also by the weatherability of the media containing uranium and its mobility in solution. This wide range of concentration, together with significant regional and local variations (due to local scale variability in geological structure), makes it impossible to estimate typical exposures to the presence of natural uranium from drinking water and by inference the likely importance of additional sources such as DU. However, it is clear from these studies that the probability of a drinking water source containing uranium at a concentration of about 2 µg/l is relatively high, getting progressively smaller over the range 5 to 10 µg/l and becoming very small above 10 µg/l. Such data indicates that many countries are likely to have drinking water supplies in which the current WHO guideline for uranium in drinking water (2 µg/l; WHO, 1998a) is likely to be exceeded.

3.3 Soil

There are few systematic studies in which uranium has been measured over larger areas with high resolution. A selection of more recent generalized studies in which significant attention has been paid to define baseline or benchmark data are presented in Annex 3. Additionally the advent of high sensitivity, high resolution airborne and seabed gamma spectrometry has enabled uranium to be routinely determined at baseline levels across relatively large areas.

The concentration of uranium in soil varies widely. This reflects the abundance of uranium in the parent geological materials from which the soils were formed, the soil development processes (for example uranium may become concentrated in organic-rich horizons) or leaching, and the addition of uranium from anthropogenic activities such as fertilizer application or military conflicts/training.

Levels of uranium in soils generally not associated with known sources of anthropogenic contamination or obvious areas of mineralisation indicate median concentrations in the order of 1 to 2 mg/kg. However, variations can be very spatially dependent and may reflect not only geologically derived sources of elevated uranium but also dispersion zones associated with the transport of river sediments. Concentrations as high as 4 mg/kg are often found in soils away from any obvious anthropogenic activity and have been suggested to represent the upper baseline level for uranium. However, even higher concentrations of uranium can be found in soils associated with mineralized environments such as those found in the vicinity of deposits of phosphate or in superficial uranium ore deposits. Such deposits are common throughout the world. For example measured levels of uranium in surface soils associated with phosphorite in North Africa and the Middle East, may reach that of the primary phosphate, i.e. approximately 200 mg/kg. In industrialized environments, uranium may also be found associated with uranium processing plants (e.g. British Geological Survey, 1992), mine tailings and process waste streams (e.g. Ledvina et al., 1996; McConnell et al., 1998), and agricultural environments in which uranium-rich phosphate fertilizers have been used (e.g. Zielinski et al., 1997).

3.4 Mobility of uranium in soil and water

The dissolution and mobility of dissolved uranium and hence DU, in soils (e.g. during the infiltration of rainwater and plant uptake) is strongly controlled by the proximity of groundwater to the soil environment, soil and water pH, soil organic carbon content and the presence and abundance of cation exchange sites such as those found in clays (e.g. Ribera et al., 1996; Burns and Finch, 1999 and US EPA, 1999; 2000b). Unlike many heavy metals, such as lead, the mobility of uranium increases under neutral to alkaline conditions, due to the formation of stable negative complexes (oxy-anions) with oxygen and carbon (Figure 3.2). For example, uranium sorption values were found to be very low in soils rich in montmorillonite and low in organic carbon, such as those found in west Anatolia and other semi-arid Mediterranean type environments (e.g. Akcay, 1998; Zielinski et al., 1997).

More accurate insights into the mobility and chemical form of uranium in soils and groundwater require the use of geochemical modelling codes such as PHREEQC (Parkhurst and Appello, 1999) or coupled chemical transport codes in which predictions concerning the physical migration of uranium are coupled to chemical processes that may retard such migration.



Figure 3.2 Eh-pH diagram showing stability fields for uranium under various Eh and pH conditions. Eh is an indicator of oxidation potential that may be related to the presence of dissolved oxygen. pH is an indicator of acidity. Note the wide stability fields (i.e. the regions bounded by lines) over environmental conditions (moderate Eh and pH) of the dissolved, highly soluble neutral and negatively charged anionic species UO_2CO_3 , $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ compared to that of the positively charged, strongly sorbed cation UO_2^{2+} and insoluble $\text{UO}_2(\text{s})$. The diagram has been constructed for a U-C-O-H system adapted from Brookins, (1988) and may be used as a first approximation to predict the chemical form and mobility of uranium species in soils and groundwaters in which Eh and pH have been determined.

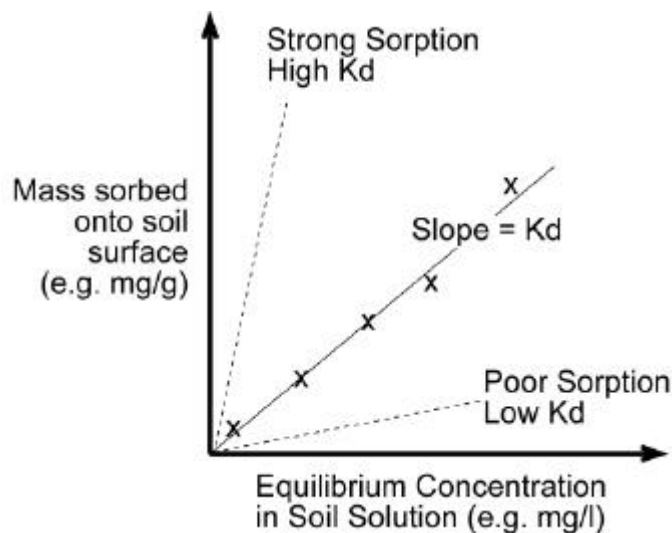


Figure 3.3 Example of a linear Freundlich isotherm illustrating the derivation of the K_d term.

One important indicator of migration potential commonly used in the assessment of pollutant mobility is the soil water distribution coefficient (K_d) (see Figure 3.3). The K_d represents a special case ‘linear’ Freundlich isotherm (an X,Y plot of the concentration of contaminants such as uranium sorbed onto the soil versus the equilibrium

concentration of the contaminant in associated soil water, where the slope of the resultant line is equal to the K_d), (Domenico and Schwartz, 1990).

Values of the K_d of uranium for various soil pH values are given in Table 3.3. It should be noted that the organic carbon content of a soil also strongly influences pH and the K_d for uranium (soils high in organic carbon having a larger K_d). There should be no differences between the values of K_d for DU and uranium because of their chemical similarity, although the value of the K_d does change with the chemical form of uranium present.

Table 3.3 Values of K_d for various soil pHs (US EPA, 1999). Higher values indicate greater sorption and hence greater retardation. Typical Northern and Central European soils have a pH range of 5 to 7 while those in Mediterranean environments and formed over limestones typically exhibit pH ranges from 7 to 9. Additions of various soil conditioners and fertilizers such as peat, lime or phosphate may significantly effect the behaviour of uranium in soils.

Soil pH	K_d ml/g
3	<1
4	0.4
5	25
6	100
7	63
8	0.4
9	<1
10	<1

3.5 Food

As a component of the natural environment uranium is likely to be present as a trace constituent in all foodstuffs. It may become incorporated into the bulk of the food or may alternatively adhere to the surface of foodstuffs as particulate contamination, with root vegetables often containing higher levels. ATSDR (1999) cites a review of the oral intake of uranium in the US with a typical range of 0.9 to 1.5 μg per day in food and the same range for drinking water, for a total intake of 1.8 to 3.0 μg per day. Harley (1998) cites a review of naturally occurring sources of radioactive contamination undertaken in several European countries and estimates dietary intakes of uranium to range between 0.5 and 2 μg per day. These compare with 0.5 to 3 μg per day in Japan and 0.5 to 0.9 μg per day in the UK which were also cited in Harley (1998). On the basis of this information these authors suggest a worldwide average daily dietary intake of 4 μg although they state that it is often unclear if drinking water exposure has been included in the reviewed dietary assessments. Spencer et al. (1990) measured the total dietary intake of uranium (excluding water and milk) in the strictly controlled diet of four patients partaking in a survey of uranium intake and excretion to be 2 $\mu\text{g}/\text{day}$. This is similar to that quoted by Hamilton (1972) and US Department of Health and Human Services (1990) of 1 to 2 $\mu\text{g}/\text{day}$.

The determination of uranium in a variety of foodstuffs from the USA and UK (Annex-3) indicates that the highest recorded concentrations have been found in shellfish, molluscs and winkles (9.5 to 31 $\mu\text{g}/\text{kg}$), presumably due to the relatively high

concentrations of uranium in seawater. Typical concentrations in staple foods such as bread and fresh vegetables were approximately two orders of magnitude lower (i.e. 2 µg/kg) whereas uranium concentrations in other foods such as rice and meat were in the range of 0.1 to 0.2 µg/kg in meat products.

Concentrations of uranium observed in a variety of tropical staple foods including cassava, matooke, maize and sweet-potato ranged from less than 1 to 11 µg/kg (unpublished data for carefully peeled foods, British Geological Survey). The unusually high phytate (or fibre) content of such diets potentially affects the uptake of uranium from the human gut in a similar manner to the uptake of other minerals (Gibson, 1994). Additionally soil is known to adhere to vegetables, particularly root crops, and the efficiency of washing is a factor that can significantly bias results (particularly as it is not often described in conjunction with the analytical results).

The mean concentration in nine different prepared beverages, including tea and coffee, was found to be 0.98 µg/l (range 0.26 to 1.65 µg/l) and in a series of mineral waters was 9.20 µg/l (Cheng et al., 1993). A survey of 56 randomly sampled bottled mineral waters from Europe by Misund et al. (1999) observed uranium concentrations to range from 0.0104 to 9.45 µg/l.

Like many trace metals, the bioavailability (i.e. gut uptake) of uranium in food may be influenced by the food's phytate (or fibre) content (Gibson, 1994; Golden and Golden, 1981) and the presence of low molecular weight ligands, such as citrate, that may promote uptake.

The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR, 2000) has estimated that the total annual intake into the human body by adults is 460 µg by ingestion of food and water and 0.59 µg from inhalation.

3.6 Other sources in the human diet

Other sources of uranium in the human diet include dusts and soils both inadvertently and deliberately eaten and uranium derived from cooking and serving wares.

3.6.1 Cooking and serving containers

Landa and Councill (1992) performed leaching studies on the release of uranium from 33 glass items and two ceramic items in which uranium had been used as a colouring agent. The uranium-bearing glasses released a maximum of 30 µg/l uranium. Experiments also showed that when a glazed ceramic plate was kept in contact with a 4% acetic acid solution for 24 hours, the concentration of uranium in the leachate was 3.1 mg/l (Landa and Councill, 1992).

Fortunately, the use of uranium in glazes by artists and potters is now rare, although, as described earlier, uranium powder is still employed in some specialist glazes used principally in the jewellery industry, and this may introduce uranium into the diet through habitual placing of the object into the mouth.

3.6.2 Uranium in dust and soil

Levels of uranium in dust and soil to which individuals and populations may be exposed to through ingestion are varied, and levels depend greatly on the existence of potentially elevated sources. For example baseline levels may be dominated by soil and dust in the

range of less than 1 to 4 mg/kg, as discussed in Chapter 3.4, while levels of uranium in soil and dust intimately associated with areas of man-made contamination or mineralisation may be considerably higher.

Additionally it is important to consider that levels of uranium determined in root crops and drinking water may include contamination from uranium present in soil and dust unless considerable care is taken during sample preparation. Where such material is likely to be present in prepared foods it should be included in the calculation of exposure to uranium.

As discussed later in Chapter 5, three distinct categories of soil/dust ingestion can be defined, and levels of uranium relevant to each category are discussed below.

(1) *Inadvertent ingestion of small quantities of soil and dust.* The high density of uranium and its chemical reactivity may lead to concentration within different particle size/density ranges. This may result in considerably elevated concentrations of uranium with the fine/dense fractions of dusts and soils with a direct impact on levels of uranium ingested as a result of inadvertent exposure.

(2) *Occasional deliberate consumption of soil and dust.* Many young children indulge in this type of exploratory behaviour for a relatively short time. However, unlike inadvertent ingestion, it is generally considered that deliberate consumption is likely to result in ingestion of the bulk soil or dust rather than any particularly mobile size or density fraction (see Figure 3.4).



Figure 3.4 Picture of child eating dirt

(3) *Geophagia*. This term refers to the persistent and purposeful consumption of soil and/or dust, often in relatively large quantities. Historically, it has been recognized as a worldwide phenomena although its prevalence now tends to be associated with traditional communities (both rural and urban) and the poorly nourished. Where geophagia is practised, large quantities of soil (often from a preferred source such as soils associated with termitaria (termite mounds)) may be consumed by children, young adults and pregnant women on a regular basis (Geissler et al., 1997). It is therefore important to determine the concentrations of uranium within preferred sources of soil in such circumstances and any methods or pre-treatment or preparation that might affect levels used in subsequent assessments of exposure.

Toxic metals and uranium in soils are generally considered to be much less bioavailable than similar substances present in food and water. It is therefore important when describing levels of uranium in soils that may be ingested to consider its potential bioavailability in the context of inadvertent and deliberate consumption. The percentage of uranium ingested in soils that might be bioavailable for uptake into the systemic circulation depends upon the physiochemical form of the uranium and the mode by which the soil is ingested. For example, if soil is eaten with foods, particularly those rich in fibre, the bioavailability of uranium may be reduced as a result of sorption by phytate present in such foods. There are also a number of other physiological parameters such as stomach pH, food consumption and stomach/intestinal residence time, which indicate that kinetic constraints of the dissolution of uranium-bearing phases within ingested soil and dust also provide an important control on metal bioavailability. A number of physiologically based extraction tests (e.g. Ruby et al., 1996) have been developed to study the bioavailability of lead and arsenic from mine wastes and other polluted soils; and these methodologies may be extrapolated, with appropriate validation, to investigate the solubility of uranium in contaminated soils.

3.7 Summary

Uranium (U) is a naturally occurring element with an average abundance in the Earth's crust of about 2 mg per kg (range 0.1 to 20 mg per kg). It is more abundant than silver or gold. Typical concentrations in air are low ranging from less than 0.01 to 0.2 ng/m³. Concentration in air may be influenced by smoking cigarettes and the presence of a range of industrial processes such as mining of uranium ore, gas releases from coal-fired power stations and nuclear fuel manufacturing facilities. Concentrations of uranium in water, food and soil are variable (typically 0.1 to 5 µg/l in water; 0.1 to 2 mg/kg in soil and 0.01 to 2 µg/kg in food) and depend largely on the presence of uranium in associated parent materials (i.e. rocks) or proximity of industries that may introduce uranium into the environment. In all cases, extreme concentrations (up to a factor of about 100 times the typical ranges quoted above) may quite naturally be found in suitable geological environments. Levels in both surface and groundwaters, as well as many bottled mineral waters commonly exceed current WHO drinking water guidelines in many countries.

The 'natural' isotopic ratio of ²³⁴U/²³⁸U may be perturbed by a variety of environmental processes, while the ratio of ²³⁵U/²³⁸U remains largely constant.

