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Distribution of Natural Radioactivity in the Environment

Land, Soil & Coast Programme

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BRITISH GEOLOGICAL SURVEY

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Distribution of Natural Radioactivity in the Environment

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Foreword

This report is the published product of a study by the British Geological Survey (BGS) in collaboration with AMEC for the Nuclear Decommissioning Authority (NDA), undertaken between March and August 2016.

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Summary

This report describes our current knowledge of the distribution of natural radioactivity in rocks, groundwater and soils of the United Kingdom. Elements of interest include Uranium (U), Thorium (Th) and Potassium (K), along with radon (Rn) and radium (Ra) in groundwater. This information is then used to describe the likely background conditions at each of the U.K.'s nuclear sites, particularly in relation to the geology.

1 Introduction

The aim of this part of the guidance is to provide information on the variation in background concentrations of naturally occurring radio-nuclides (Th, U and K) in rocks, groundwater, soils in the UK. The review does not aim to calculate background radioactivity as this was undertaken previously for soils, sediments and waters (EA, 2007). However a key aim is to identify processes which may lead to variation from the background concentrations.

2 The distribution of natural radioactivity in rocks

The principal naturally-occurring radioactive elements that contribute the majority of the background radioactivity in rocks are uranium (U), thorium (Th) and potassium (K).

2.1 URANIUM

2.1.1 Uranium and its daughter radionuclides

Uranium has three natural isotopes: ^{238}U, ^{235}U and ^{234}U (Wedepohl, 1978a). All three isotopes are radioactive, and ^{238}U and ^{235}U are the progenitor parent isotopes for two separate decay series, which ultimately lead to the formation of the lead daughter isotopes ^{206}Pb and ^{207}Pb, respectively (Figure 1). 238U is the most abundant isotope, and the ^{238}U/^{235}U ratio today is 137.5 ± 0.5 (Wedepohl, 1978a). This ratio has increased over time due to faster radioactive decay of ^{235}U (half-life; 7.04 x 10^8 years) relative to ^{238}U (half-life 4.47 x 10^9 years). ^{234}U, which is produced by the decay of ^{238}U and has a relatively short half-life (2.45 x 10^5 years), comprises approximately 0.0056 % of total natural uranium (Wedepohl, 1978a).

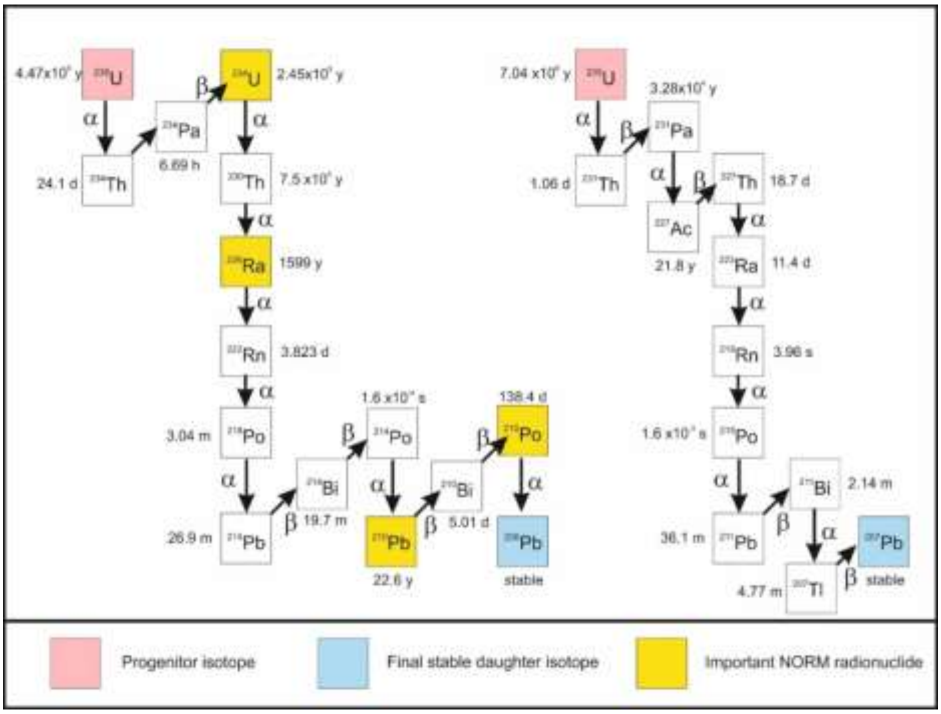

Figure 1. Schematic drawing of the 238U and 235U decay chains showing the decay path and radionuclide half-life (nuclide half-life data taken from Bourdon et al., 2003).

With very long half-lives ^{238}U (4.47 x 10^9 years), ^{235}U (7.04 x 10^8 years) and ^{234}U (2.45 x 10^5 years) are the most commonly encountered uranium isotopes in most rocks. However, some of the longer-lived daughter nuclides (Figure 1), principally ^{226}Ra (half-life; 1599 years), ^{210}Pb (half-life; 22.6 years) and ^{210}Po (half-life; 138.4 days), can also be important naturally-occurring radionuclides. These can be concentrated in some naturally-occurring radioactive material (NORM) wastes from industrial operation: e.g. well and pipeline scale deposits from UK onshore and offshore oil and gas wells (Bassignani et al., 1991; Ceccarello et al., 2004; Read et al., 2004; Garner et al., 2015); mineral processing – in particular, processing ores of titanium, rare earth elements (REEs) and zirconia, phosphate fertilizer production and China clay processing (Beddow et al., 2006).

Radon (^{222}Rn), a gaseous daughter radionuclide produced from the decay of ^{226}Ra within the ^{238}U decay series, is a particularly important natural environmental hazard over uranium-rich rocks in some parts of the UK (Scheib et al., 2013). It may be concentrated in the air of buildings and other places (e.g. underground in caves, tunnels and mines) where ventilation is inadequate or restricted, and is considered to be the largest contributor to radiation exposure in the UK (Watson et al., 2005). Watson et al (op. cit.) estimate that about half of the average annual dose from natural radiation to the UK population comes from radon exposure indoors.

2.1.2 Uranium abundance

Uranium is a relatively rare element, with an average abundance in the Earth’s crust of between 1 to 3 ppm (Basham and Kemp, 1993; Hazen et al., 2009; Fayek et al., 2011; Cumberland et al. 2016). A generic summary compilation of the distribution of uranium in common rock types is given in Table 1

Table 1. Global ranges of uranium abundance in common rocks and waters

Igneous Rocks		**Sedimentary Rocks**	
Syenites and phonolites	0.1-26 ppm	Shales, clays, mudrocks	1-5 ppm
Granites and rhyolites	2-50 ppm	Black shales (organic-rich)	2-1250 ppm
Intermediate rocks	1-6 ppm	Phosphorite-black shales	≤700 ppm
Basalts and other mafic rocks	0.1-1 ppm	Sandstones	0.5-4 ppm
Ultramafic	0.001-1 ppm	Limestones, dolomites	<0.1-9 ppm
		Coals, lignites, peats	1-6000 ppm
Metamorphic Rocks		Pure evaporites	<0.1 ppm
Low-grade	<1-5 ppm	**Water**	
Medium-grade	<1-5 ppm	Oceanic seawater	0.3-3 ppb
High-grade	<1-7 ppm	Groundwater	<0.1-460 ppb

[based on data from Wedepohl, 1978a; Bowie, 1979; Basham et al., 1989; Ball and Milodowski, 1989; Basham and Kemp, 1993; Hobday and Galloway, 1999; U.S. Geological Survey, 1997;

Cuney, 2010; Kreuzer et al., 2010; Bowell et al., 2011; Douglas et al. 2011; Alloway, 2013; Cumberland et al., 2016; Guidez and Gabriel, 2016].

2.1.2.1 URANIUM ABUNDANCE IN IGNEOUS ROCKS

It is a lithophile element i.e. its primary occurrence in igneous rocks is generally in association with rocks containing dominantly light elements (Basham and Kemp, 1993). In general, uranium content increases with magmatic fractionation (Wedepohl, 1978a). Felsic igneous rocks are relatively enriched in uranium: globally, granitic and rhyolitic rocks generally contain between 2 and 15 ppm U, and silicic alkaline rocks often have higher uranium contents (up to 26 ppm U) (e.g. Wedepohl, 1978a; Basham and Kemp, 1993; Cumberland et al., 2016). Some granites can be more uraniferous (Alloway, 2013), with up to 50 ppm U found within some Proterozoic granites in Australia (Kreutzer et al., 2010). Intermediate igneous rocks typically contain between 1 and 6 ppm U. Mafic rocks range from 0.1 to 1 ppm U: average basalt is around 1 ppm U (Alloway, 2013; Cumberland et al., 2016), whereas ultramafic igneous rocks are relatively low in uranium, usually with considerably less than 1 ppm U (Wedepohl, 1978a; Basham and Kemp, 1993).

2.1.2.2 URANIUM ABUNDANCE IN METAMORPHIC ROCKS

Metamorphic rocks generally contain less uranium than granitic or silicic alkaline igneous rocks. A review by Basham and Kemp (1993) suggests that the uranium concentration in metamorphic rocks is typically between 0.1 to 4 ppm U, and that depletion of uranium takes place with increasing metamorphic grade. However, this is an oversimplification, and as might be expected for rocks derived from a variety of parent materials and under a variety physical-chemical conditions, the variation in uranium content of metamorphic rocks is quite large. Data presented by Wedepohl (1978a) shows a much greater range of compositions from 0.1 to 45 ppm U, with typical values of 1 to 4 ppm U irrespective of metamorphic grade.

2.1.2.3 URANIUM ABUNDANCE IN SEDIMENTARY ROCKS

The concentration of uranium in sedimentary rocks is highly variable. Two of the major factors that influence the uranium content are: (i) the detrital source mineralogy, and; (ii) the redox-chemistry of uranium, which is strongly influenced by the geochemical processes operating during weathering of source rock and sediment transport, within the depositional environment, and during subsequent burial diagenesis. Uranium is redox-sensitive, and although it can exist in 3+, 4+, 5+ and 6+ oxidation states (http://www.rsc.org/periodic-table/element/92/uranium), only 4+ and 6+ are significant in nature. The occurrence of pentavalent uranium (U^{5+}) has been discovered in the mineral wyartite [$CaU^{5+}(UO_2)_2(CO_3)O_4(OH).7H_2O$] (Burns and Finch, 1999), but its occurrence in nature is very rare. Consequently, uranium concentrations in sedimentary rocks can be significantly higher in sedimentary rocks (Table 1) than in the parent igneous rocks (Cumberland et al, 2016). Exceptionally high sedimentary-diagenetic uranium concentrations (>20%) have been produced in the Precambrian, in the Oklo natural reactors, in Gabon (Gauthier-Lafaye et al., 1989). However, these concentrations of uranium are “the exception rather than the rule” in most sedimentary rocks (Table 1):

- sandstones typically contain between 0.5 to 4 ppm U;
- shales and mudrocks typically contain between 1 to 5 ppm U;
- limestones are generally low in uranium – typically about 2 ppm (Wedepohl, 1978a), although some more uraniferous limestones have been reported (e.g. Basham and Kemp, 1993; Milodowski et al., 1989);

- pure evaporites are typically very low in uranium, <0.1 ppm U (Wedepohl, 1978a).

In general, much of the uranium in siliciclastic sedimentary rocks (sandstones, shales, mudrocks) is contained within resistate detrital heavy minerals (e.g. zircon, xenotime, apatite, titanite (sphene), monazite), which occur as trace components, or as inclusions preserved in major detrital minerals such as quartz, feldspars and micas (e.g. Wedepohl, 1978a; Milodowski and Hurst, 1989; Hurst and Milodowski, 1976). In carbonate rocks, the trace concentration uranium is considered to substitute in the lattice in place of calcium.

Organic-rich and phosphatic sediments and sedimentary rocks often host significantly higher concentrations of uranium (Table 1). Phosphorites are often enriched in uranium, with up to 700 ppm reported in some formations (cf. Wedepohl, 1978a; Bowell et al., 2011; Cumberland et al., 2016). Black shales and organic sediments (coals, lignites, peats) display a large variation in uranium content (1 to 6000 ppm: Table 1) with very high concentrations of uranium reported from some formations (e.g. Wedepohl, 1978a; Bowell et al., 2011; Cumberland et al., 2016), including localised concentrations in UK peat deposits (Ball and Milodowski, 1989; Basham et al., 1989; Milodowski et al., 1989).

2.1.3 Uranium host minerals

As mentioned earlier, uranium is a lithophile element: all uranium minerals contain oxygen and it does not occur naturally as the native element nor in combination with sulphur as a sulphide mineral. Over 160 minerals have been identified in which the uranium is essential part of the crystal structure. In addition, uranium can be present as a minor or trace component in a large number of other minerals, incorporated intrinsically by substitution of major ions within the crystal structure (e.g. for Ca^{2+} in calcium carbonates; titanite and apatite; for Zr^{4+} in zircon; and rare earth elements (mainly Ce and Y) in rare earth minerals such as monazite and xenotime; niobium-tantalum-titanium minerals, and; iron oxides and oxyhydroxides). Uranyl ions may also be adsorbed on clay minerals, zeolites, oxides and hydroxides iron, manganese and titanium, or may be adsorbed, reduced or form organic-metallic species with organic matter. It is not possible to describe all the uranium-bearing minerals here. Comprehensive lists and accounts of the mineralogy of uranium can be found in Frondel (1958), Henrich (1958), Wedepohl (1978a), and in reviews by Smith (1984), Finch and Murakami (1999), and Cumberland et al. (2016). Many of these uranium minerals are rare. A brief overview of the uranium principal minerals is given here.

2.1.3.1 MINERALS CONTAINING TETRAVALENT U^{4+}

Minerals where uranium is present as a major component in the reduced tetravalent (U^{4+}) state can be divided into three main groups, and the most important minerals are summarised below:

(i) Simple oxides and silicates	Uraninite-thorite [UO_2-ThO_2]
	Coffinite [$U(SiO_4)_{1-x}(OH)_{4x}$]
	Uranothorite-thorite [$(U,Th)SiO_4$]
(ii) Complex (multiple) oxides	Brannerite [$(U, Ca, Y, Ce, La)(Ti, Fe)_2 O_6$]
	Davidite [$(La, Ce)(Y,U,Fe)(Ti,Fe)_{20}(O,OH)_{38}$]
(iii) Phosphate	Ningyoite [$(U,Ca,Ce)_2(PO_4)_2.1{-}2H_2O$]

Uraninite is the most important and abundant U^{4+} mineral, and occurs as a primary accessory igneous mineral, and as primary mineral in hydrothermal deposits, and is the main ore mineral of uranium. It is often partially oxidized and commonly referred to as “pitchblende”,- a term often used to reflect partially altered and poorly crystalline uraninite.

Coffinite is also a relatively common U^{4+} mineral and an important uranium ore mineral. It is isostructural; with thorite ($ThSiO_4$) and zircon ($ZrSiO_4$) but unlike these generally magmatic accessory minerals, coffinite is formed at low temperature, either by direct precipitation or often as an alteration product of uraninite. It is nearly always very fine grained and usually poorly crystalline.

Uranothorite is also isostructural with thorite and zircon, often occurring as a primary accessory mineral in alkaline granites, syenites and associated pegmatites (Basham and Kemp, 1993).

Brannerite is the third most important mineral containing U^{4+} (Basham and Kemp, 1989). It occurs as an igneous or metamorphic accessory mineral, and as a low-temperature phase. Its principal occurrence is in pegmatites, where is may be associated with uraninite. It may also be found in sedimentary rocks, associated with secondary titanium oxide (anatase, rutile) formed as a diagenetic alteration product of primary detrital ilmenite and magnetite (e.g. Milodowski et al., 1989).

Davidite is a complex oxide. It is uncommon and found in rare earth element-rich pegmatites. Ningyoite, named after the type locality in Japan where it was first discovered, is also rare and occurs a low temperature hydrothermal mineral in sedimentary uranium deposits.

2.1.3.2 MINERALS CONTAINING HEXAVALENT U^{6+}

There is a great diversity of minerals, where uranium is present as a major component in the oxidised hexavalent (U^{6+}) state. Uranium is present as the uranyl ion ($[UO_2]^{2+}$), often combining with other oxyanion species, including CO_3^{2-}, PO_4^{3-}, AsO_4^{3-}, SO_4^{2-} and VO_4^{3}. Complex substitution and replacement can occur within both the cationic and anionic groups, giving rise to a wide range of mineral compositions:

- $A(UO_2)(RO_4).xH_2O$
- $B(UO_2)_2(RO_4)_2.xH_2O$
- $B(UO_2)(CO_3)_2.xH_2O$
- $B(UO_2)(SiO_3)_2.xH_2O$

Where: $R=P^{5+}, As^{5+}, V^{5+}$

$A = K^+, Na^+, H^+$

$B = Ca^{2+}, Ba^{2+}, Mg^{2+}, Fe^{2+}, Pb^{2+}$

In addition, many of these minerals are hydrous and contain significant water of crystallisation. Many of these minerals are brightly coloured. They occur as low-temperature secondary minerals, formed within supergene oxidising groundwater and near-surface weathering environments, largely as alteration products of primary uranium mineralisation containing U^{4+} minerals. However, oxidation of U^{4+} to much more soluble U^{6+}, coupled with solution and transport within the supergene environment can result in either concentration and redeposition of uranium from a distant large-volume low-level source such as a granite, or to wider dissemination as minor surface coatings from a localised primary uranium concentration such as an orebody (Hazen et al., 2009; Cumberland et al., 2016).

The uranyl phosphates and arsenates represent the most common group of these minerals. They occur in a wide range of geological environments, and exhibit the greatest range of compositions. The autonite ($Ca(UO_2)_2(PO_4)_2$) – meta-autonite ($Ca(UO_2)_2(PO_4)_2.6H_2O$), torbernite ($Cu[(UO_2)(PO_4)]_2\cdot 10–12H_2O$) – metatorbernite ($[Cu(UO_2)_2(PO_4)_2\cdot 8H_2O]$), zeunerite

(Cu $(UO_2)_2(AsO_4)_2.8H_2O$) and troegerite ($H_2(UO_2)_2(AsO_4)_2..8H_2O$) groups are probably the most widespread of these. This reflects both the natural abundance of P and As in groundwaters around ore deposits and the ready formation of UO_2-PO_4 and UO_2-AsO_4 aqueous complexes, and their ability to precipitate in the presence of a variety of cations (Basham and Kemp, 1993). Uranophane is a common uranyl silicate, forming as an oxidative alteration product of primary uranium ores. It has a very variable composition (Cumberland et al., 2016). Hydrated uranyl oxides are also common low-temperature secondary uranium minerals. Schoepite ($Ca(H_3O)_2(UO_2)(SiO_4)_2(H_2O)_3$) is probably the most common of these.

2.2 THORIUM

2.2.1 Thorium and its daughter radionuclides

Thorium has only two long-lived natural isotopes, both of which are radioactive (Wedepohl, 1978a). ^{232}Th is the major isotope, with a very long half-life (1.41 x 10^{10} years), and is the parent of a long radioactive decay series ending with stable ^{208}Pb (Figure 2). The other important natural thorium isotope is ^{230}Th, which is a decay product of ^{238}U (Figure 1). It has a much shorter half-life (7.5 x 10^4 years) and is generally present in minerals containing uranium (Wedepohl, 1998a).

Most of the daughter isotopes of ^{232}Th are very short-lived but ^{228}Ra (half-life 5.75 years) can be an important component in some NORM wastes.

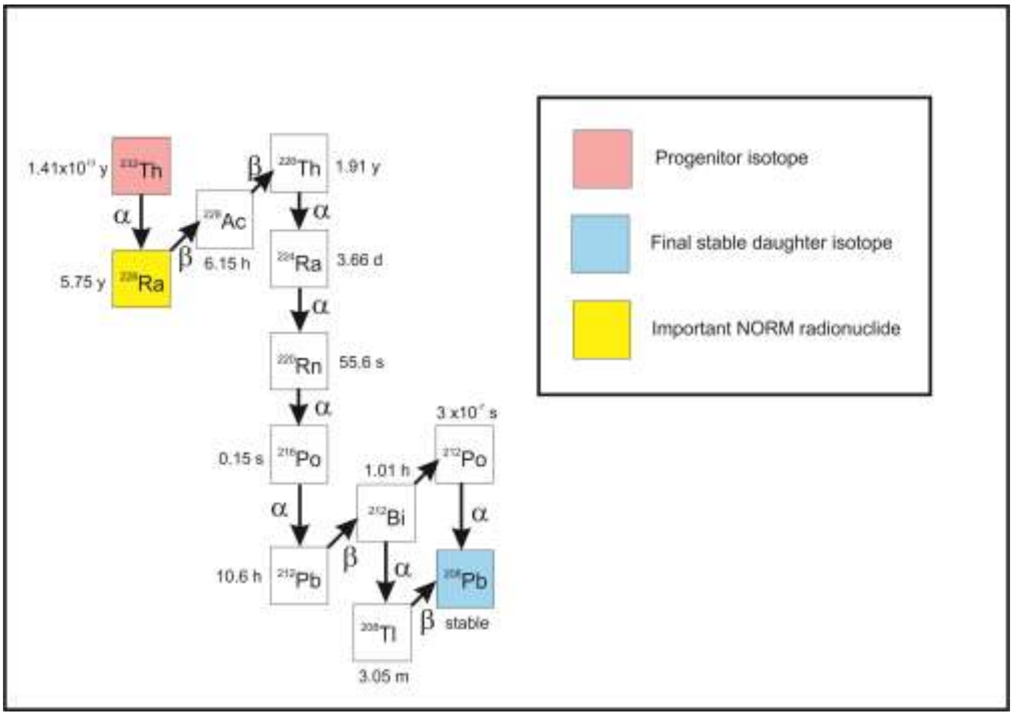

Figure 2. Schematic drawing of the ^{232}Th decay chains showing the decay path and radionuclide half-life (nuclide half-life data taken from Bourdon et al., 2003).

2.2.2 Thorium abundance

Like uranium, thorium is a relatively rare element, with an average abundance in the Earth's crust in the range of 6-10 ppm, and more abundant than uranium with an average crustal Th:U ratio of about 3:1 (Adams and Weaver, 1958; Wedepohl, 1978a; Basham and Kemp, 1993; Hazen et al., 2009). Thorium only occurs in the tetravalent oxidation state (Th^{4+}) and, in contrast to highly-soluble hexavalent uranium (U^{6+}), is highly immobile. Consequently, during oxidative alteration, weathering and leaching of primary uranium-thorium minerals, uranium is transported away in solution whereas thorium precipitates locally and is concentrated in residual deposits resulting in geochemical separation (Adams and Weaver, 1958). It forms very few primary minerals and virtually no equivalents of the complex secondary minerals that are characteristic of hexavalent uranium. Typical ranges of thorium concentration for common rock types are summarised in Table 2.

Table 2. Global ranges of thorium abundance in common rocks and waters

Igneous Rocks		**Sedimentary Rocks**	
Syenites and phonolites	0.7-35 ppm [typically >10 ppm]	Shales, clays, mudrocks	10-13 ppm
		Pelagic clays and siliceous oozes	2-30 ppm
Granites, rhyolites and intermediate igneous rocks	8-56 ppm	Sandstones	1-7 ppm
Basalts and other mafic rocks	0.1-4 ppm	Phosphorites	1-5 ppm
Ultramafic rocks	<0.1 ppm	Limestones, dolomites	<0.05-3 ppm
		Bauxites	~50 ppm
Metamorphic Rocks		**Waters**	
Highly variable, typically	6-10 ppm	Seawater	0.009 ppb
		River water	<0.26 ppb

[based on data from Wedepohl, 1978a; Hazen et al., 2009].

2.2.2.1 THORIUM ABUNDANCE IN IGNEOUS ROCKS

It is a lithophile element and is predominantly associated with silicic alkaline igneous rocks. Granites and granodiorites may contain around 10 ppm Th, whereas syenites are generally more enriched with up to 35 ppm Th in some cases (Wedepohl, 1978a; Hazen et al., 2009). Basalts and mafic intrusive rocks typically contain between 0.1 to 4 ppm and ultramafic rocks may have even less thorium (Wedepohl, 1978a).

2.2.2.2 THORIUM ABUNDANCE IN SEDIMENTARY ROCKS

The thorium content of sedimentary rocks is highly variable (Wedepohl, 1978a). As discussed above, thorium is highly immobile and tends to be geochemically-separated from mobile uranium during weathering and alteration of primary minerals in igneous parent rocks. Consequently, it is concentrated in resistate detrital heavy minerals such as zircon, monazite, xenotime, apatite etc., or if it is released during weathering then thorium is strongly sorbed onto clays and iron and manganese oxide alteration products. As a result, thorium is often concentrated in residual deposits such as bauxites and heavy mineral placer deposits.

Summary data in Wedepohl (1978a) indicate typical values of around 12 ppm Th for shales and mudrocks; 1 to 7 ppm Th for sandstones; very low values in limestones (because thorium does not enter into the carbonate lattice); 1 to 5 ppm Th in phosphatic rocks, and; >20 ppm in residual deposits such as bauxites and bentonites.

2.2.2.3 THORIUM ABUNDANCE IN METAMORPHIC ROCKS

The concentration of thorium in metamorphic rocks is highly variable, and is dependent on the thorium content of the original parent igneous or sedimentary rock. Wedepohl (1978a) indicates that thorium concentration can range from <0.1 ppm in marble to >67 ppm in some high-grade feldspathic rocks. However, most metamorphic rocks probably have thorium contents close to the crustal average of between 6-10 ppm Th.

2.2.3 Thorium host minerals

There are only a very small number of primary thorium minerals which contain thorium as an essential component (cf. Wedepohl, 1978a, Basham, 1993). The principal thorium minerals include: thorite ($ThSiO_4$), uranothorite ($[Th,U]SiO_4$), thorianite (ThO_2), uranothorianite ($[Th,U]O_2$), thorogummite ($Th(SiO_4)_{1-x}(OH)_{4x}$ - analogous to, and isomorphous with, coffinite), and monazite - in particular, the variety cheralite ($[Th,Ca,Ce][PO_4,SiO_4]$).

Thorite-uranothorite, thorianite-uranothorianite and monazite (cheralite) occur as primary accessory minerals in alkaline granitic rocks, syenites and associated pegmatites. Monazite has also been found to form as a low-temperature concretionary authigenic mineral in Lower Palaeozoic mudrocks and low-grade metamorphic rocks in the U.K. and elsewhere (Milodowski and Zalasiewicz, 1991, and references therein). However, authigenic monazites are typically low in thorium. In the UK and Eurpope, they appear to be restricted to rocks of Lower Palaeozoic age (Milodowski and Zalasiewicz, 1981), although recently they have also been found in Triassic rocks from Iran (Alipour-Asli et al., 2012).

Thorogummite typically occurs as a low-temperature secondary mineral, forming from the alteration, weathering or metamictisation of primary thorite or thorium-rich minerals. It is usually fine grained and poorly crystalline (Basham and Kemp, 1993).

2.3 POTASSIUM

2.3.1 Potassium abundance

Potassium is abundant in the Earth’s crust, with an average crustal concentration of about 2.5% (Wedepohl, 1978b). It has three isotopes, ^{39}K (93.1% isotopic abundance), ^{40}K (0.01% isotopic abundance) and ^{41}K (6.88% isotopic abundance), of which only ^{40}K is radioactive. ^{40}K decays with a half-life of 1250 million years via a combination of beta decay to ^{40}Ca and gamma emission to yield ^{40}Ar. Potassium is a major element in many silicate rocks but may only be present in minor to trace amounts in some sedimentary rocks such as limestones, dolomites and some chemically-precipitated sedimentary rocks. The potassium contents of common rock types is summarised in Table 3.

Table 3. Global ranges of potassium abundance in common rocks

Igneous Rocks		**Sedimentary Rocks**	
Syenites and phonolites	3-6 %	Shales, clays, mudrocks	<0.01-7.1 %
Granites, rhyolites and intermediate igneous rocks	2.5-4.5 %	Sandstones	<0.01-5.6 %
Basalts and other mafic rocks	1-2 %	Evaporites: *Pure gypsum, anhydrite, halite* *Sylvite (KCl)*	variable *0 %* *52.4 %*
Ultramafic rocks	<10 ppm - 1 % [av. ~0.6 %]		
Metamorphic Rocks		Limestones, Dolomites	<0.01-5 % [av. limestone ~0.3 %] [av. dolomite ~0.6 %]
Dependent on parent rock (see igneous and sedimentary)			

[based on data from Wedepohl, 1978b].

2.3.1.1 POTASSIUM ABUNDANCE IN IGNEOUS ROCKS

The abundance and range of concentrations of potassium in common igneous rocks has been collated by Wedepohl (1978b) and is summarised in Table 3.

Potassium is enriched in the more fractionated alkaline silicic rocks and has the lowest concentration in the silica-poor ultramafic rock types. Its concentration primarily reflects the abundance of major potassium silicate minerals, principally: alkali feldspars (orthoclase, sanidine, microcline), micas (biotite, muscovite, phlogopite, paragonite), feldspathoids (nepheline) and alkali-bearing amphiboles:

- Alkali igneous rocks, which include granites, granodiorites, rhyolites, trachytes, typically vary between about 2.5 to 4.5 % K;
- Syenites and phonolites are more alkali-rich and have potassium concentrations between 3 to 6 % K;
- Intermediate igneous rocks, which include diorites and andesites, typically have potassium concentrations between about 1 to 2 % K;
- Mafic igneous rocks, which include, gabbros and basalts, have potassium concentrations typically in the range 0.5 to 1.3 % K;
- Ultramafic rocks, which include pyroxenites, anorthosites, dunites, peridotites, and eclogites, typically have very low potassium. However, potassium concentrations vary considerably from <10 ppm K in some dunites and peridotites to about 1 % in some anorthosites. An average concentration for ultamafic rocks is about 0.6 %.

2.3.1.2 POTASSIUM ABUNDANCE IN SEDIMENTARY ROCKS

The concentration of potassium in sedimentary rocks is highly variable (Table 3). and dependent on detrital mineralogy, primary chemically-precipitated sedimentary minerals (i.e. evaporite mineralogy), and alteration during sediment burial (diagenesis).

Carbonate rocks and sediments can contain between <0.01 to 5 % K. The bulk of the potassium in these materials is essentially contained in the non-carbonate fraction. This largely comprises detrital silicate minerals such as alkali feldspars, micas and clay minerals (particularly potassium-rich clay minerals such as illite, smectite or mixed-layer illite-smectite). Pure limestones and dolomites contains only trace amounts of potassium (Wedepohl, 1978b).

The potassium content of mudrocks (clays, shales, mudstones, siltstones) is largely controlled by the clay mineralogy, with subordinate contribution from K-feldspar (Wedepohl, 1978b). There is usually a strong positive correlation between potassium concentration and clay mineral content. This is also reflected in the wireline gamma-logs of sedimentary sequences, where clay-rich strata normally correlate with an enhanced gamma response (Serra, 1984; Hurst, 1990). The most common and major potassium-bearing clay mineral in mudrocks is illite and clay-grade detrital micas. Less potassic mixed-layer illite-smectite and smectite may also contribute in some clays. Glauconite, which is usually of detrital origin, can also be an important source of potassium in some sedimentary sequences

The potassium content of sandstones is principally controlled by three main minerals: K-feldspar, mica and glauconite. K-feldspar may be detrital or authigenic in origin. The amount of detrital K-feldspar and mica decreases with increasing sediment maturity. Glauconite is usually formed in situ as authigenic mineral during burial diagenesis. The amount of clay present (which reflects the “cleanliness” or degree of sorting of the sandstone) also influences the potassium content: poorly sorted clay-rich sandstones usually contain more potassium than well-sorted low-clay sandstones.

The potassium content of evaporite rocks is a function of the presence or absence of potassium-rich salts that are precipitated from highly-evolved brines during late-stage extreme evaporation. Pure gypsum, anhydrite and halite contain only minor or trace amounts of potassium. The potassium content of evaporites dominated by these minerals will be influenced largely by the presence of detrital clay minerals. However, late-stage evaporite sequences may include potash deposits formed by the precipitation of potassium salts. There are a large number of potassium salts but the volumetrically most important potassium mineral in evaporites is sylvite (KCl). The mixed salt carnallite ($KMgCl_3.6(H_2O)$), and the sulphate salt polyhalite ($K_2Ca_2Mg(SO_4)_4.2H_2O$), are also important potassium-bearing evaporite minerals.

2.3.1.3 POTASSIUM ABUNDANCE IN METAMORPHIC ROCKS

Metamorphic rocks contain a wide variation in potassium concentration. This primarily reflects the nature of the original parent igneous or sedimentary precursor rock. For example, pelitic rocks derived by the metamorphism of mudrocks contain major mica and consequently will contain significant potassium. In contrast, quartzite formed by the metamorphism of a clean quartz-rich sandstone (orthoquartzite) will contain little-or-no potassium.

2.4 DISTRIBUTION OF BACKGROUND RADIOACTIVITY FROM ROCKS IN THE UK

The BGS undertook an assessment of distribution of background γ-radioactivity in the UK in 1983 (Plant et al., 1983), which is summarised in Figure 3. Subsequent assessments for radon potential (Miles et al., 2007; Scheib et al., 2013) provide further information on the distribution of radioactivity in the UK. The distribution of radioactivity closely reflects the underlying bedrock geology (Figure 4).

High background radioactivity is principally associated with large granitic bodies, in particular the evolved potassium-rich alkaline granites, including: the Hercynian southwest England batholith (Dartmoor, Bodmin Moor, Carnmenellis, St Austell and Land’s End granites); Shap and Skiddaw in the Lake District, Cairngorm and Etive in northern Scotland; Caledonian granites of the Southern Uplands of Scotland and northeast England (e.g. Criffell Granodiorite and Cheviot Granite), and the Altanabreac Granite in Sutherland and Caithness, northeast Scotland. These granites contain high concentrations of uranium, thorium and potassium (Plant et al., 1983 and references cited therein). Most of the uranium and thorium in these granitic rocks is hosted within primary igneous accessory minerals such as uraninite/pitchblende, thorite, thorianite, zircon, xenotime, monazite- cheralite, apatite, titanite, allanite and apatite.

High levels of background radioactivity also correspond to the interbedded lacustrine rocks of the Middle Old Red Sandstone (Devonian) of the Orcadian Basin of Caithness, Sutherland, Orkney and Shetland in northeast Scotland. These rocks contain significant uranium closely associated with organic-rich strata, phosphatic fossil-fish beds and localised carbonate-sulphide fracture mineralisation (where minor amounts of uranium minerals are often associated with residual bitumen related to hydrocarbon mobilisation (e.g. Milodowski et al., 1989 and references therein).

The highest levels of total natural radioactivity are associated with localised hydrothermal polymetallic vein mineralisation. The main occurrences include: minor vein mineralisation at the margins of the Criffell Granodiorite on the Solway Coast, at Needle’s Eye, near Dalbeattie (Miller and Taylor, 1965; Gallagher et al., 1976; Basham et al., 1989); Broubster, near Dounreay in Caithness (Gallagher et al., 1976; Ball and Milodowski, 1989; Milodowski et al., 1989), and several other small vein deposits in Caithness and Orkney (Gallagher et al., 1976); and numerous localities in the southwest of England mining region where uranium is concentrated in hydrothermal vein deposits, the most significant of which is at South Terras on the St Austell Granite where uranium was mined commercially in the late 19th and early 20th century (Dines, 1956; Hooker et al., 1989; Read et al., 1991). The principal uranium mineral associated with these vein deposits is uraninite, sometimes associated with coffinite (Basham et al.,1982) Secondary oxidation, leaching and mobilisation of uranium by percolating groundwater has resulted in the formation of a wide range of secondary low-temperature uranyl minerals associated with many of these deposits. In the case of the Needle’s Eye (Solway Coast) and Broubster (Caithness) uranium mobilised by groundwater from the primary vein mineralisation has been locally concentrated by re-deposition in adjacent organic-rich near-surface sediments (peats and intertidal sediments) to levels in excess of 1000 ppm U (Basham et al., 1989; Ball and Milodowski, 1989; Milodowski et al., 1989).

Moderately-high radioactivity is associated with localised sedimentary facies such as: phosphatic limestone horizons in the Lower Carboniferous Dinanian limestones, mostly in north England; organic-rich marine bands in Namurian and Westphalian mudrocks (e.g. Bowland Shale, Edale Shale); the ironstones and limestones within the Jurassic – i.e. Lias, Inferior Oolite Group (including the Northamptonshire Sand Formation, previously referred to as the Northamptonshire Ironstone) Great Oolite Group and Bridport Sand Formation (Plant et al., 1983; Hodgkinson et al., 2006; Schreib et al., 2013).

The areas of lowest background radioactivity correspond to: the Cretaceous Chalk, Tertiary sedimentary rocks, and unmineralised Lower Carboniferous Limestones in England; granulite-facies Lewisian metamorphic rocks of northwest Scotland, and; areas underlain by mafic and ultramafic rocks in general (e.g. the lizard, Cornwall), Tertiary basalts of northwest Scotland, and mafic and ultramafic rocks of the Grampians and Aberdeenshire).

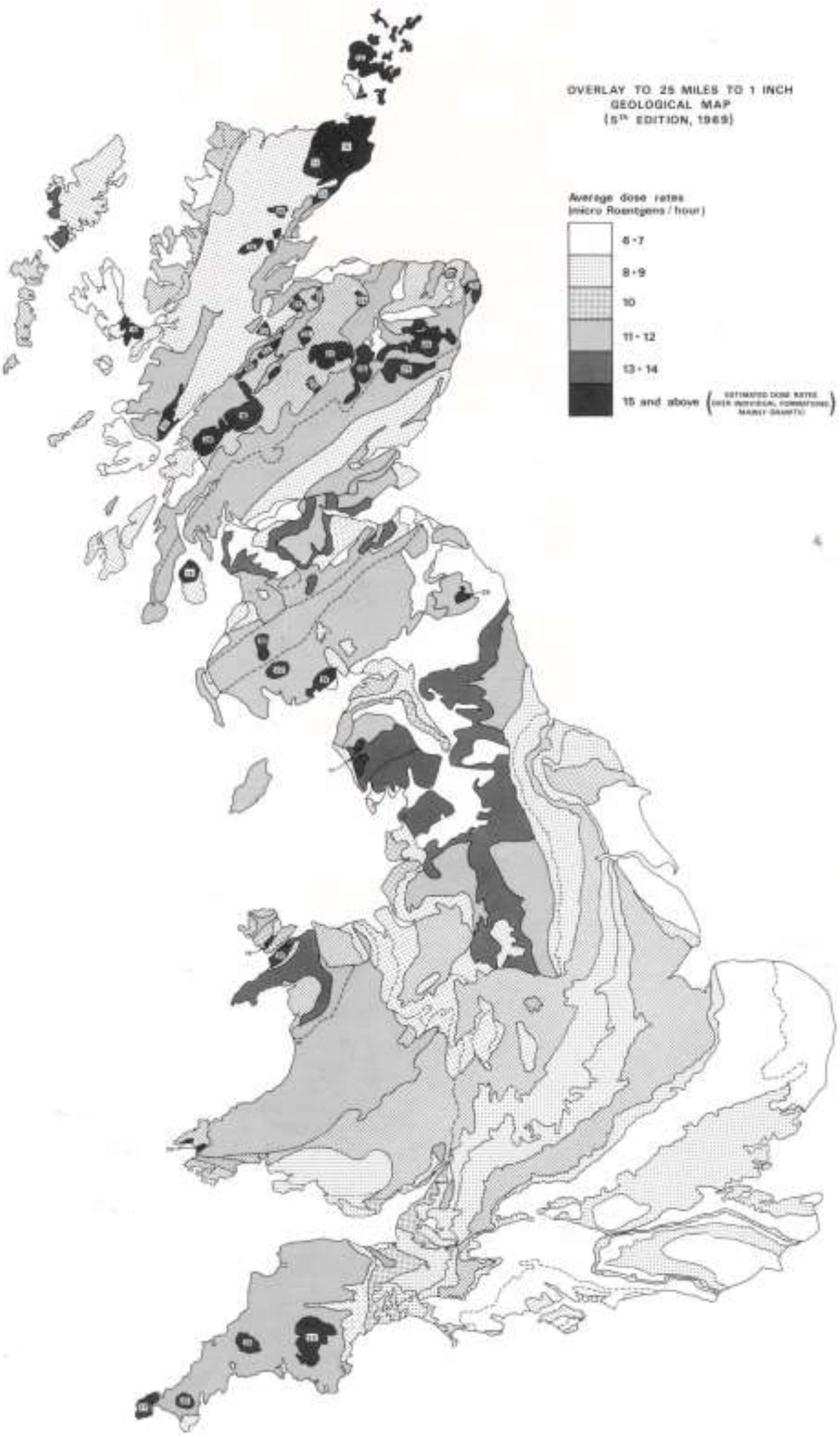

Figure 3. Distribution of radioactivity in the U.K. (data from Plant et al., 1983 ©Crown Copyright, 1983).

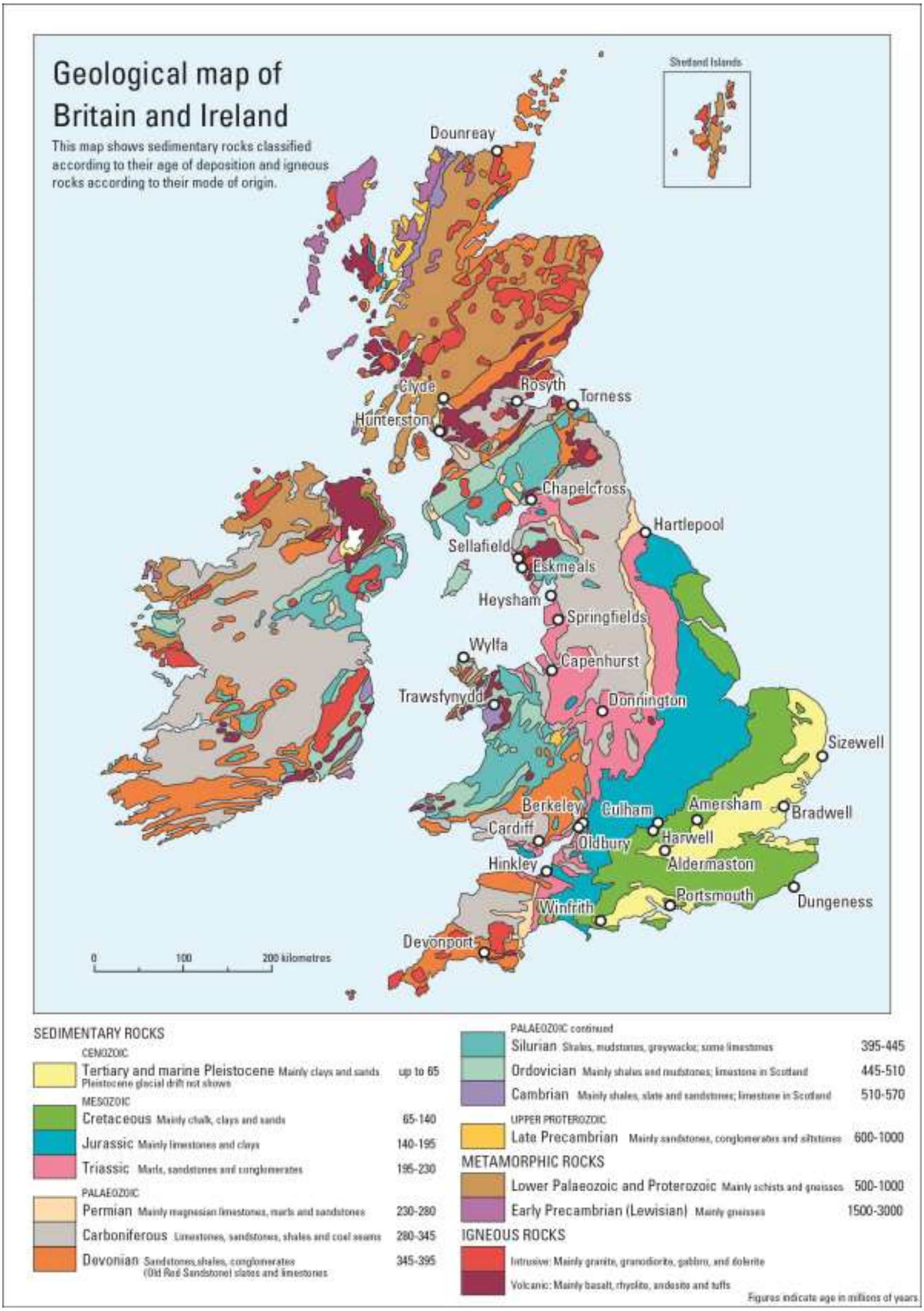

Figure 4. Simplified geological map of the U.K showing the main geological units with the locations of the main sites relevant to the NDA (base geological map $^{©}$British Geological Survey, 2016).

Other areas of elevated background radioactivity are associated with shale and volcanic lithologies of the Ordovician and Silurian of Wales and the Southern Uplands of Scotland, and the Devonian of southwest England (Figure 3 and Figure 4). Some of these areas are associated with moderate-to-high radon risk (e.g. Environment Agency, 2007; Miles et al., 2007; Schreib et al, 2013), and petrographic analysis indicates that uranium is hosted largely within detrital heavy minerals (zircons etc.), iron-rich clays, goethite alteration products, and phosphatic (apatitic) cements (Hyslop and Pearce, 1999; Hodgkinson et al., 2006 and unpublished BGS data).

2.5 NATURAL BACKGROUND RADIOACTIVITY AT UK NUCLEAR SITES

Figures 4 and 5 indicate that, with the exception of Dounreay, Clyde, Rosyth, Hunterston, Torness and Trawsfynydd, most of UK nuclear sites relevant to the responsibility of the NDA are most probably located in areas with low- to moderately-low background radioactivity.

2.5.1 Dounreay

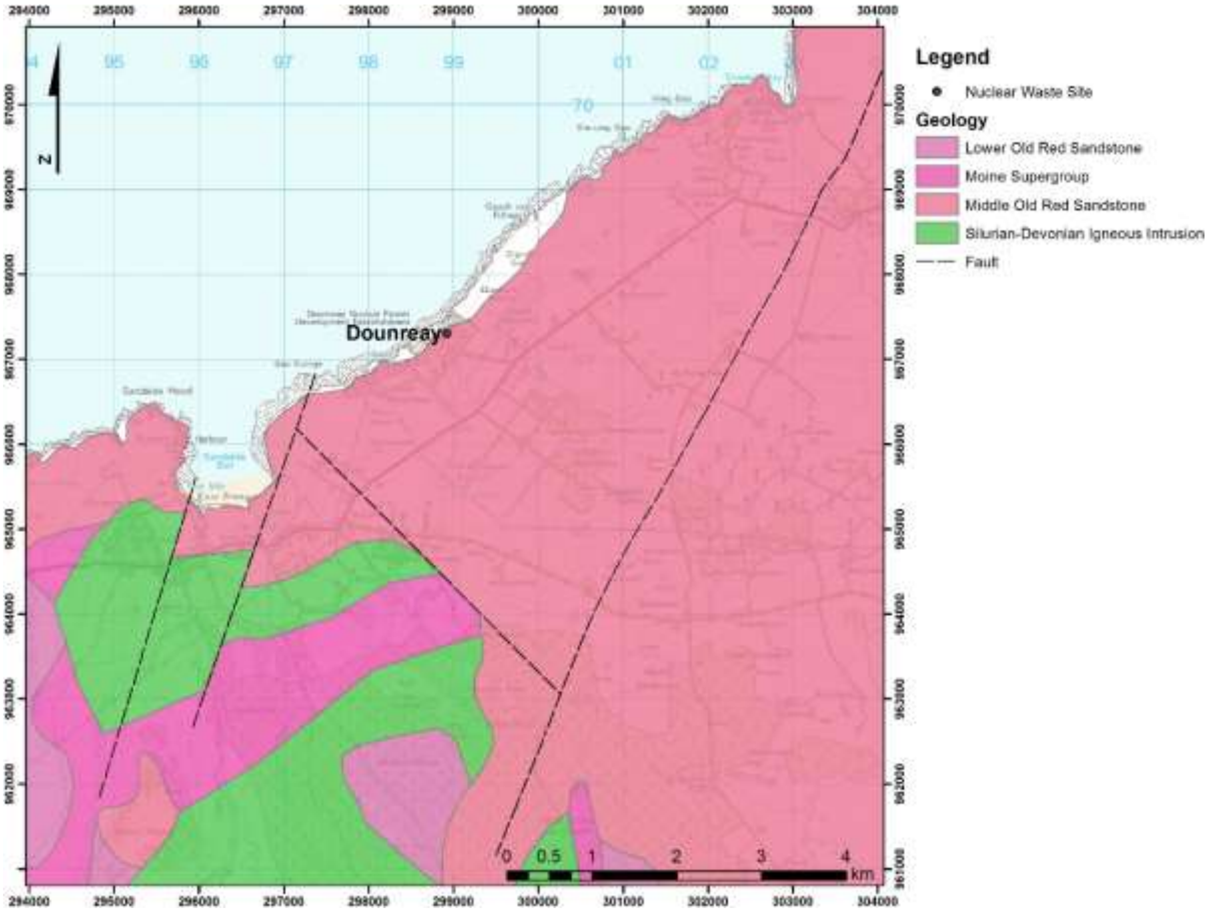

Figure 5 Bedrock geology of the Dounreay area.

Dounreay is located on the Middle Old Red (Devonian), Caithness Flagstone Group bedrock (Figure 5). These unconformably overly Moine (Late Precambrian) metasedimentary rocks (semipelites and psammites), bodies of dioritic and amphibolitic metamorphosed igneous rocks; intruded by: later Caledonkian (Silurian-Devonian) diorite and granodiorite (Reay Diorite). These crystalline basement rocks outcrop to the south and west of the Dounreay site (Figure 5).

Detailed mineralogical and chemical analyses of these rocks have been reported as part of the UK Nirex site investigations and generic Nirex Safety Assessment Research Programme (NSARP) studies at Dounreay (Milodowski et al., 1991; Hyslop and Milodowski, 1994; Hyslop and Milodowski, 2000; Milodowski et al., 2000)

The Caithness Flagstone Group has a relatively high background radioactivity (Figure 3, and Plant et al., 1983). These rocks are predominantly a succession of lacustrine deposits, comprising a cyclic sequence of feldspathic to subfeldspathic and micaceous sandstones, siltstones, finely-laminated organic-rich shales, and finely-laminated organic-rich limestones sometimes containing abundant phosphatic fossil fish remains (Donovan, 1980). The potassium concentration in the Caithness Flagstone Group rocks at Dounreay ranges from 0.7 to 4.7 % K_2O (Hyslop and Milodowski, 1994). Within the sandstones, the potassium is hosted largely within detrital K-feldspar and micas, and illite clay matrix. The shales and muddy laminae in the limestones are dominated by detrital chlorite and illite, and therefore illite is probably the main, potassium source. Uranium concentrations in this formation at Dounreay are generally between 1-5 ppm U. However, some horizons are significantly more uraniferous with between 10-25 ppm U (Hyslop and Milodowski, 1994). Fault-rock mineralised by calcite, sulphides and bitumen containing abundant inclusions of uranium silicate (probably coffinite) was encountered within the Caithness Flagstone Group during drilling of the Nirex borehole NDN1 at Dounreay, and found to contain 10-80 ppm U. This produced a strong wireline gamma log response during geophysical logging of the borehole. Thorium is present at concentrations between 5 to 12 ppm Th (Hyslop and Milodowski, 1994). It is present largely in detrital heavy minerals (e.g. monazite). However, traces of authigenic monazite have also been found as authigenic inclusions associated with minor to trace amounts of residual bitumen in the Caithness Flagstone Group (e.g. Milodowski et al., 1989; 1991).

Early BGS mineral exploration studies identified common enrichments of uranium (up to 1500 mg/kg) associated with the phosphatic and black shale horizons throughout the Caithness Flagstone Group of northeast Scotland (Michie et al. 1972). The phosphatic enrichments are typically associated with the fish beds (Donovan's (1980) lithological association A). Elevated concentrations of lead, zinc, copper, molybdenum and silver are also commonly associated with the uranium enrichments (Michie et al. 1973, Michie, 1970), and zinc and / or molybdenum can be particularly enriched in black shale horizons (Tweedie, 1981). There is strong association between uranium and phosphate content in these rocks (100 ppm U / 1% P_2O_5; Tweedie, 1981), which is consistent with the enhancement of uranium in the fossil fish debris.

A detailed study by Milodowski et al. (1990) of a site of particular enrichment at nearby Broubster to the soth of Dounreay (Michie, 1970) also found uranium largely present within the carbonate lattice of limestone laminae in beds of interlaminated siltstone laminae, limestone and organic laminae (Facies A: Donovan, 1980), and to a lesser extent (although in greater enrichment) in the organic-rich and phosphate-bearing siltstone-mudstone beds (Facies B: Donovan, 1980), where it occurs spatially related to diagenetic pyrite. Additionally, uranium was found associated with early diagenetic hydrocarbons as discrete included minerals, and in calcite-dolomite-barite vein mineralisation containing minor copper and zinc sulphides, uraninite, and residual bituminous hydrocarbon Detailed petrographical studies (Milodowski et al. (1991, 1994; Evans, 1996) observed similar minor diagenetic (matrix)- and fracture-hosted uranium mineralisation associated with residual bitumens elsewhere in the MORS, including in core samples from the Dounreay Shaft area (Milodowski et al., 1991) and from the Nirex Dounreay Borehole NDN1 (Milodowski et al., 1994; Evans, 1996).

Uranium enrichment is also found along the unconformity surface between the MORS and the Moine basement in the Dounreay area. Hyslop and Milodowski (2000) examined the MORS unconformity with the Reay Diorite at Achvarasdal (2.5 km east of Reay) and Borlum House (1 km south of Reay), on granite and amphibolite at Portskerra (~12km west of Dounreay), and on granite at Baligill (15 km west of Dounreay. They found uranium to be concentrated along the

Devonian palaeoweathered horizon (regolith), and hosted largely within fine grained secondary iron and titanium oxides, and accessory secondary light rare earth element (La,Ce,Nd) phosphates. These secondary minerals were associated closely with the weathering and alteration of biotite and amphiboles to chlorite, and the breakdown of primary ilmenite and or titaniferous magnetite to anatase (TiO_2) and poorly crystalline secondary Fe-Ti oxide phases. Up to 500 ppm U was found within these secondary phases, although it is unclear whether the uranium is sorbed onto, or if it is incorporated within the crystal structure of, the iron-titanium oxides. Thorium was also found to be present in the same phases.

Detailed autoradiography studies have revealed that uranium mobilisation and enrichment is also encountered on fracture surfaces and within the adjacent altered wallrock matrix in the Caithness Flagstone Group, in association with iron oxyhydroxides formed by near-surface weathering and shallow oxidative groundwater alteration (Milodowski et al., 1990, 1991). The iron oxyhydroxide formation is related to the dissolution and oxidation of ferroan calcite, ferroan dolomite and ankerite cements, and iron sulphides in fracture mineralisation and matrix diagenetic cements. This alteration is associated with alteration in the present-day weathering and shallow groundwater environments.

Detailed mineralogical and petrographical analysis of drillcore from the Nirex Dounreay Borehole NDN1 found minor but significant uranium silicate and uranium-titanium oxide mineralisation, closely associated with calcite and residual bitumen cementing a large fault breccia within a broad silicified zone of Facies A rock in the Caithness Flagstone Group sequence at around 305 m depth. This uranium mineralisation corresponds to the anomalously high gamma response recorded at this depth on the borehole gamma log. The uranium minerals are accompanied by minor amounts of pyrite, galena and barite. Similar uranium silicate and uranium-titanium oxide minerals are found as trace authigenic minerals closely hosted as inclusions within scattered bitumen globules in the matrix of the Caithness Flagstone Group Facies A rocks and occasionally in the more sandstones and siltstones (Milodowski et al., 1994). The same uranium minerals are also found mineralising fossil fish, and accounts for the high degree of radioactivity reported from these fossil fish (Milodowski et al., 1994, and AE Milodowski, unpublished data)

2.5.2 Clyde

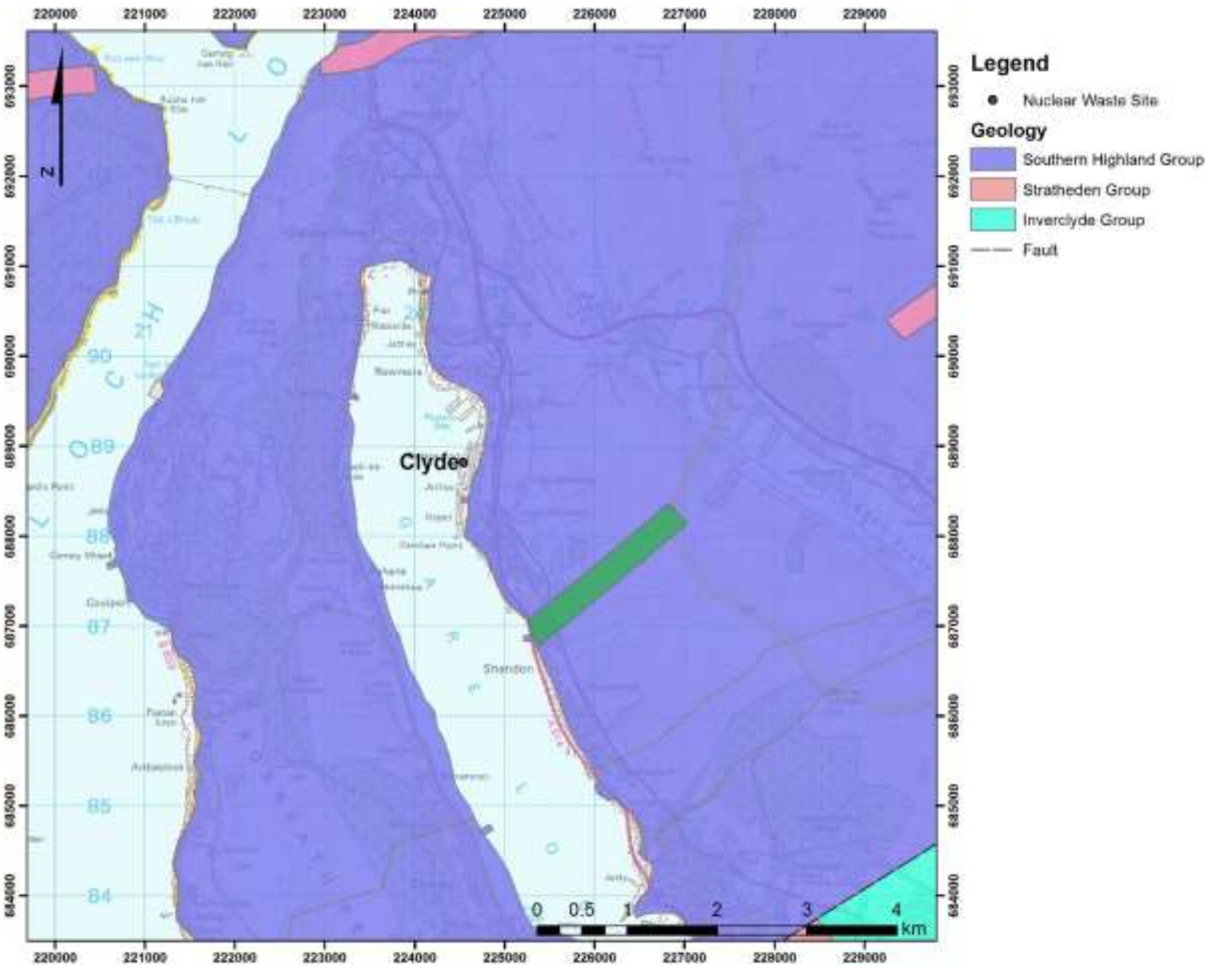

Figure 6. Bedrock geology of the Clyde area.

The Clyde site is located on bedrock belonging to the Southern Highland Group (Figure 6). These form part of Dalradian Supergroup, and are probably of Ordovician age. Regionally, they comprise greenschist facies schistose pebbly grits, schistose grits and greywackes, schistose semi-pelites and pelites, together with purple or black phyllites and dark fine-grained limestones. (Roberts, 1977). No specific rock data for uranium, thorium and potassium are available from this site. However, these rock types will be mica (biotitic and / or muscovite) rich, and also likely to contain significant K-feldspar. Consequently, they will be relatively high in potassium. No significant uranium or thorium mineralisation is recorded in this area and uranium and thorium are expected to be generally close to average crustal concentrations.Figure 3 indicates that these rocks moderately radioactive, which would be consistent with most background radioactivity being derived largely from potassium in these mica and feldspar-rich rock types.

2.5.3 Hunterston

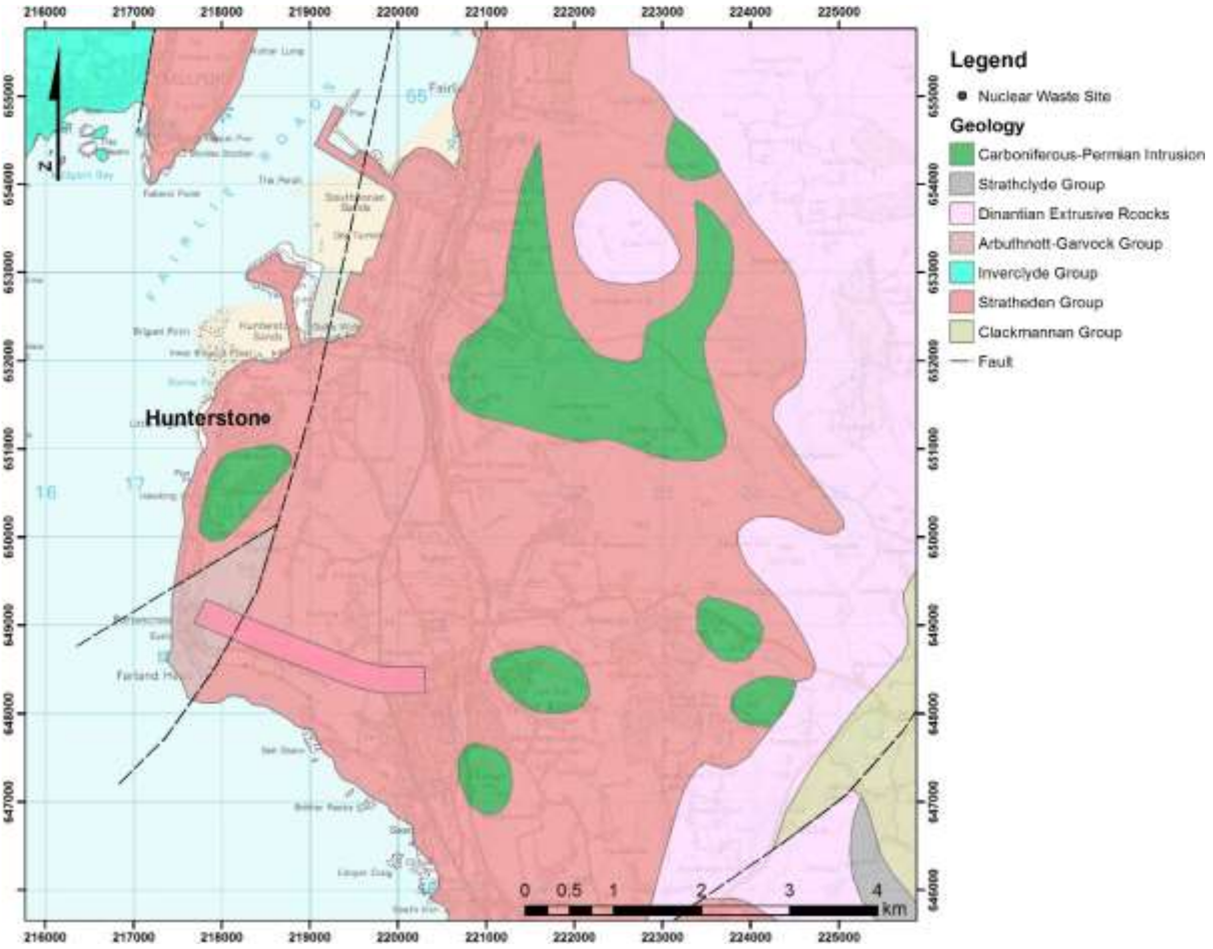

Figure 7. Bedrock geology of the Hunterston area.

The Hunterston site is located on bedrock belonging to the Late Devonian Stratheden Group Group (Figure 7). Regionally, these rocks consist mainly of red-brown sandstones with subordinate conglomerates and mudstones (Brown et al., 2001). No specific rock data for uranium, thorium and potassium are available from this site. However, Figure 3 indicates that these rocks have a relatively high total background radioactivity. Petrographic analyses of this formation from elsewhere in the Midland Valley of Scotland (Milodowski and Rushton, 2008; Monaghan et al., 2012) shows the sandstones are commonly subfeldspathic to sublithic arenites with detrital quartz and minor K-feldspar, albite, muscovite, biotite and chlorite. Mudstones and siltstones are commonly composed of illitic clay with minor quartz, muscovite, biotite and chlorite. Therefore, at least part of the radioactivity will be derived from potassium decay in these potassium-rich minerals. However, it is also possible that the enhanced radioactivity may be related to the presence of phosphatic fossil fish in this formation (Brown et al., 2001).

2.5.4 Rosyth

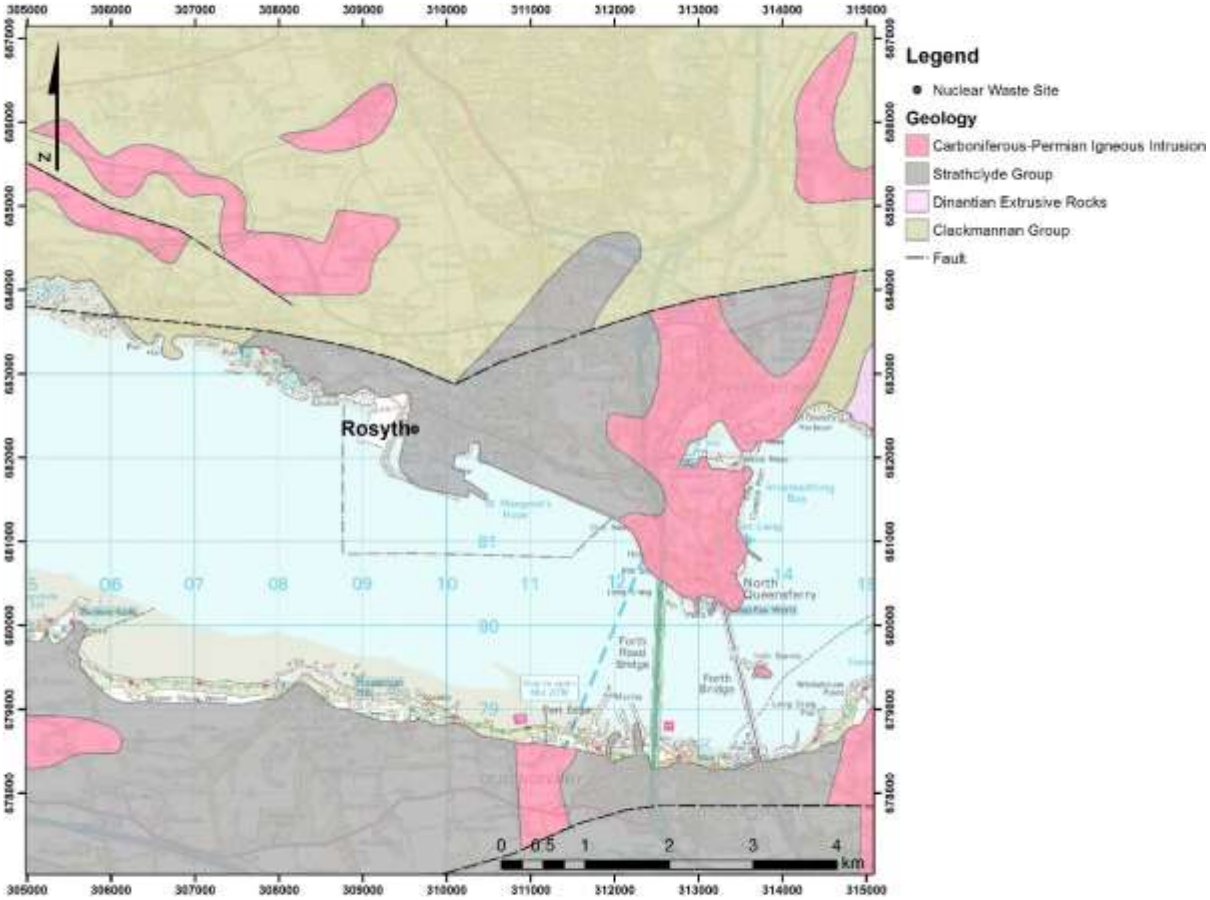

Figure 8. Bedrock geology of the Rosyth area.

Rosyth is situated on bedrock belonging to the Lower Carboniferous Strathclyde Group (Figure 8). In the Fyfe region these rocks comprise a sequences of interbedded sandstones with mudstones, mudstones and siltstones with minor limestone, mudstone, and mudstones and siltstone with limestone and dolomite and minor sandstones (Monaghan et al., 2012). The mudrocks in this sequence are organic-rich and include minor oil shales and coals. Nearby to the north, the Strathclyde Group rocks are overlain by, and faulted against, younger Carboniferous strata belonging to the Clackmannan Group. These rocks also comprise cyclical sandstone, mudstone and siltstone with minor limestone, minor coal and sideritic ironstone (Monaghan et al., 2012). Mineralogically, the sandstones are commonly subfeldspathic to sublithic arenites with detrital quartz and minor K-feldspar, albite, muscovite, biotite and chlorite. Mudstones and siltstones are commonly composed of illitic clay with minor quartz, muscovite, biotite and chlorite.

No detailed information for uranium, thorium or potassium are available. Like Hunterston (above) Figure 3 suggests that these Carboniferous rocks have a relatively high total background radioactivity. Some of this radioactivity will be contributed from potassium in detrital K-feldspar, micas and illite, which are abundant in these rocks. However, it is possible that the enhanced background radioactivity could potentially be associated with more organic-rich strata (black shales, coals and oil shales) present in the sequence. These rock types are commonly associated with elevated uranium concentrations (cf. Table 1)

2.5.5 Torness

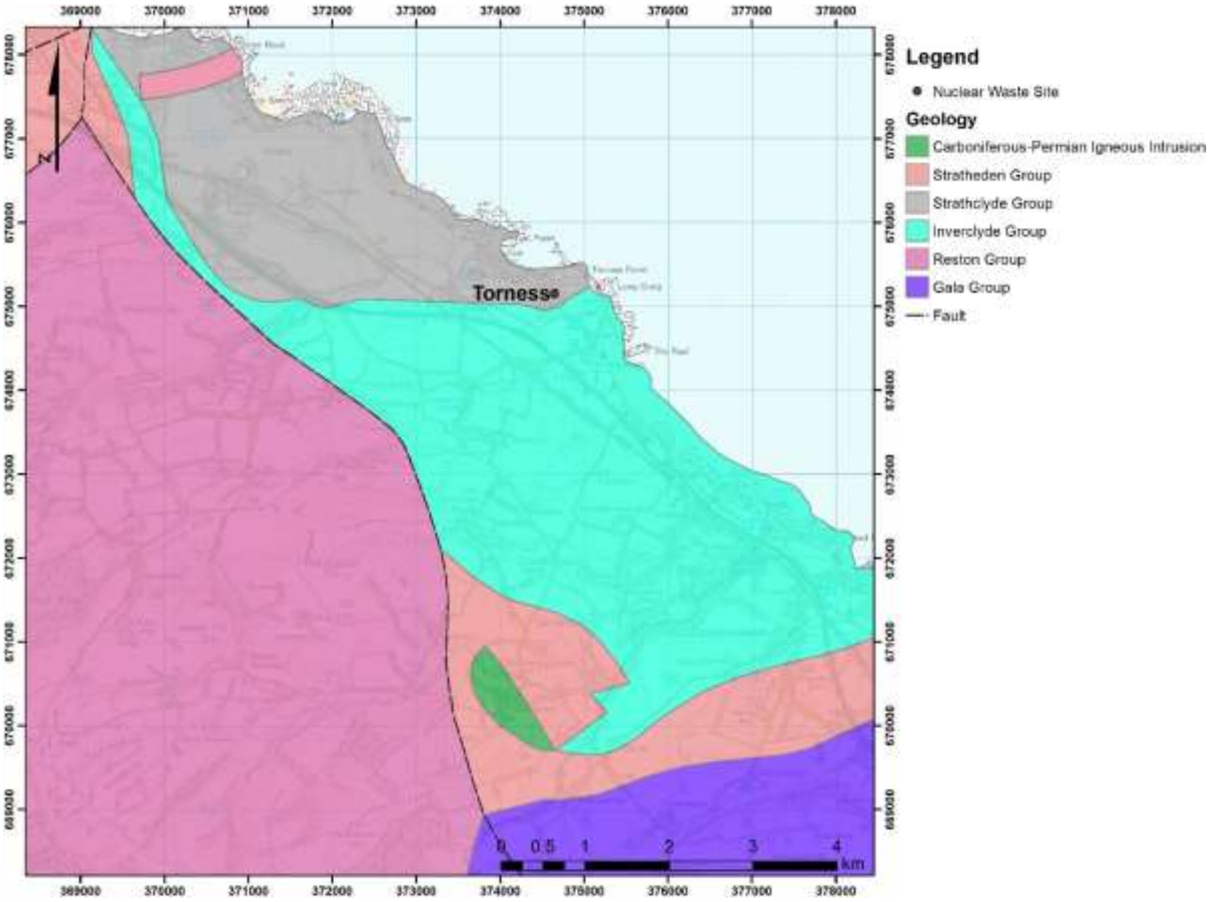

Figure 9. Bedrock geology of the Torness area.

The Torness site is underlain by the Lower Carboniferous Strathclyde Group, which close to the south of the site these rocks overly the Lower Carboniferous Inverclyde Group (Figure 9). In the East Lothian Region the Strathclyde Group comprises cyclical sandstone, siltstone and mudstone with minor coal, seatrock, limestone and ironstone (Monaghan et al., 2012). The underlying Inverclyde Group is dominated by sandstones with some mudstones and pedogenic carbonate rocks (dolostone and calcrete limestone) (Monaghan et al., 2012). Little specific mineralogical data is available but by comparison with rocks of similar age in the Midland Valley to the north (Milodowski and Rushton, 2008; Monaghan et al., 2012), and to the south and from the Southern North Sea (Shaw, 2006), they probably include feldspathic to subfeldspathic sandstones and a clay mineralogy comprised of kaolinite, chlorite and illite.

No detailed information is available for uranium, thorium and potassium in the bedrocks from this site. The total background radioactivity appears to be low to very low. Most of this activity is possibly related to potassium-bearing minerals (K-feldspars and illite).

2.5.6 Chapelcross

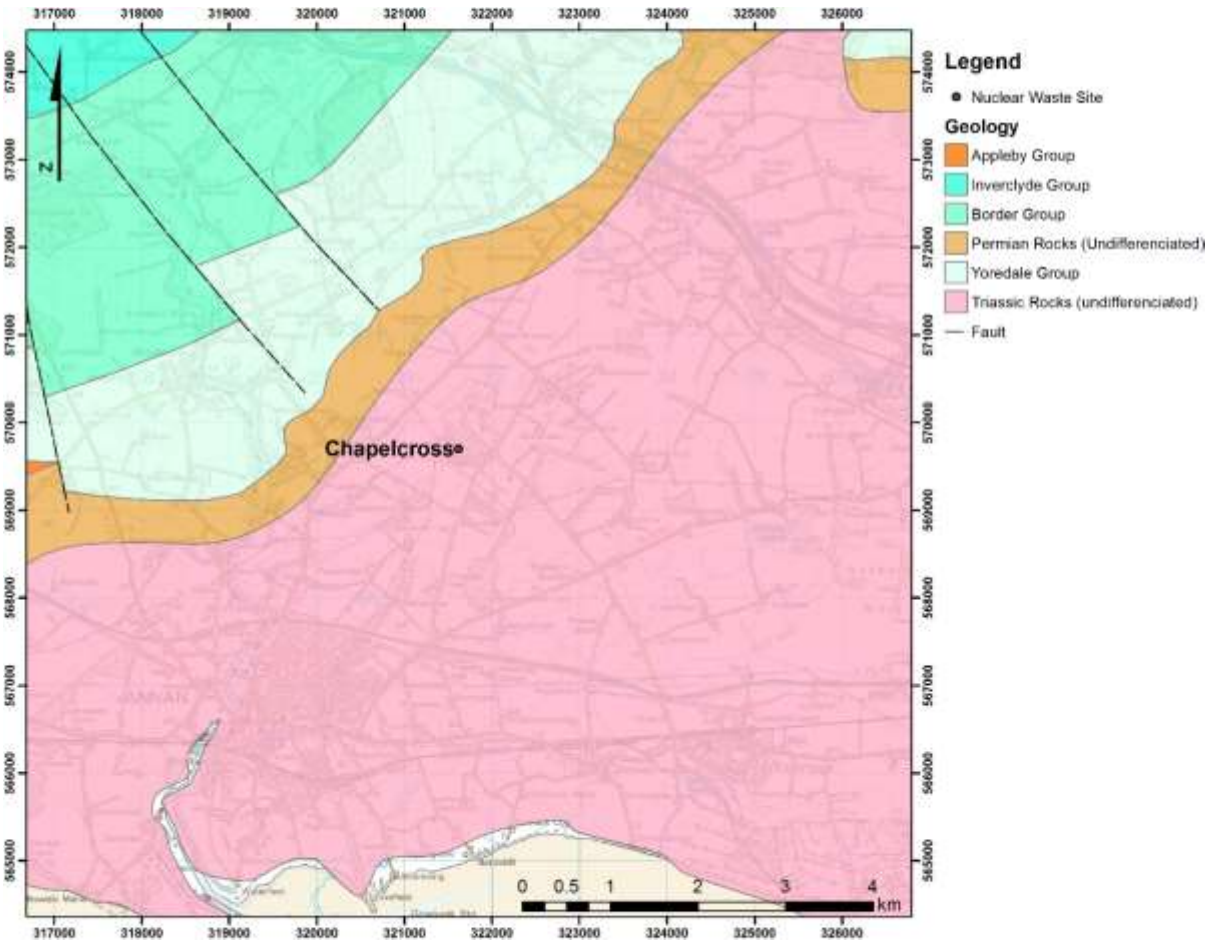

Figure 10. Bedrock geology of the Chapelcross area.

Chapelcross lies within the Permo-Triassic Carlisle Basin. The site is underlain by the St Bees Sandstone Formation of the Sherwood Sandstone Group (Triassic) (Figure 10). These rocks comprise sporadically micaceous and/or silty, some beds grade up to medium-grained, and intraformational mud clasts are common at some levels (Stone et al., 2012). Thin partings of siltstone, silty mudstone and mudstone may be present.

This area appears to have very low background radiation (Figure 3). No detailed petrological and geochemical data for uranium, thorium and potassium are available for the St Bees Sandstone at this site. However, based on data from elsewhere in northwest England (Strong and Kemp, 1997; Ackhurst et al., 1997; Milodowski et al., 2000; Hyslop et al., 2000) these rocks are likely to be dominated by subfeldspathic sandstones containing minor detrital K-feldspar and mica, and illitic clay present either as matrix clay in poorly-sorted sandstones and mudstone clasts and laminae. Similar sandstones from west Cumbria contain <1 to 4 ppm U, 3 to 9 ppm Th, and 2 to 4 % K_2O (e.g. Strong and Kemp, 1997; Milodowski et al., 2000; Hyslop et al., 2000). These values are typical of those normally found sandstones globally (Tables 1 to 3, and Wedepohl, 1978a,b). Uranium and thorium are likely to be located principally in detrital heavy minerals – zircon, monazite and apatite. (Milodowski et al., 2000; Hyslop et al., 2000). Fine grained hematitic coatings and hematitic clay matrix material may also contain a minor proportion of the uranium and thorium (Milodowski et al., 2000; Hyslop et al., 2000). The major hosts for potassium with be detrital K-feldspar, mica and illite.

2.5.7 Sellafield

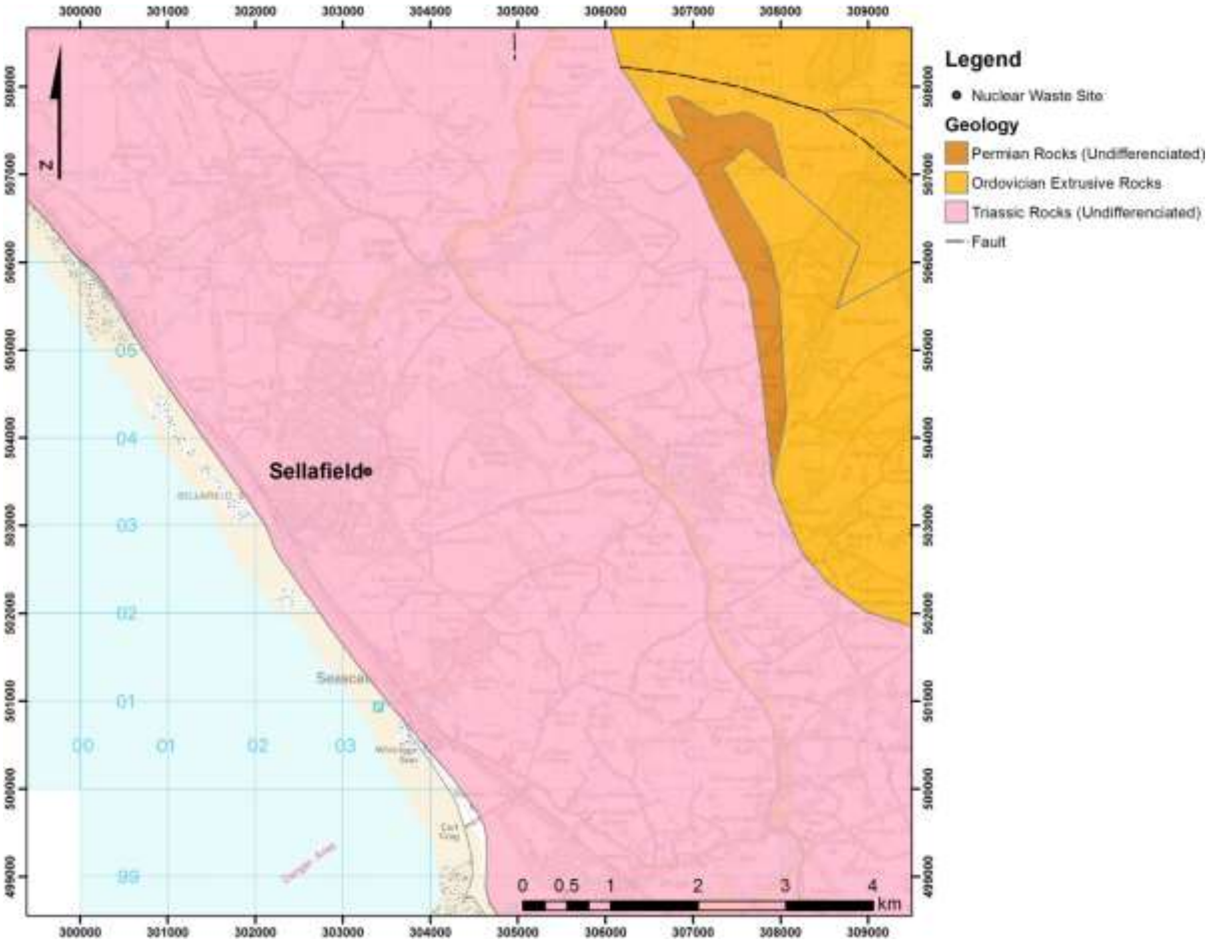

Figure 11. Bedrock geology of the Sellafield area.

The bedrock at the Sellafield site (Figure 11) is the St Bees Sandstone Formation, which form the lower part of the Triassic Sherwood Sandstone Group (Ackhurst et al., 1997). The area has relatively low total natural radioactivity (Figure 3).

The mineralogy, petrology and geochemistry of these rocks was studied in detail as part of the UK Nirex Limited site investigation programme at Sellafield (1990 to 1997) and within the generic Nirex Safety Assessment Research Programme (NSARP). The sandstones are dominated by subfeldspathic sandstones containing minor detrital K-feldspar and mica, and illitic clay present either as matrix clay in poorly-sorted sandstones and mudstone clasts and laminae (e.g. Strong and Kemp, 1997; Milodowski et al., 2000; Hyslop et al., 2000). They contain <1 to 4 ppm U, 2 to 11 ppm Th, and 2 to 4 % K_2O (e.g. Strong and Kemp, 1997; Milodowski et al., 2000; Hyslop et al., 2000), which are typical of those normally found sandstones globally (Tables 1 to 3, and Wedepohl, 1978a,b).

The principal mineral hosts for potassium in these rocks are K-feldspar, mica and detrital illite. Uranium and thorium are hosted largely in detrital accessory minerals: zircon (typically several hundred ppm U), monazite (>500 pmm U), and apatite. (up to 50 ppm U) (Milodowski et al., 2000; Hyslop et al., 2000). Uranium is also present in lower concentrations and at variable levels) in secondary sites associated with altered lithic grains (typically several tens of ppm), where is appears to be associated with fine grained hematite (Milodowski et al., 2000).

Calcite vein mineralsation appears to have had little effect on the distribution of uranium in the adjacent wallrock. However, secondary manganese and iron oxyhydroxides, coating the fracture surfaces and penetrating into the adjacent sandstone wallrock of fractures associated with modern groundwater movement, show enhanced levels of uranium (Hyslop et al., 2000). Radium is also concentrated in the secondary manganese-iron oxyhydroxide, which may also be barium-rich (Hyslop et al., 2000). The manganese and iron oxyhydroxide alteration is associated with weathering and oxidation of ferroamanganoan calcite and dolomite vein mineralisation and matrix cements, and alteration of iron-bearing detrital minerals by percolating shallow groundwater (Milodowski et al., 1998).

The Triassic bedrock at Sellafield is covered a thick sequence of till and fluvial-glacial deposits (Ackhurst et al., 1997; McMillan et al., 2004, which may mask the underlying sandstones. These unconsolidated Devensian deposits are, for the large part derived from the underlying local bedrocks. No information is available on the distribution of uranium and thorium in these sediments. However, it is possibly similar to that seen in the St Bees Sandstone Formation.

2.5.8 Eskmeals

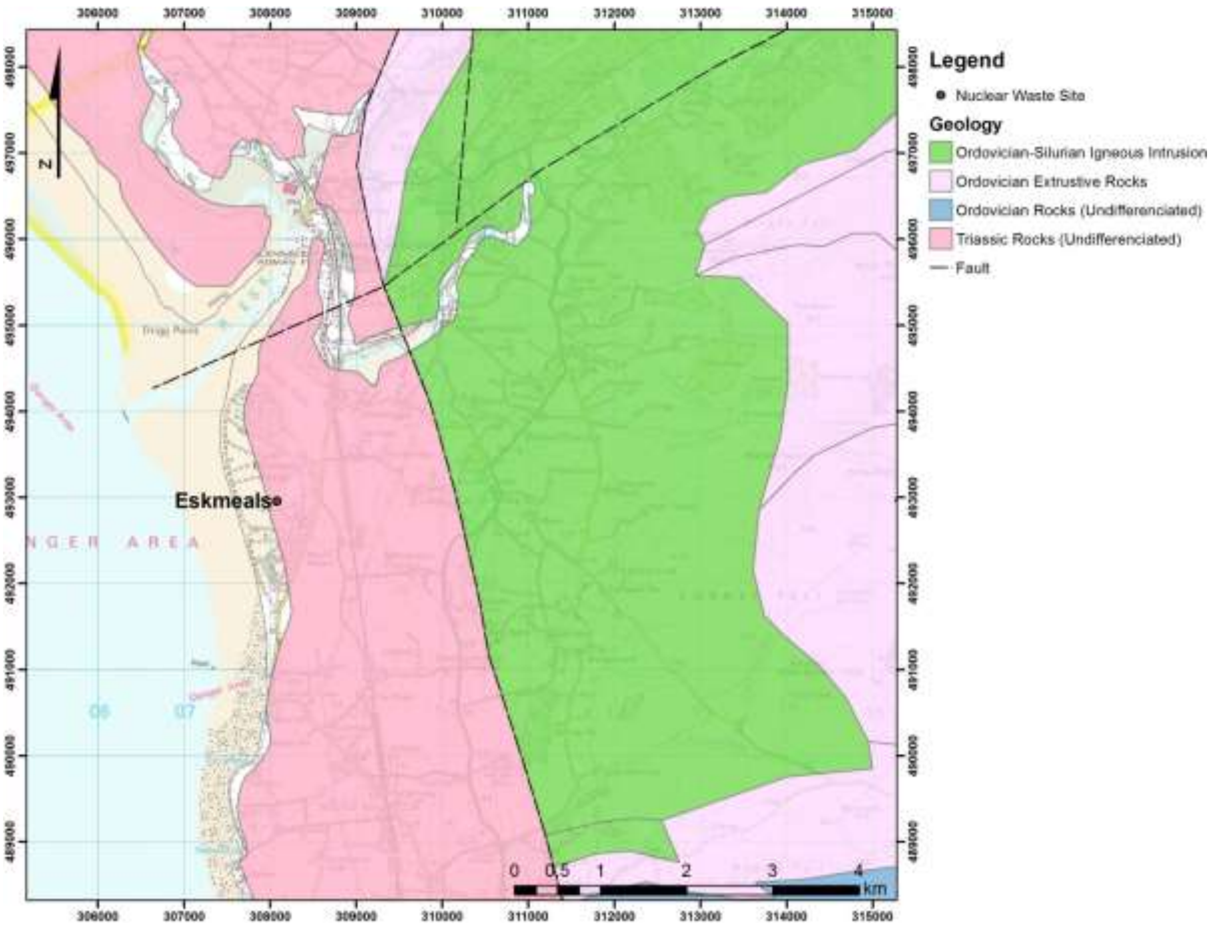

Figure 12. Bedrock geology of the Eskmeals area.

The Eskmeals site occupies a region of Holocene coastal dunes and interdunes, and shoreface and beach deposits (sand, gravel and boulders) south of the mouth of the River Esk on the margin of the Eastern Irish Sea. These Holocene deposits probably overly a complex sequence of

Devensian and older glacigenic deposits that may be up to 70 m thick, which will comprise interbedded tills and glaciofluvial sands, gravels, silts and clays. The bedrock (Figure 12) beneath the superficial deposits will be largely fine- to medium sandstones belonging to the Calder Sandstone Formation - the upper part of the thick sequence of Sherwood Sandstone Group (Triassic) that extends westwards beneath the Irish Sea (Ackhurst et al., 1997; McMillan et al., 2004).

As at Sellafield, the area appears to have a low natural background radioactivity (Figure 3) There are no regional background data for U and Th in soils for Eskmeals. However, BGS GBASE stream sediment data report 2.5 to 2.7 ppm U over glaciofluvial deposits to the south-east of the area, and 2.7 to 3.2 ppm U over the marine deposits that underlie most of the area. Regional data indicates that the natural background concentration of uranium and thorium in Sherwood Sandstone Group bedrock is probably between <1 to 4 ppm U and 2-11 ppm Th. Most of the uranium and thorium will probably reside within resistant trace detrital minerals such as zircon, monazite, apatite and xenotime, although some may also be associated with disseminated iron oxides and sorbed on clay minerals (cf. Hyslop et al., 2000; Milodowski et al., 2000).

2.5.9 Hartlepool

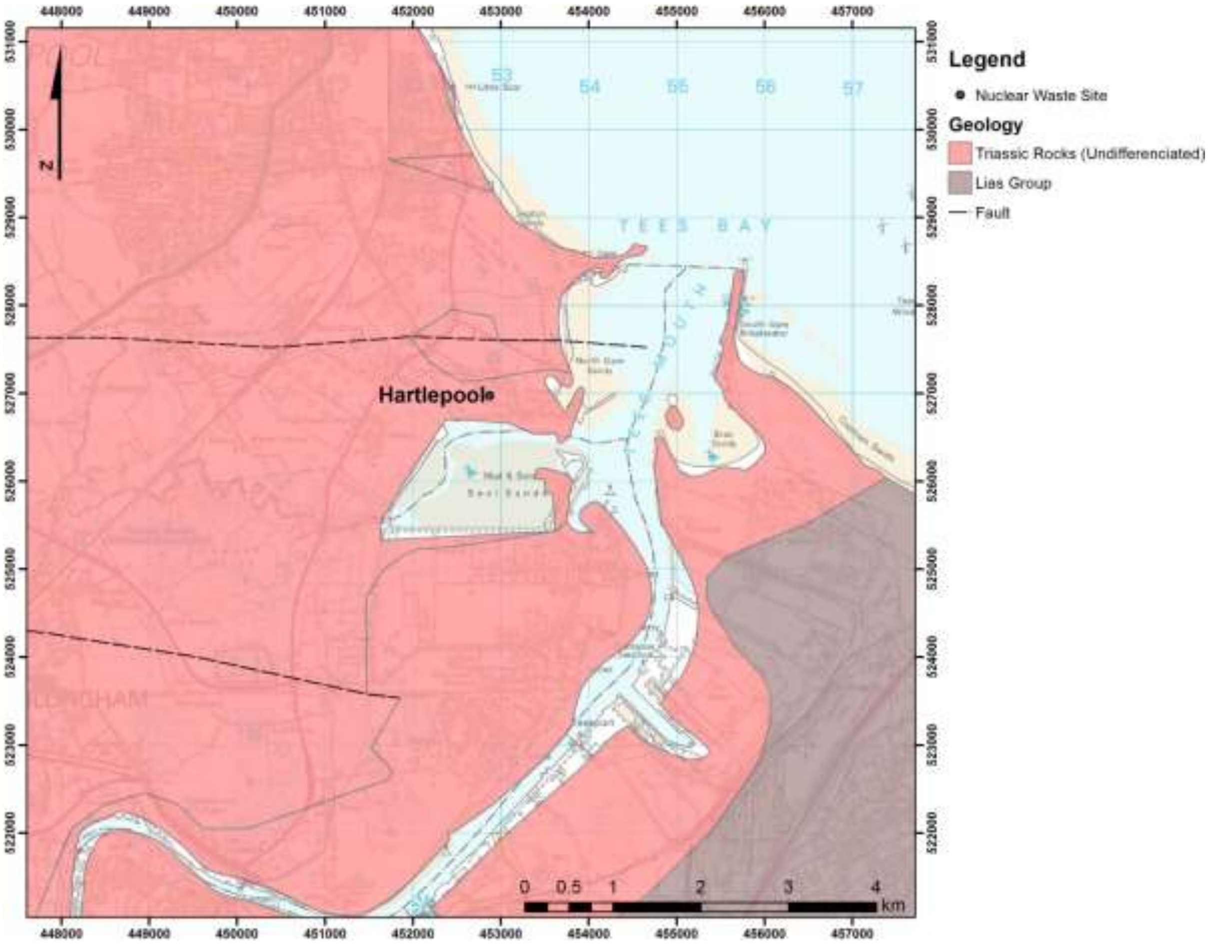

Figure 13. Bedrock geology of the Hartlepool area.

The Hartlepool site is underlain by Mercia Mudstone Group and Sherwood Sandstone Group rocks of Triassic age (Figure 13). The area appears to have a moderate degree of natural background radioactivity (Figure 3). The Sherwood Sandstone Group is dominated by feldspathic to subfeldspathic sandstones (similar to those described by Monaghan et al., 2012). The clay mineralogy of the Mercia Mudstone Group in northeast England is dominated by assemblage of major illite or mica and chlorite, variable amounts of corrensite (1:1 mixed-layer chlorite-smectite) (Jeans et al., 2006a). Most of the natural background radioactivity is likely to be contributed by potassium hosted predominantly in the illite-mica-rich Mercia Mudstone Group, and detrital K-feldspar in the Sherwood Sandstone Group (with contributions from illite in more clay-rich sandstone lithologies). Uranium and thorium will be present in trace amounts in accessory detrital phases – principally zircons, monazite, apatite and xenotime.

Further south, enhanced radioactivity may be encounted over the Liassic rocks. The Liassic rocks can give to enhanced radon risk in other parts of the UK but the radon potential map presented by Scheib et al. (2013) suggests this is not problematic in the Hartlepool area.

2.5.10 Heysham

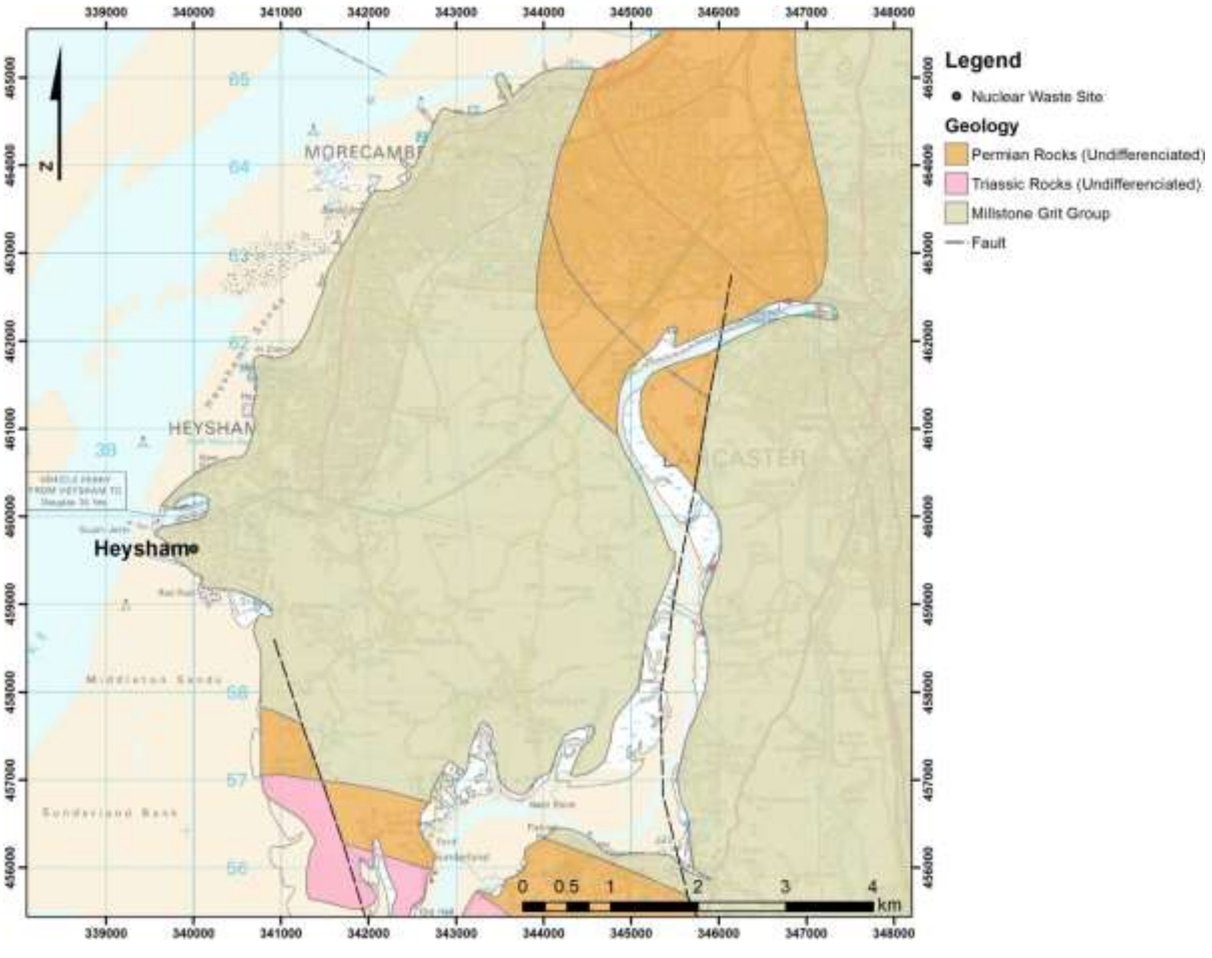

Figure 14. Bedrock geology of the Heysham area.

Heysham is located on the Millstone Grit Group (Namurian). These Carboniferous strata of the Central Pennines of Yorkshire and Lancashire thick, massive sandstone horizons form discrete aquifers separated by intervening mudstones and shales. They include coarse-grained and feldspathic pebbly sandstones. The bedrock in this area has a moderate to high background radioactivity (Figure 3). This probably reflects the radiation contributed by potassium in the feldspathic sandstones, and illite and mica-rich mudstones (cf. Shaw, 2006). Petrographic studies of Namurian sandstones further south showed only very low concentrations of uranium and thorium, hosted predominantly with accessory detrital phases, including zircon, monazite, xenotime, apatite and some organic material (Hyslop and Pearce, 1999).

Interbedded dark mudstones may also be organic-rich, and these could contribute enhanced radioactivity of uranium associated with organic matter (see Table 1).

2.5.11 Springfields

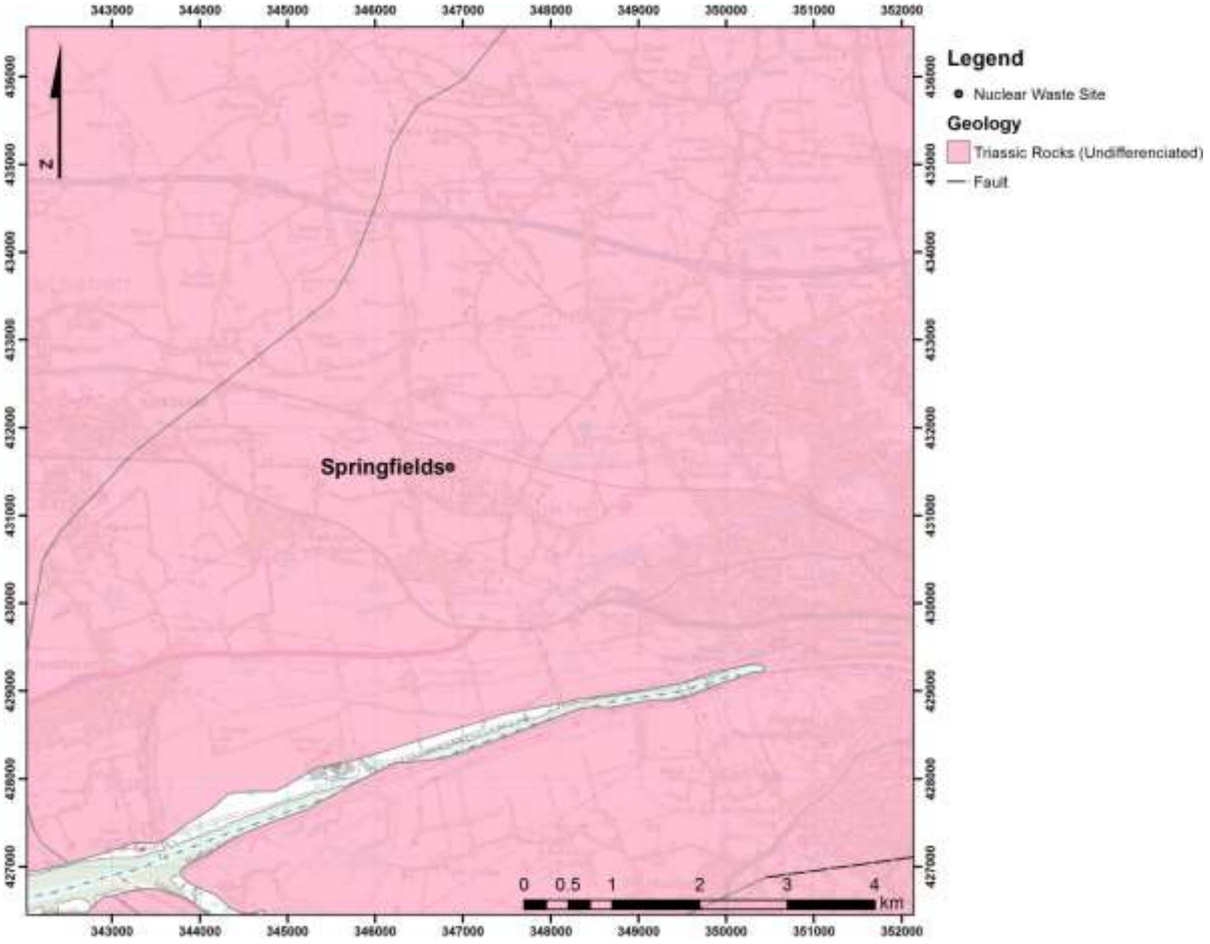

Figure 15. Bedrock geology of the Springfields area.

The Springfields site is located on the Permo-Triassic strata (Figure 15), close to the junction of the Mercia Mudstone Group with the underlying Sherwood Sandstone Group. The area has a moderate natural background level of radioactivity (Figure 3). No detailed background geochemical are readily available for the immediate site. However, petrographic analysis of Sherwood Sandstone Group rocks from the nearby Kirkham borehole (Strong, 1993) show that the sandstone is predominantly subfeldspathic, containing significant K-feldspar with accessory amounts of ilmenite, zircon and apatite, as well as thin mudstones. The clay mineralogy of the sandstone in this area is also illite-dominated (Strong, 1993). Illite is a major component of the Mercia Mudstone Group rocks in this region (Jeans, 2006a). Further south in the Cheshire Basin, both the Sherwood Sandstone Group and the Mercia Mudstone Group are characterised by high potassium and low uranium and thorium (Plant et al., 1999). It seems likely that the geochemistry of these formations in the Springfield area will be similar. Therefore, the moderate natural background radioactivity in this site is due to high levels of potassium in the illitic mudstones of Mercia Mudstone Group and the abundance of K-feldspar in the feldspathic sandstones of the Sherwood Sandstone Group.

2.5.12 Capenhurst

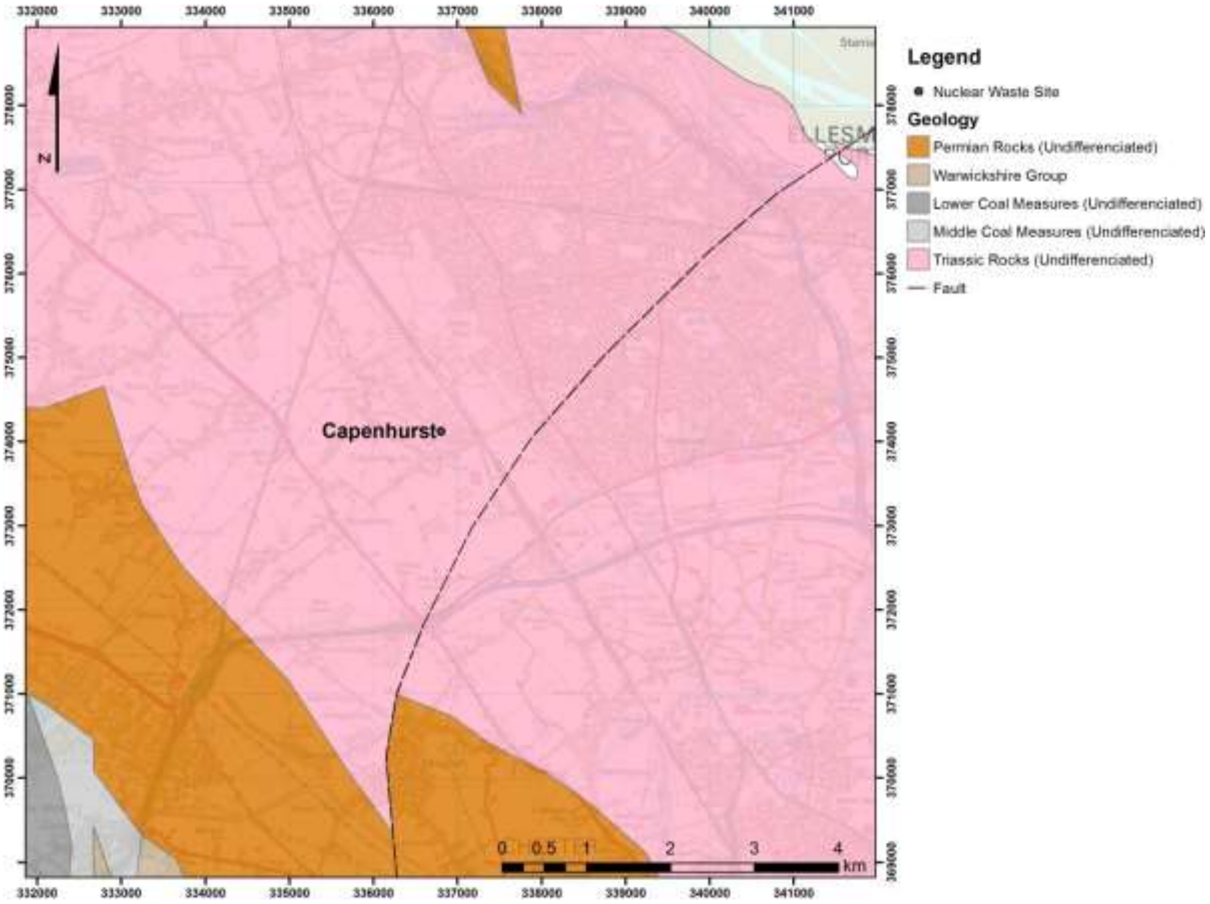

Figure 16. Bedrock geology of the Capenhurst area.

The Capenhurst site is located on Lower Triassic Sherwood Sandstone Group Permo-Triassic bedrock at the northerm margin of the Cheshire Basin (Figure 16). This area has a moderate natural background level of radioactivity (Figure 3). Detailed petrographic analysis of Sherwood Sandstone Group rocks show that these sandstones in the Cheshire Basin are predominantly feldspathic to subfeldspathic, containing significant K-feldspar with accessory amounts of ilmenite, zircon, monazite and apatite, as well as thin illitic mudstones and illite clay matrix material (Plant et al., 1999). Illite is a major component of the Mercia Mudstone Group rocks in this region (Jeans, 2006a). Whole-rock geochemical analyses show that they are characterised by high potassium and low uranium and thorium, although trace accessory minerals such as zircon, monazite and apatite can contain uranium in high concentrations (Plant et al., 1999). However, since these phases are only present in trace amounts it is unlikely that they contribute significantly to the background radioactivity. Therefore, it seems likely that the moderate natural background radioactivity in this site is due to high levels of potassium in the Sherwood Sandstone Group.

2.5.13 Wylfa

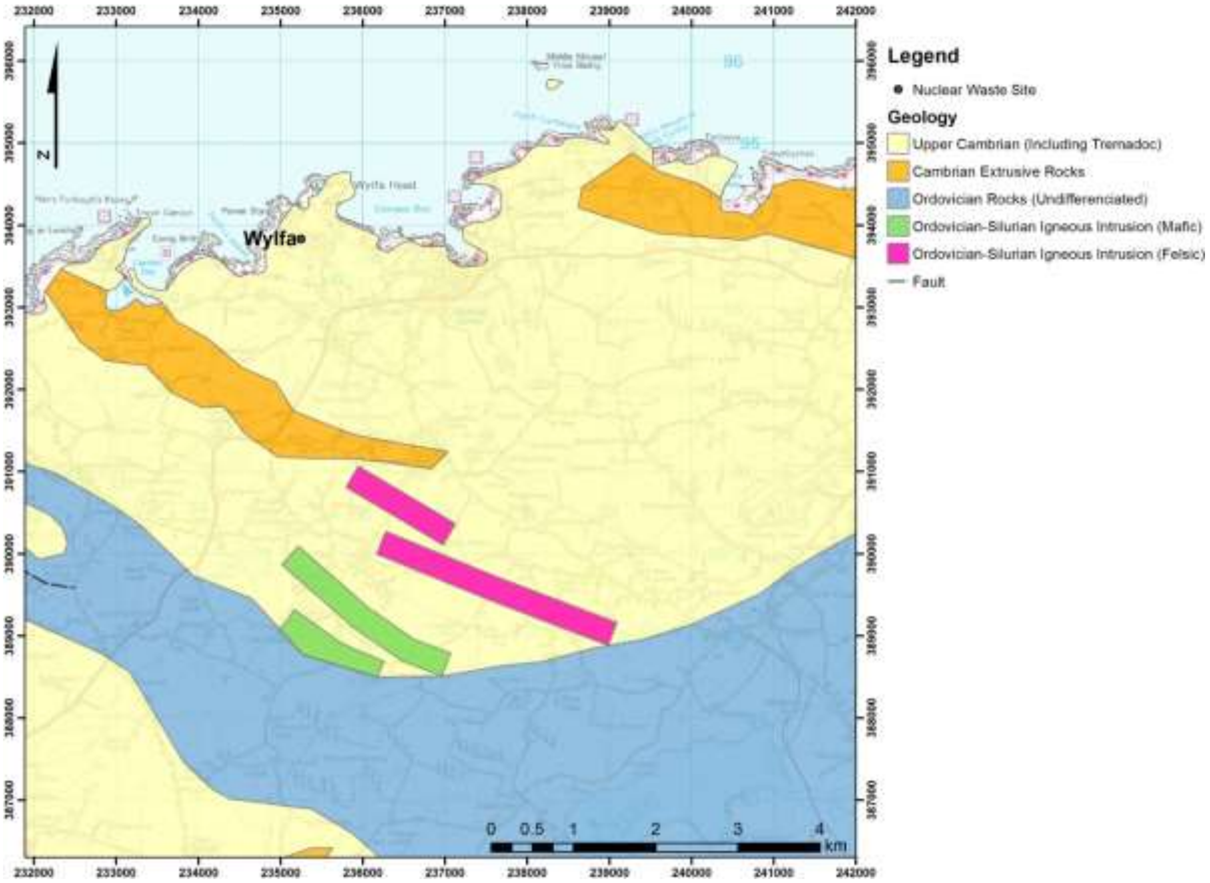

Figure 17. Bedrock geology of the Wylfa area.

Wylfa is located on bedrocks consisting of Upper Cambrian, poly-deformed and metamorphosed (greenschist to sub-greenschist facies) chlorite-mica-schists and phyllites (Figure 17). These are predominantly interbedded metamudstones, metasiltstones metasandstones, and red cherts (Phillips, 2011). This area has low to moderate natural background radioactivity (Figure 3), which is largely reflects the abundance of potassium in these mica- and K-feldspar- rich metamorphic strata.

2.5.14 Trawsfynydd

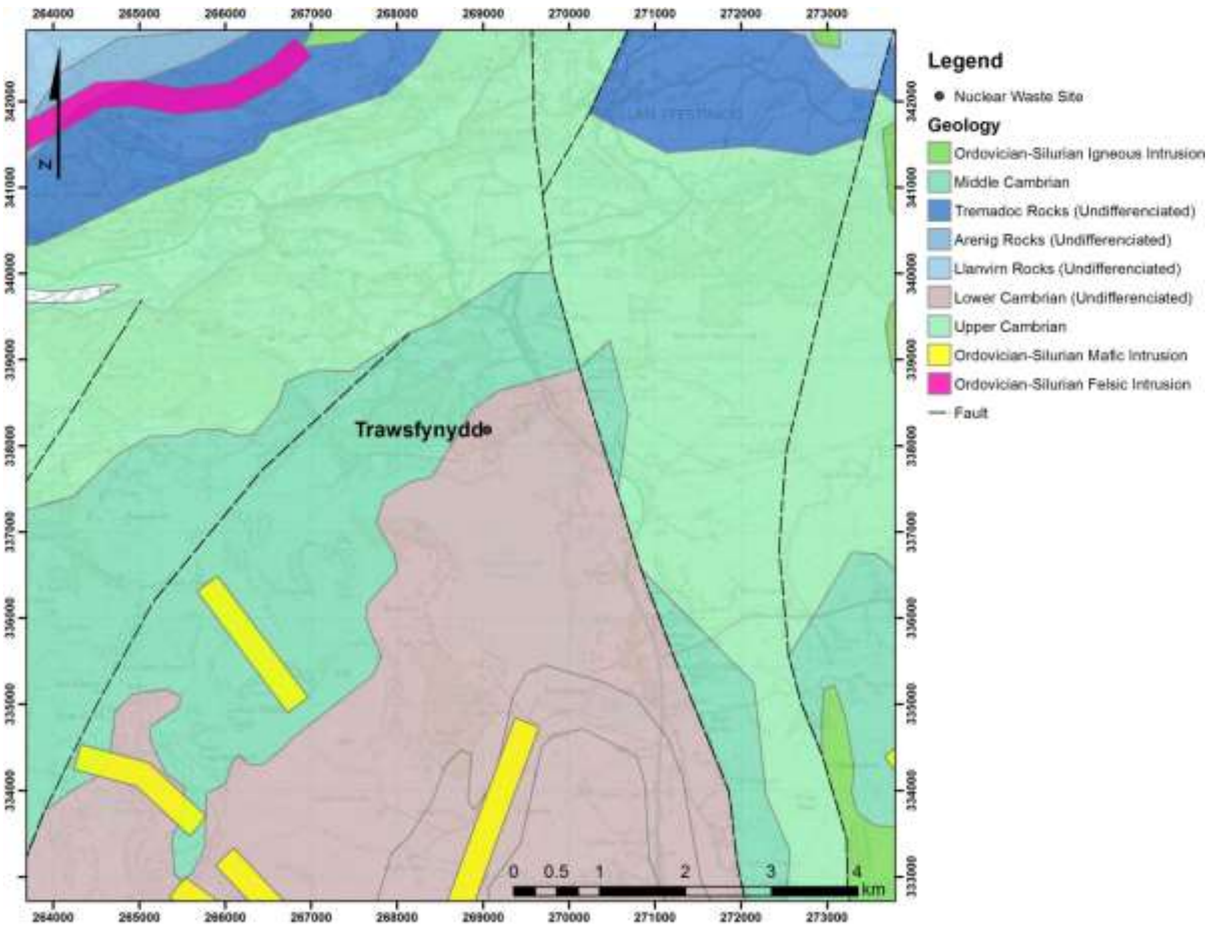

Figure 18. Bedrock geology of the Trawsfynydd area.

Trawsfynydd rests on Lower Cambrian and Middle Cambrian rocks (Figure 18). These rocks are predominantly metapelites and slatey mudrocks of high (epizonal) metamorphic grade (Merriman, 2006). The rocks are dominated by quartz, and well-crystallised muscovite and chlorite. The area has a moderate to relatively high natural background of radioactivity (Figure 3). Much of this enhanced radioactivity may reflect the abundance of potassium-rich mica in these rocks. However, there is little information on the distribution of uranium and thorium.

2.5.15 Donnington

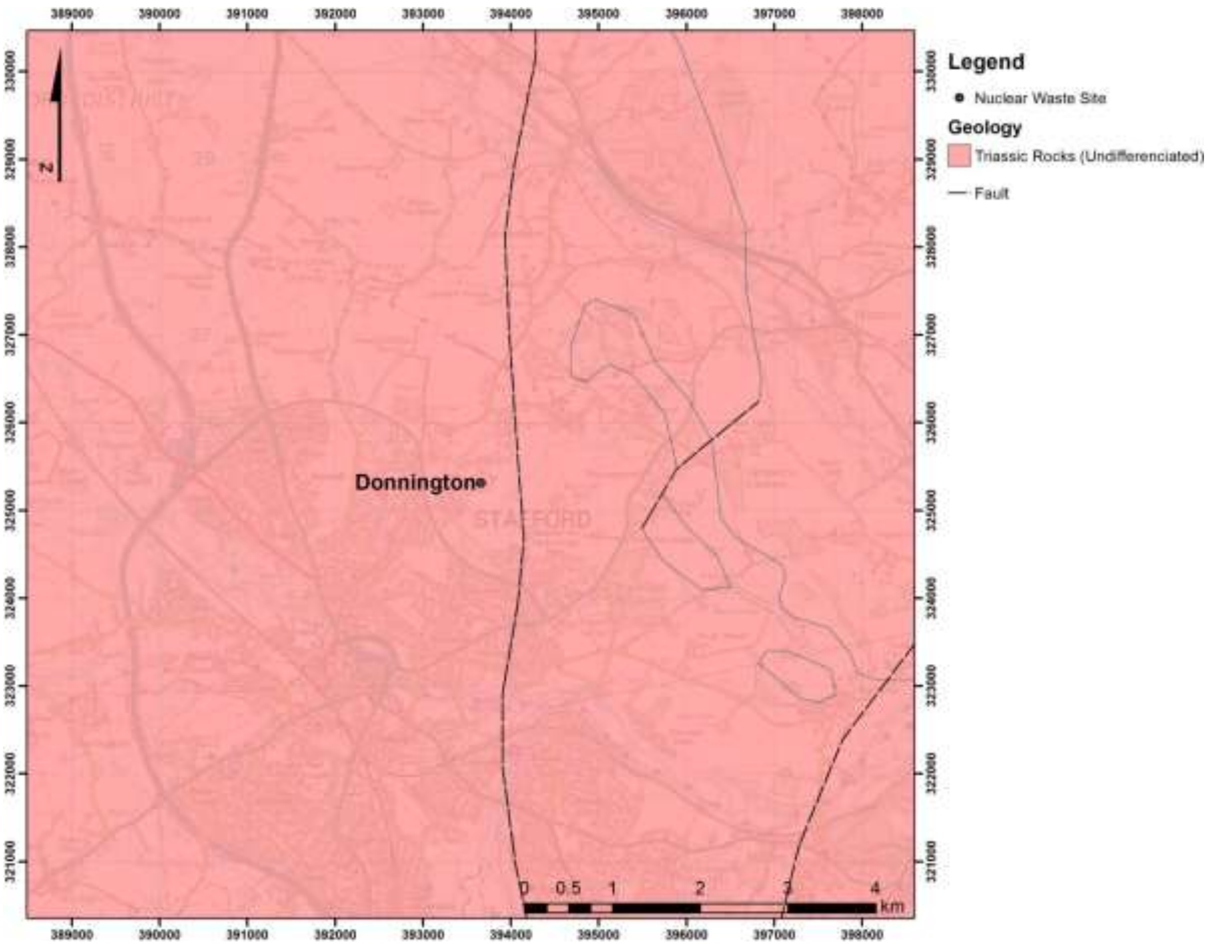

Figure 19. Bedrock geology of the Donnington area.

Donnington is located on Triassic bedrocks of the Mercia Mudstone Group (Figure 19). This area has a moderate natural radioactivity background (Figure 3). As discussed previously, the Mercia Mudstone Group is characterised by high potassium and low uranium and thorium mudrocks (Plant et al., 1999). Therefore, it seems likely that most of the background radioactivity derived from potassium hosted within these illite-rich mudrocks (Jeans, 2006a).

2.5.16 Sizewell

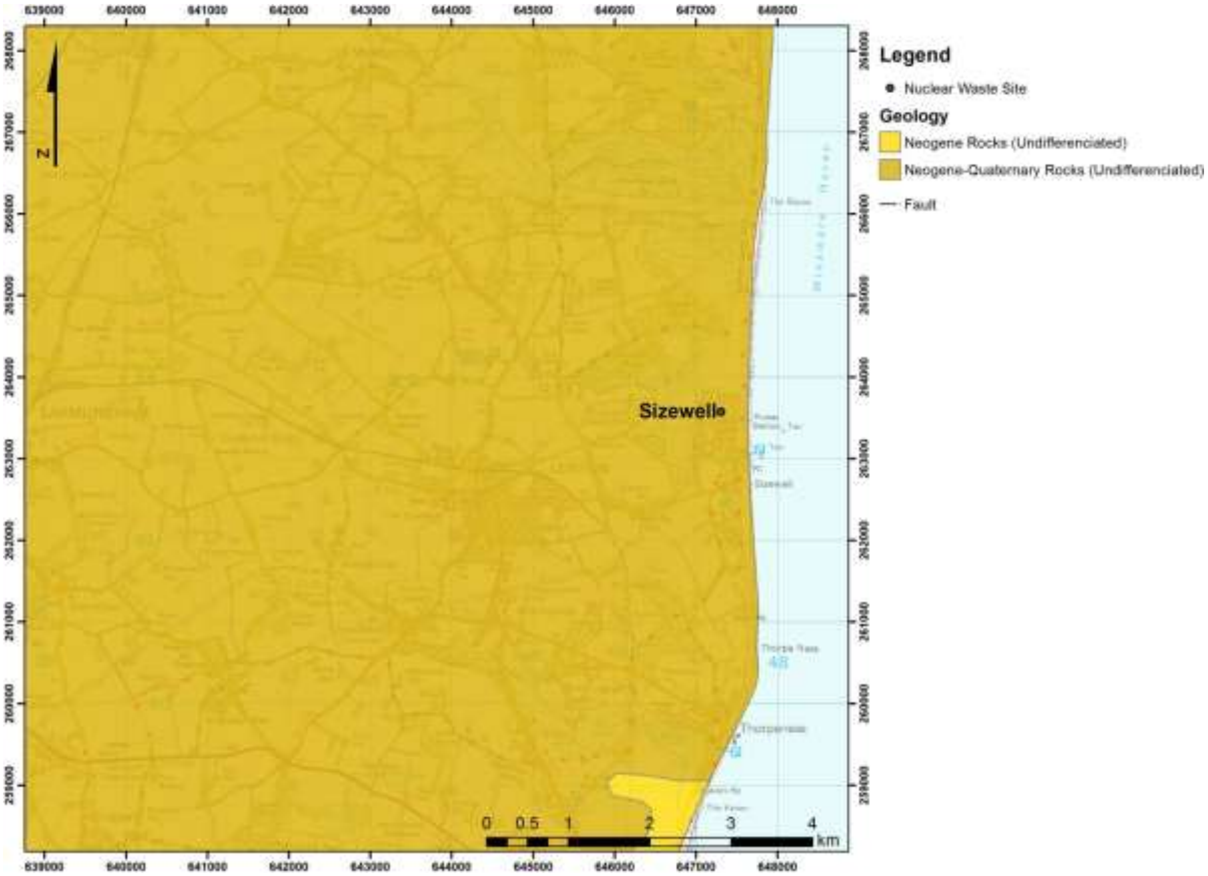

Figure 20. Bedrock geology of the Sizewell area.

Sizewell site is located Neogene and younger Quaternary rocks (Figure 20). The area has a very low level of natural background radioactivity. However, there is little readily-available information on the bedrock mineralogy and chemistry, and further investigation is required to evaluate the sources and distribution of any natural radioactive elements.

2.5.17 Bradwell

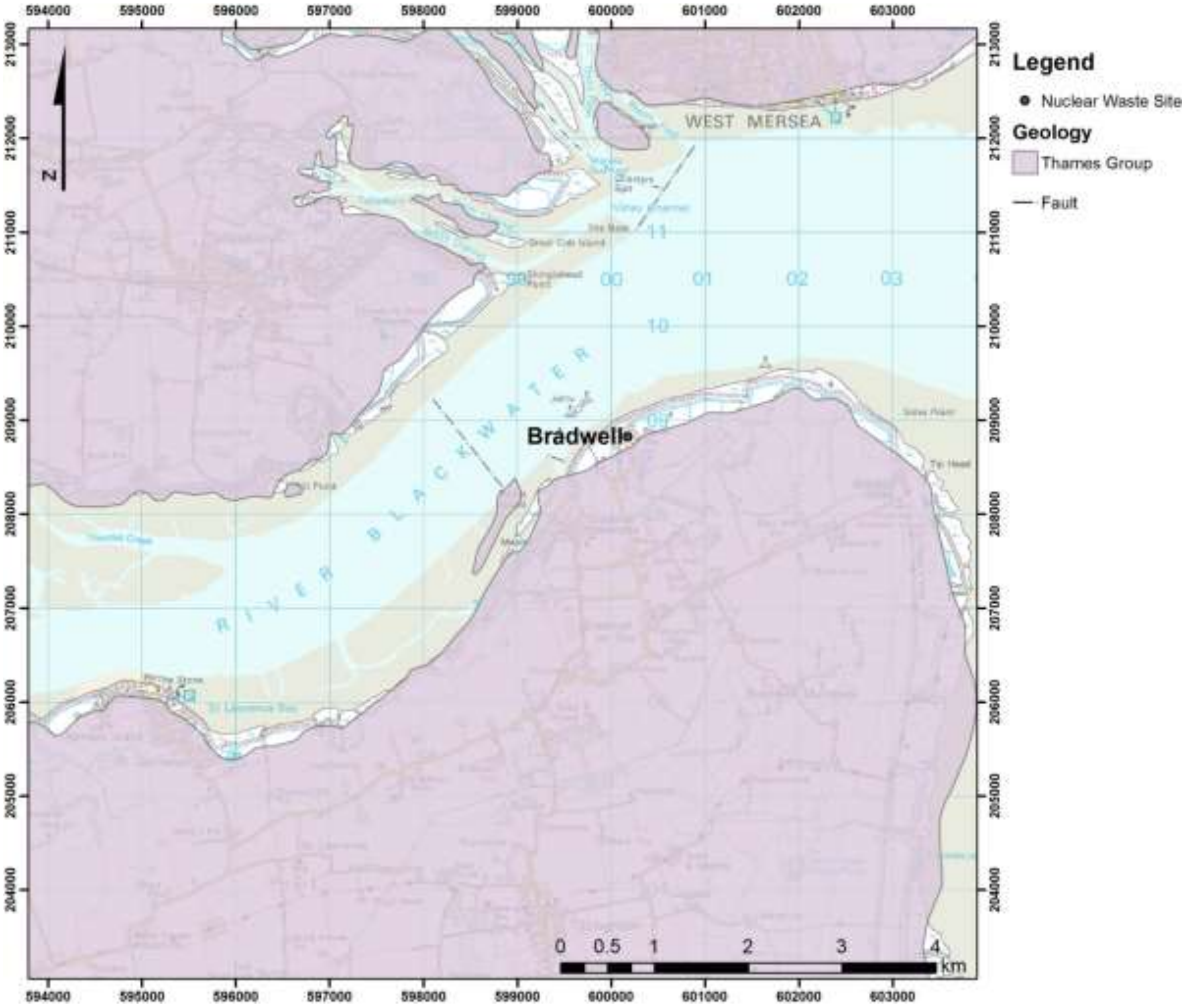

Figure 21. Bedrock geology of the Bradwell area.

Bradwell site is located on bedrocks forming part of the Tertiary Thames Group (Figure 21). Regionally, these rocks have a relatively low level of background radioactivity (Figure 3). The bedrock comprises predominantly mudstone, with subordinate muddy sandstones and thin beds of volcanic ash (Huggett and Knox, 2006). The rocks are smectite rich with subordinate illite and mixed-layer illite-smectite (Huggett and Knox, 2006). Although trace amounts of authigenic rare earth phosphate have been identified from the mudstones at the Bradwell site (Bloodworth et al., 1990), it seems likely that much of the low-level background radioactivity is probably derived from potassium hosted by illite. However, little is known about the distribution of uranium and thorium in these rocks and their contribution to background radioactivity.

2.5.18 Amersham

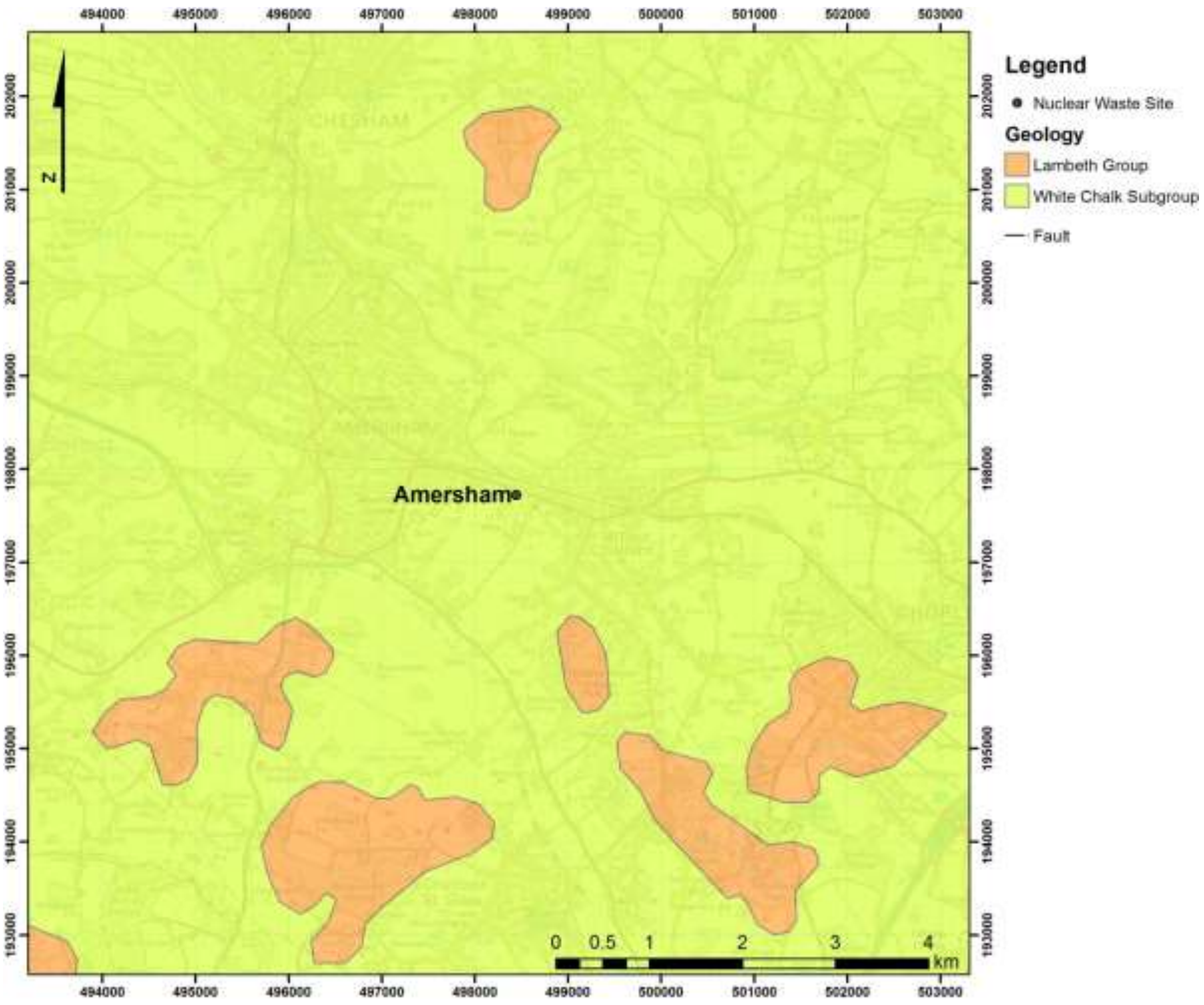

Figure 22. Bedrock geology of the Amersham area.

Amersham is situated of the Cretaceous White Chalk Subgroup (Figure 22). The crop of the White Chalk corresponds to a very low radioactivity background (Figure 3). Essentially, the White Chalk is a very pure calcium carbonate sediment composed largely of calcite with only very minor to trace amounts of clay minerals and detrital components. Consequently, it is expected to have very low concentrations of potassium, uranium and thorium, which is consistent with its low background radioactivity.

2.5.19 Culham

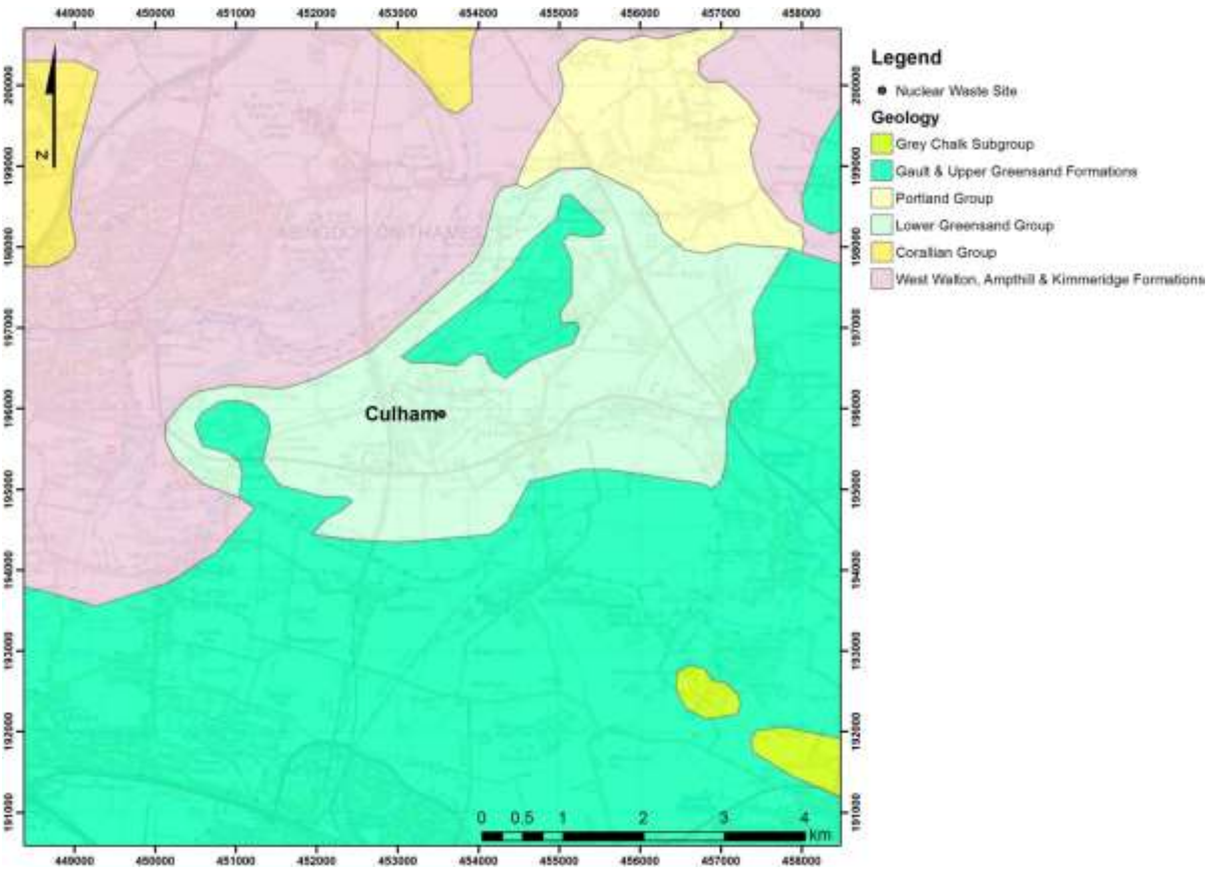

Figure 23. Bedrock geology of the Culham area.

The Culham site is located on Lower Greensand Group rocks (Figure 23). These rocks have a moderate to low natural background radioactivity (Figure 3), probably largely because the Lower Greensands contain significant illite, and often glauconite a iron-rich micaceous clay mineral (Jeans, 2006b). Limited mineralogical and chemical analyses reported from drillcore samples recovered from the Lower Greensand Group further south at the Harwell site show the presence of major mica (which includes glauconite) as the dominant clay mineral present, and potassium concentrations of 0.6 to 2 % K_2O (Wilmot and Morgan.1982). The concentration of thorium is the same material is between 2 to 6 ppm. No data for uranium is available but the low level of thorium suggests that there is little contribution of uranium from accessory heavy mineral phases.

2.5.20 Harwell

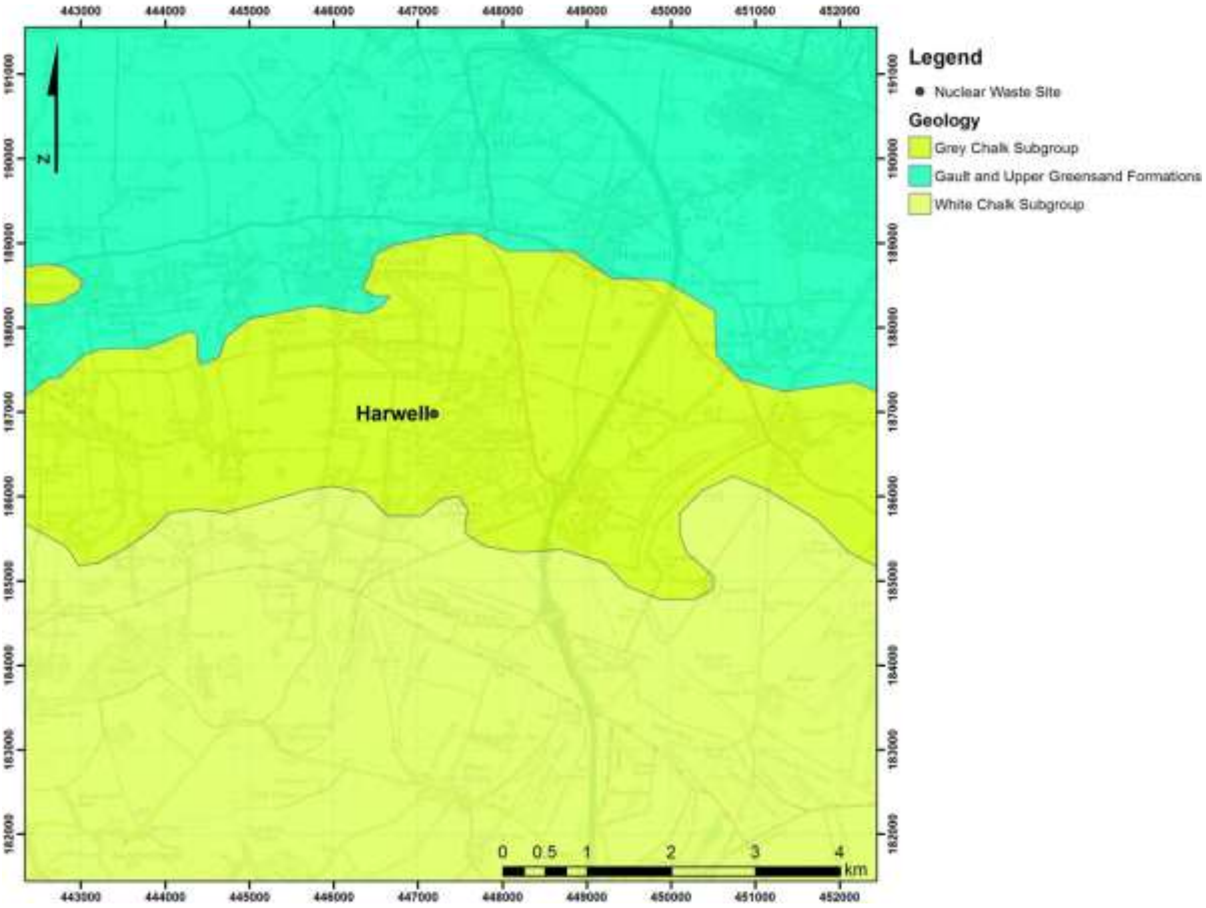

Figure 24. Bedrock geology of the Harwell area.

The Harwell site is located on the Grey Chalk Subgroup, that represents the basal part of the Cretaceous Chalk sequence (Figure 24). This has a very low level back of natural background radioactivity (Figure 3). The geochemistry and mineralogy of samples from Grey Chalk Subgroup at the Harwell site have been described by Wilmot and Morgan (1982). The clay mineralogy is dominated by illite and smectite, but it typically has very low concentrations of potassium (0.6 to 1 % K_2O) and thorium (1-2 ppm Th). Unfortunately, no data were reported for uranium by Wilmot and Morgan (1982).

2.5.21 Aldermaston

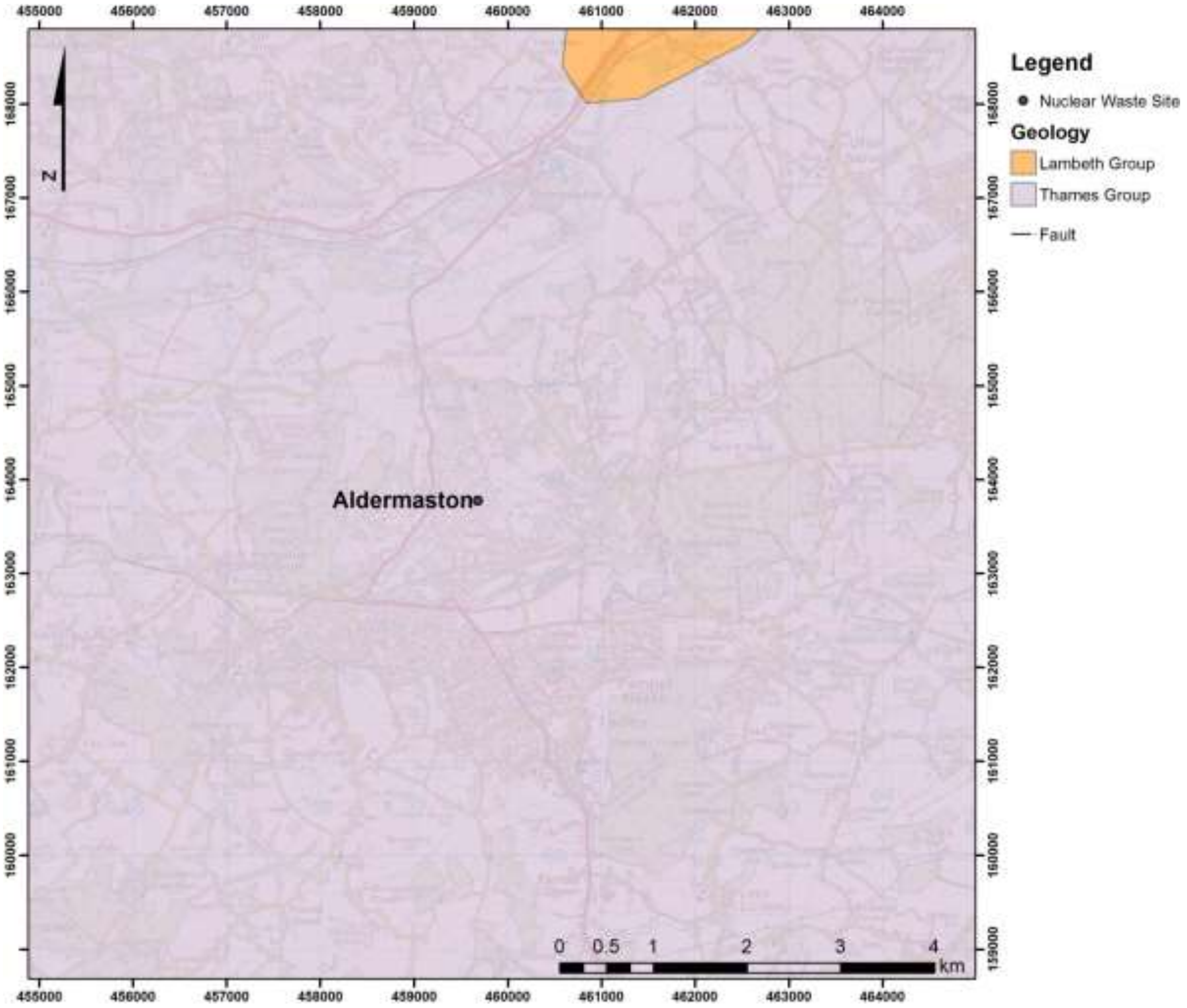

Figure 25. Bedrock geology of the Aldermaston area.

Aldermaston is located on bedrocks forming part of the Tertiary Thames Group (Figure 25). This bedrock at this site has a relatively low level of background radioactivity (Figure 3). It comprises predominantly mudstone, with subordinate muddy sandstones and thin beds of volcanic ash (Huggett and Knox, 2006). The Thames Group rocks in this area contain major smectite and illite, with minor chlorite and kaolinite (Huggett and Knox, 2006). Data summarised by Huggett and Knox (2006) suggests that the Thames Group in the Aldermaston area contains significantly more illite than at Bradwell. The natural background radioactivity at this site is probably contributed mainly by potassium hosted illite-rich clay. However, little is known about the distribution of uranium and thorium in these rocks and their contribution to background radioactivity.

2.5.22 Berkley and Oldbury

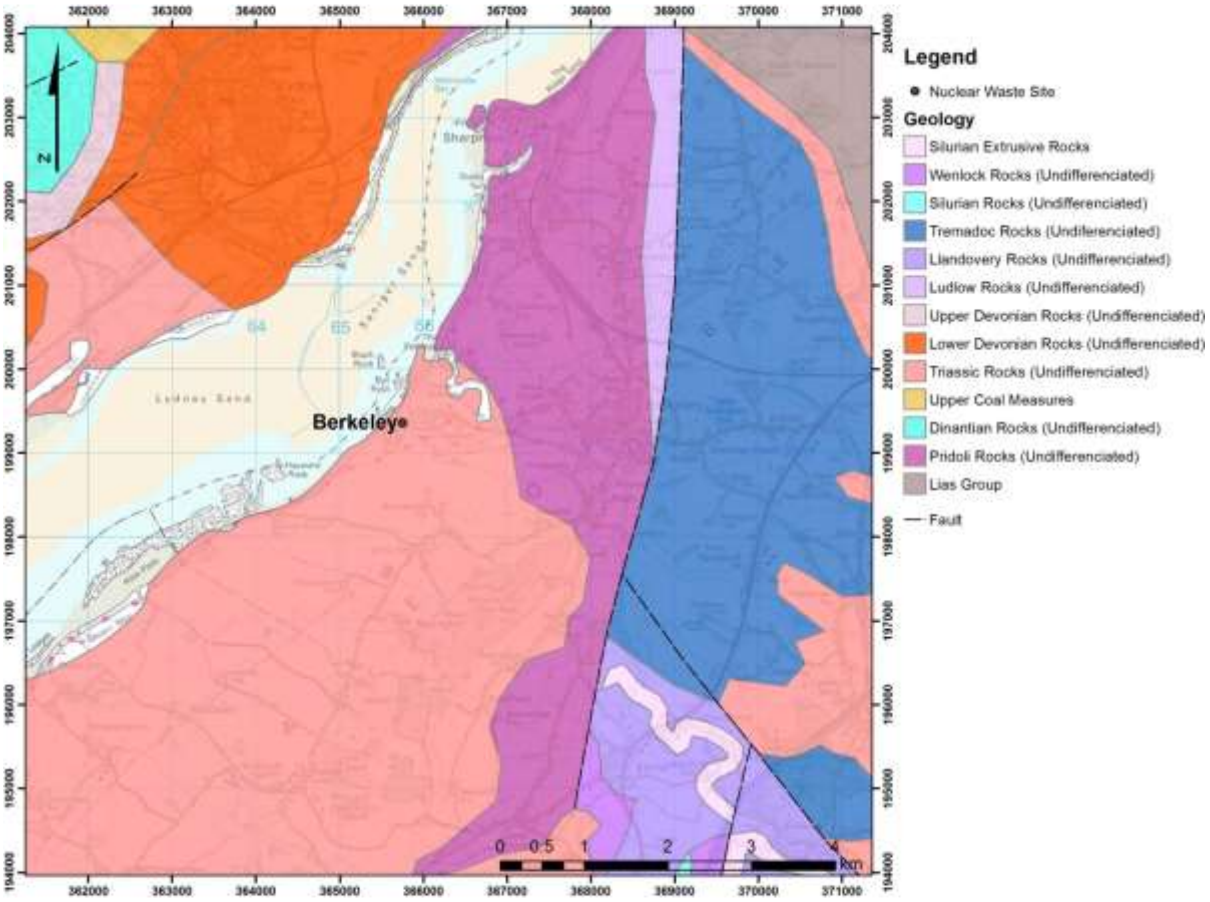

Figure 26. Bedrock geology of the Berkley area.

Berkley and Oldbury sites and situated on Triassic bedrocks within the Worcester Graben (Figures 26 and 27). The natural background radioactivity over these strata in moderate to low (Figure 3), and broadly similar to the background radioactivity encountered over other areas underlain by Mercia Mudstone Group and Sherwood Sandstone Group rocks described previously. It is therefore likely that most of the background radiation is derived from potassium hosted in illite and K-feldspar within similar feldspathic sandstones and illitic mudstones.

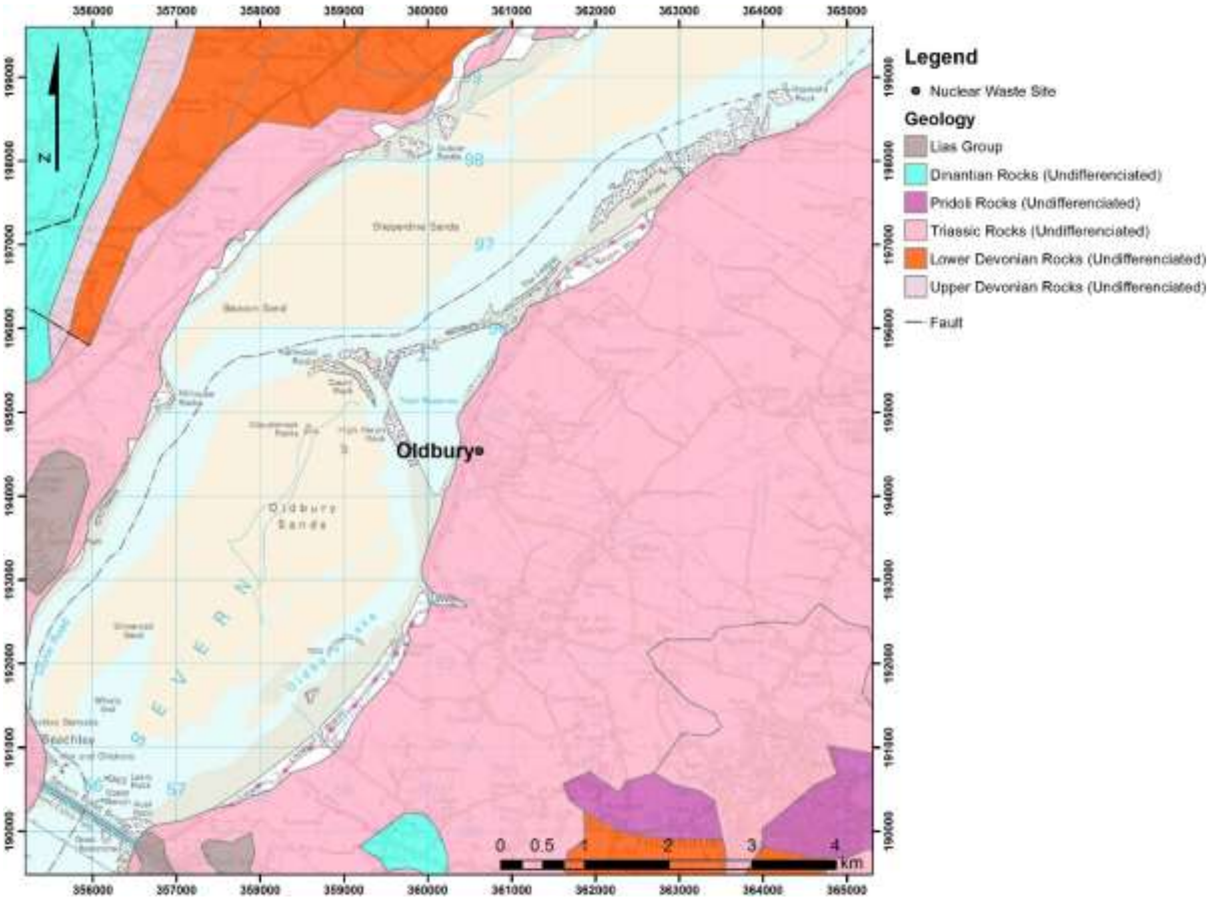

Figure 27. Bedrock geology of the Oldbury area.

2.5.23 Cardiff

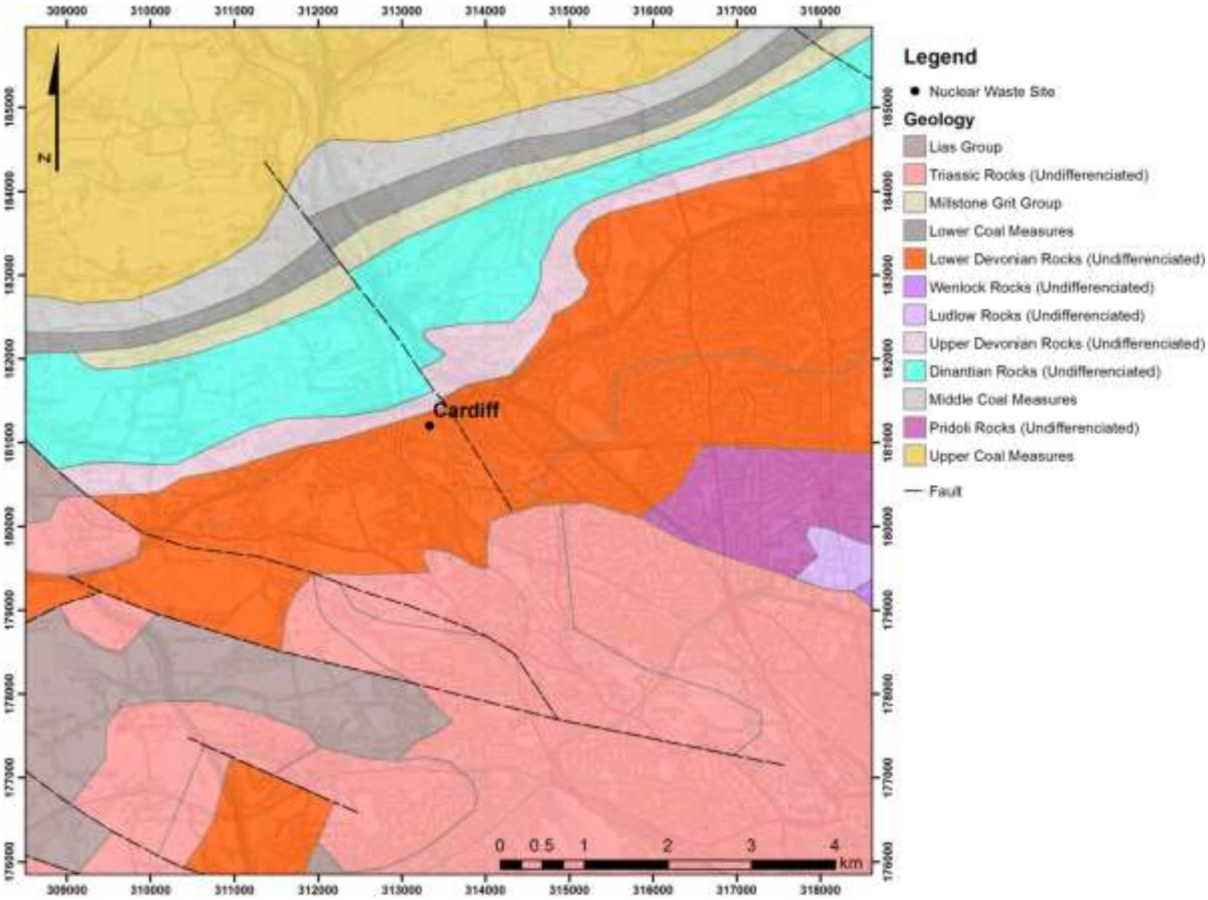

Figure 28. Bedrock geology of the Cardiff area.

The geology of the Cardiff area (Figure 28) includes a wide variety of rocks types ranging from Lower Palaeozoic to Jurassic age. These include mudstones (Lias Group, Mercia Mudstone Group (Upper Triassic), Carboniferous Coal Measures, Devonian strata), sandstones Sherwood Sandstone Group (Triassic), Carboniferous Millstone Grit Group and Coal Measures), and limestone (Dinantian). The area overall has a moderate degree of natural background radioactivity (Figure 3). However, there is little information available on the distribution of uranium, thorium and potassium in these lithologies.

Given the wide range of rock types present the significant variation in uranium, thorium and potassium would be expected, in keeping with the lithological ranges shown in Tables 1 to 3. The more organic-rich or phosphatic horizons within the Coal Measures sequence might be expected to yield significantly higher concentrations of uranium, and consequent higher background radioactivity. Limestone strata may give rise to low background values. Further work is required to understand the controls on the background radioactivity.

2.5.24 Hinkley Point

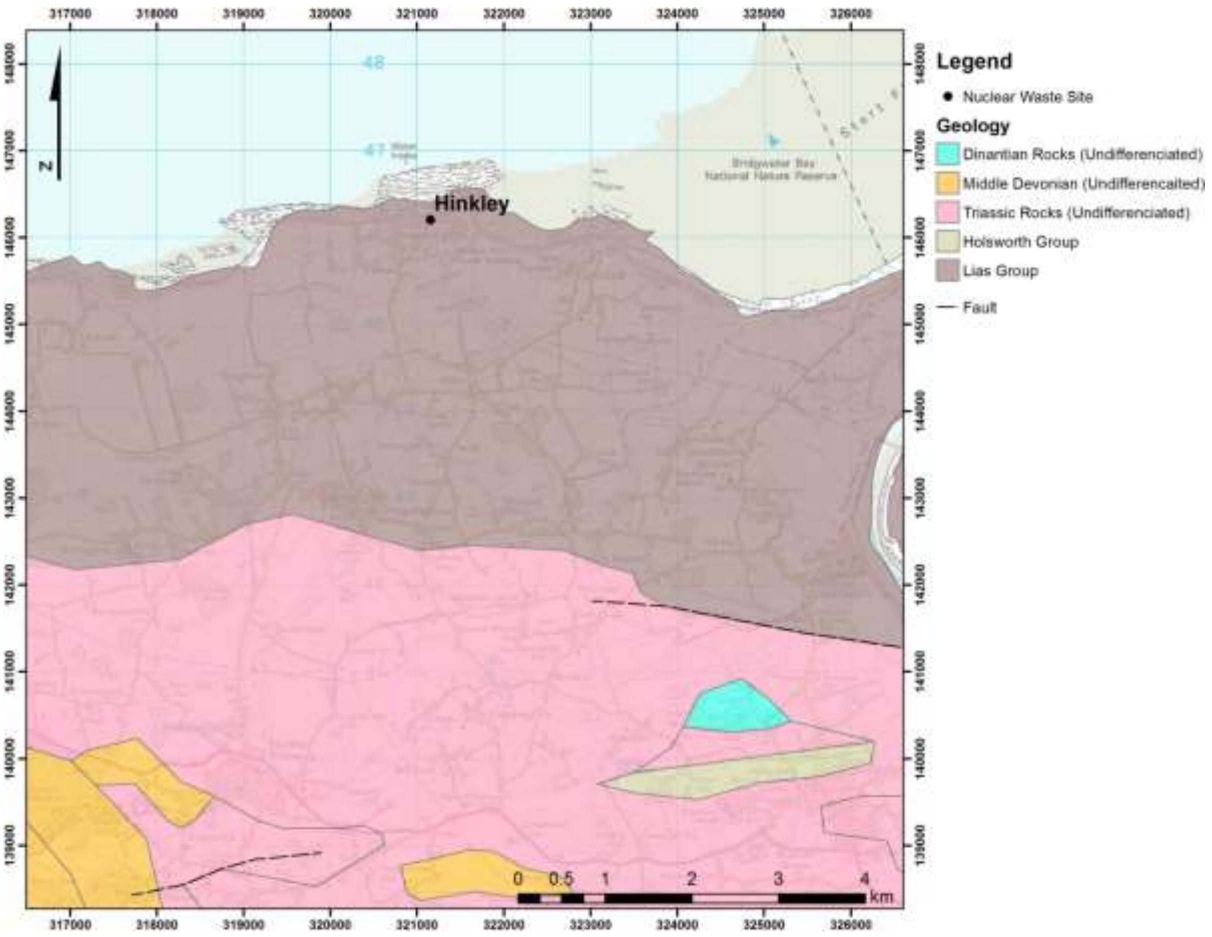

Figure 29. Bedrock geology of the Hinkley Point area.

Hinkley Point is located on Lias (Lower Jurassic) bedrock (Figure 29). The Lias strata are composed largely of interbedded mudstones and limestones. The area is characterised by low to moderate total background radioactivity (Figure 3).

Some Lias and other Jurassic strata can be responsible for high background radon levels in the UK (Scheib et al., 2013), which would infer enhanced uranium in the bedrock, probably within more phosphatic horizons. However, this does not appear to be the case for the Lias in the Hinkley Point area. Most of the radioactivity is probably contributed potassium in illitic clay in the mudstones. However, little is known about the distribution of uranium and thorium in these rocks and their contribution to background radioactivity.

2.5.25 Winfrith

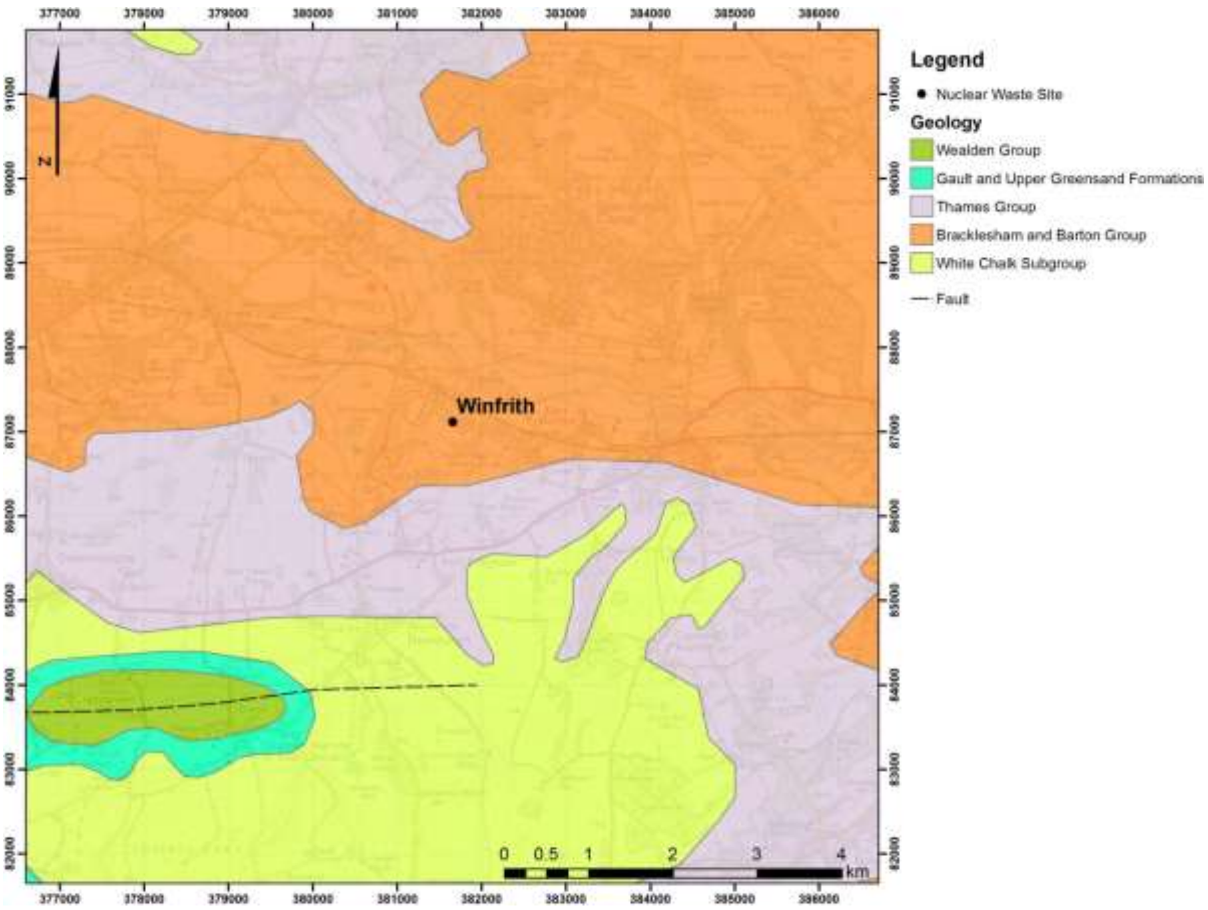

Figure 30. Bedrock geology of the Winfrith area.

Winfrith site is located on bedrock belonging to the Bracklesham and Barton Group, within the Hampshire Basin (Figure 30). These rocks are of Eocene age. This area appears to have relatively low background radioactivity (Figure 3).

The Bracklesham beds comprise interbedded to interlaminated clays, silts and mostly fine- or medium-grained sands, locally shelly. Glauconite occurs in the mid part of the sequence. Minor coarse-grained sands, fine gravelly sand, gravel beds, sandstones or ironstone concretions occur in places. The Barton beds are represented by yellow weathering, green-grey clay, with discrete fine-grained sand bands, yellow-pale grey weathering fine-grained sand, green-grey, sandy clay and clayey, silty fine-grained sand. Both units are rich in smectite and illite clay (Huggett and Knox, 2006). Most of the radioactivity is probably contributed by potassium in this illitic clay. However, little is known about the distribution of uranium and thorium in these rocks and their contribution to background radioactivity.

2.5.26 Portsmouth

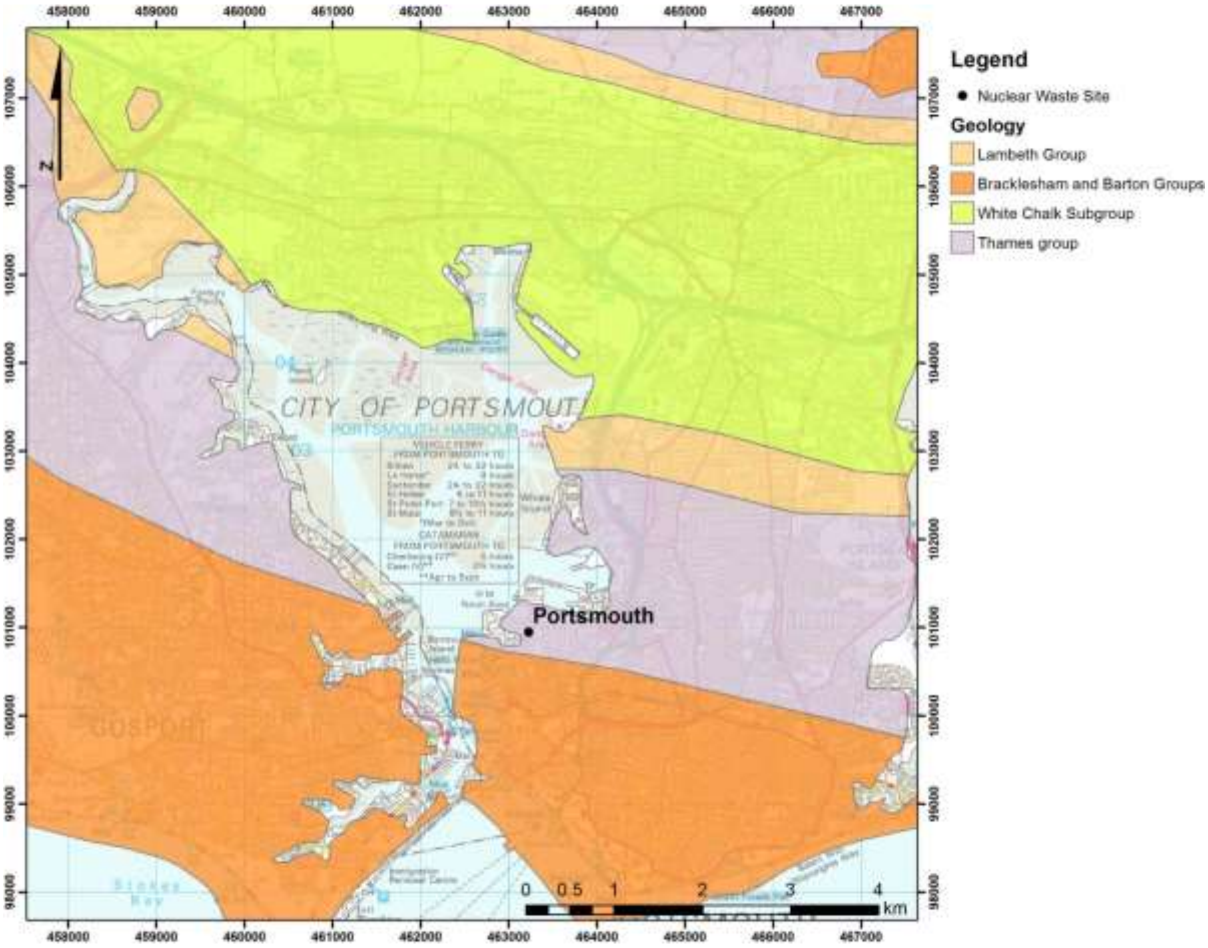

Figure 31. Bedrock geology of the Portsmouth area.

The Portsmouth site is located on Tertiary Thames Group strata, with Bracklesham and Barton Group rocks cropping close by to the south (Figure 31). The area appears to correspond to low natural background radioactivity (Figure 3). As at the Bradwell, Aldermaston and Winfrith sites, these Tertiary strata contain major smectite and illite clay (Huggett and Knox, 2006). Much of the radioactivity is therefore likely to be contributed by potassium from the illite. However, little is known about the distribution of uranium and thorium in these rocks and their contribution to background radioactivity.

2.5.27 Dungeness

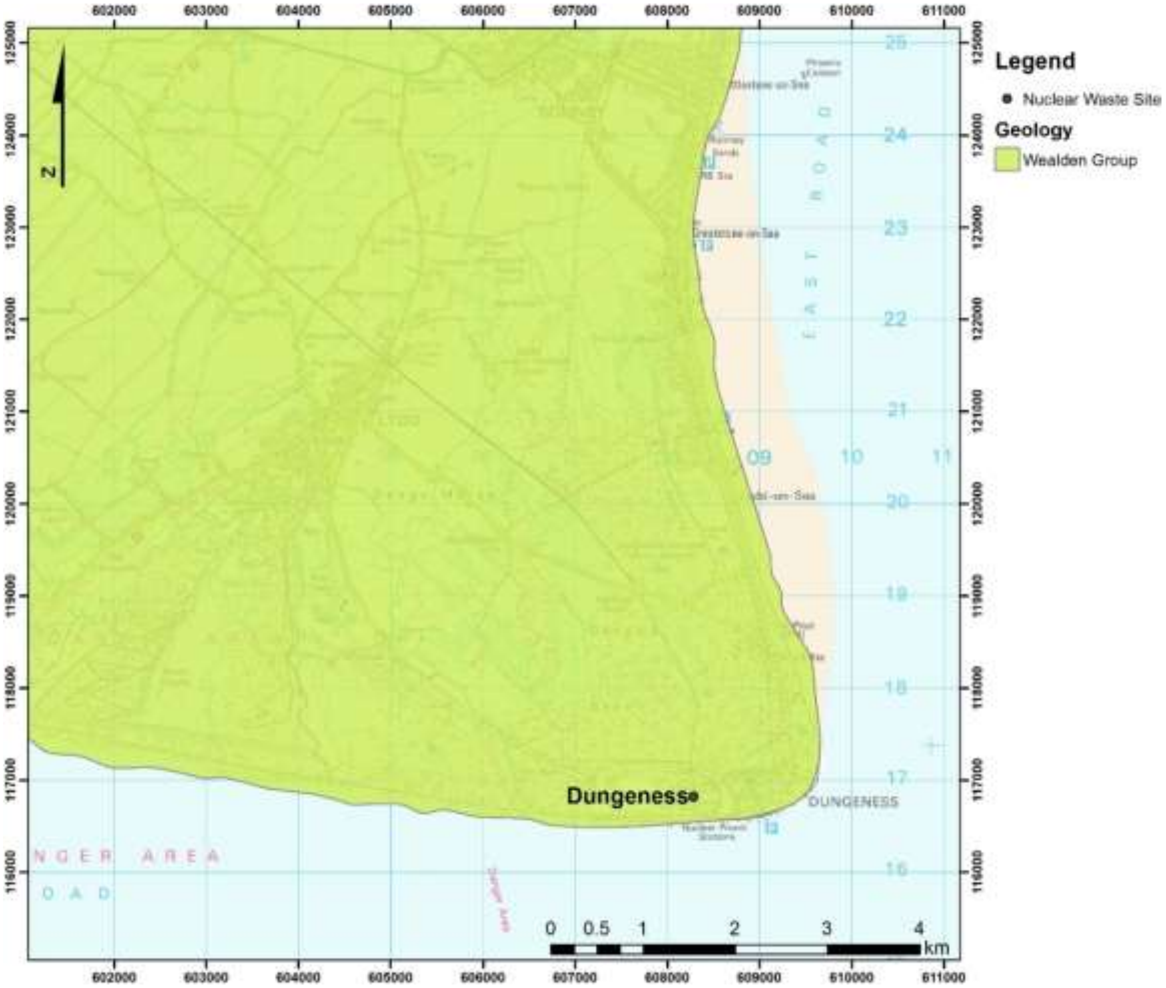

Figure 32. Bedrock geology of the Dungeness area.

The bedrock to the Dungeness site is the lower Cretaceous Wealden Group. In the Wealden Basin these rocks are represented by interbedded thick sandstones, siltstones, mudstones ("shales"), limestones and clay ironstones of predominantly non-marine facies. The Weald area corresponds to a generally low radioactive background (Figure 3).

The mineralogy and chemistry of samples of Wealden Group rocks from southern England has been described by Kemp et al. (2012). Whole-rock XRD analysis indicates that the samples from the Wealden Group are composed of variable amounts of quartz (25-69%) and phyllosilicates/clay minerals (25-74%) together with a variable range of minor-trace phases including K-feldspar, calcite, dolomite, siderite, anatase, rutile, hematite, pyrite, halite and gypsum. Ironstone horizons are cemented by manganoan-calcian siderite. Typically, the clay assemblages are dominated by mixed-layer illite-smectite (mean 38%) and kaolinite (mean 41%) with minor proportions of illite (mean 18%) and traces of chlorite (mean 2%). These results are similar to other analyses reported elsewhere (Jeans, 2006b). Traces of discrete smectite were identified in some samples. Potassium concentrations range from 0.6 to 3.7 % K_2O, uranium is present at between 2 to 6 ppm, and thorium ranges from <1 to 19 ppm. The mineralogical distribution of uranium and thorium is unknown but much of the radioactivity can probably be attributed to potassium hosted in illite-smectite clay.

2.5.28 Devonport

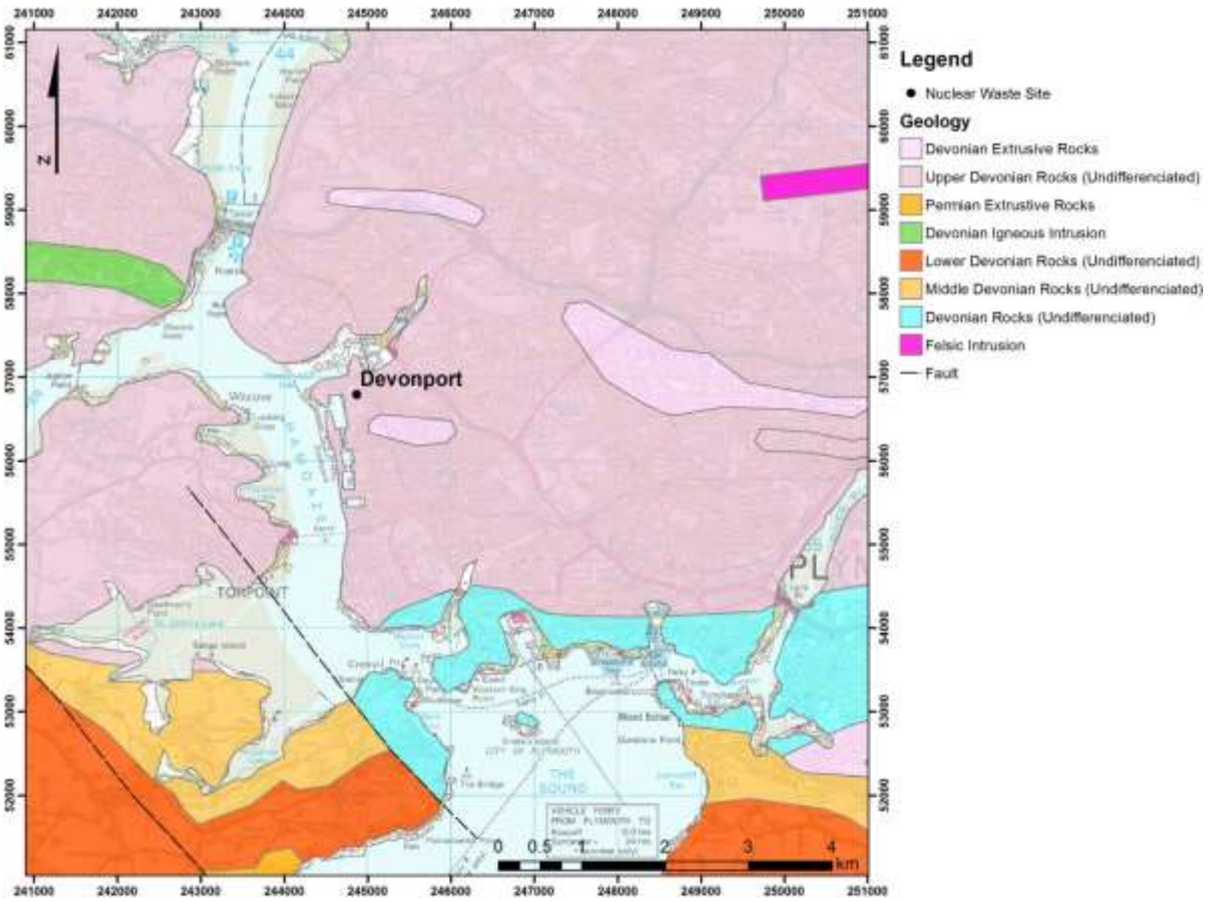

Figure 33. Bedrock geology of the Devonport area.

Devenport is located on marine upper Devonian strata (Figure 33) and correspond to a moderate to high degree of background radioactivity (Figure 3). These rocks comprise largely slates, pelites semipelites and psammites of epizontal to anchizonal metamorphic grade, with major K-mica and chlorite (Hillier et al., 2006). Much of the radioactivity is probably attributable to potassium in micas and K-feldspar. However, the mineralogical distribution of uranium and thorium and its contribution to background radioactivity is unknown.

3 Geogenic radionuclides in British groundwater

3.1 INTRODUCTION

Under natural conditions, the radioactivity of groundwater is produced dominantly by radionuclides in the uranium and thorium decay series. Contributing solutes include uranium, radon and radium. ^{40}Potassium also contributes radioactivity from subsurface radioactive decay. Data for naturally-occurring radionuclides in British groundwater are very limited, but vary depending on specific regional studies or their application and utility as tracers. Activities of ^{222}Rn and ^{226}Ra have been investigated as indicators of short-term groundwater residence time or where health concerns have been raised. A limited number of uranium radionuclide studies have also investigated ^{234}U/^{238}U activity ratios as indicators of groundwater flow paths, reactions and residence times.

In the absence of data for individual radionuclides, total-element analyses can give indications of occurrence of their respective radionuclides in groundwater, assuming equilibrium proportions. This section describes the distribution and occurrence of naturally-occurring radionuclides of environmental relevance in British groundwater (uranium, radium, radon) where data exist. In the absence of individual radionuclide data, whole-element analyses for potassium, thorium and uranium are described. These latter have been compiled from BGS databases acquired from a number of regional and national baseline studies(e.g. Ó Dochartaigh et al., 2011; Shand et al., 2007). Summary statistical data (mean, percentiles) for these elements are provided for various aquifers across Britain, calculated using non-parametric Kaplan Meier (KM) or semi-parametric robust ROS (random on order statistics) methods, depending on percentage of values above detection limits (KM for <50% non-detects). Where >80% of values are non-detects, only observed ranges are given.

3.2 POTASSIUM

3.2.1 Occurrence and controls

Potassium is an alkali metal with three naturally-occurring isotopes: ^{39}K (93.3%), ^{40}K (0.0117%) and ^{41}K (6.7%). ^{40}K has a half-life of 1.25 x 10^9 years.

Principal silicate mineral sources of potassium include feldspars and clays. Evaporite minerals may also include potassium salts (e.g. sylvite, polyhalite). Feldspars and clays are ubiquitous rock-forming minerals; occurrences of potassic evaporites in Britain are limited to the Whitby area of North Yorkshire.

Potassium is one of the eight principal ions in groundwater. Nonetheless, dissolved concentrations are limited and fresh groundwater usually has concentrations below around 10 mg/L. Potassium is released to solution substantially by weathering of silicate minerals but its transport is strongly limited by incorporation into secondary clays. Potassium is also a nutrient with an important role in the biosphere. Release of K from agricultural soils occurs via vegetation decomposition, soil leaching and runoff. Wood ash (potash) is also an enriched source (Hem, 1992).

3.2.2 Concentrations in groundwater

Concentrations of potassium in British groundwater are typically in the range 1–10 mg/L, but with occasional observed maxima of 100 mg/L or more. Median values are around 2–4 mg/L (Table 2, Figure 34). Anomalously high observed concentrations may be a feature of saline groundwater or water affected by agricultural pollutants. Among the highest concentrations appear to occur within groundwater from the Crag aquifer of East Anglia. These are moderately mineralised with around half in the BGS database having electrical conductance of greater than 1000 µS/cm (Ander and Shand, 2005).

Table 2. Statistical summary data for potassium (K) in groundwater from various aquifers in Great Britain (BGS databases).

Stratigraphy	n	ncens	Min	mean	Max	P5	P10	P25	P50	P75	P90	P95
Ashdown & Hastings Beds	8	0	1.34	2.84	11.1	1.34	1.34	1.36	1.56	1.7	5.11	8.09
Bridport Sands	52	0	0.4	2.41	10.5	0.6	0.90	1.40	2.00	3.1	4.1	4.7
Carboniferous	80	0	0.64	8.2	92.2	1.16	1.36	2.43	4.78	8.58	12.7	25
Carboniferous Limestone	223	12	<0.5	2.93	65.3	0.34	0.50	0.9	1.60	2.97	6.25	9.00
Chalk	736	2	<0.4	4.49	175	0.7	0.92	1.3	2.10	3.84	7.8	13.7
Coal Measures	12	0	0.88	5.95	15.7	0.88	0.89	1.17	2.50	7.27	15.5	15.6
Corallian	62	0	0.5	5.23	80.4	0.72	1.1	1.45	2.41	4.8	9.6	11.9
Crag	81	2	<0.5	16.5	220	0.9	1.3	2.6	4.80	20.0	34.8	63.0
Fell Sandstone	3	0	2.08	2.22	2.33	2.08	2.08	2.08	2.26	2.30	2.32	2.32
Granite	197	6	<0.5	4.44	66.8	0.7	0.90	1.5	2.50	4.1	8.7	13.2
Igneous extrusive	13	0	0.52	1.92	10.9	0.52	0.58	0.75	0.850	1.8	2.42	5.80
Igneous intrusive	18	0	0.88	3.05	13.6	0.88	1.02	1.29	2.51	3.78	4.82	6.14
Lincolnshire Limestone	19	0	2.76	5.74	11	2.76	2.84	3.81	4.15	8.82	10.8	10.9
Lower Greensand	154	0	0.83	3.96	20	1.2	1.50	2.1	2.90	5.1	8.2	9.28
Lower Palaeozoic	115	16	<0.5	1.93	33.7	0.094	0.171	0.339	0.80	1.8	4.3	8.99
Magnesian Limestone	120	0	0.613	4.92	169	1.48	1.76	2.19	2.82	3.84	6.56	8.75
Millstone Grit	178	0	0.34	2.76	14.8	0.70	0.77	1.0	1.84	3.7	5.97	7.38
Old Red Sandstone	185	3	<0.5	4.13	201	0.60	0.89	1.47	2.10	3.2	5.44	9.3
Oolite	117	2	<0.5	2.84	71.5	0.40	0.6	1.2	2.06	2.8	3.7	5.3
Ordovician	8	0	0.517	1.63	4.06	0.518	0.518	0.759	1.22	1.52	3.23	3.64
Palaeogene	73	0	0.9	9.08	105	1.20	1.4	2.6	4.61	7.67	18.6	37.6
Permo-Triassic Sandstone	786	3	<0.6	5.47	136	1.60	1.9	2.47	3.50	5.2	8.8	13.0
Precambrian	37	0	0.44	2.14	6.27	0.72	1.02	1.22	1.73	2.63	3.84	5.95
Sand & gravel	18	0	1.25	7.86	49.1	1.25	1.49	3.18	5.54	7.81	13.0	18.4
Silurian	40	0	0.342	1.76	5.7	0.456	0.761	0.996	1.27	1.74	3.61	5.58
Tunbridge Wells Sand	6	0	0.85	12	66.5	0.85	0.85	0.87	1.08	1.59	34.0	50.3
Wealden Group	2	0	0.76	1.19	1.63	0.76	0.76	0.76	1.19	1.41	1.54	1.59

ncens: number of censored points (non-detects); P5–95: percentiles

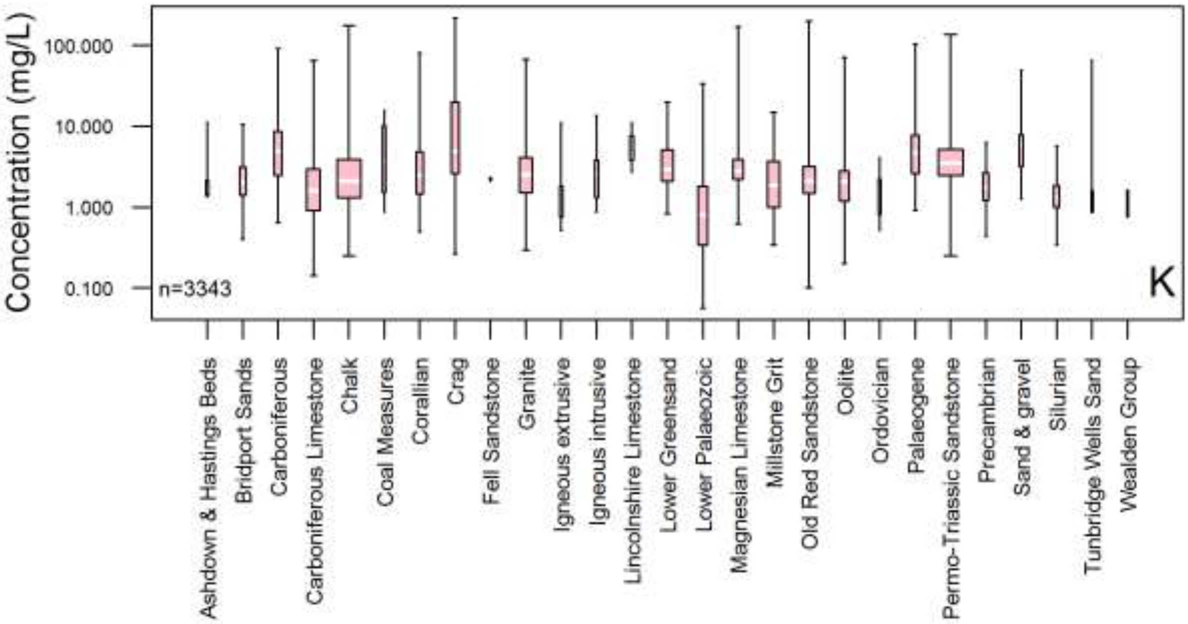

Figure 34. Boxplots showing potassium concentrations in groundwater from British aquifers; whiskers show the range of concentrations (box widths are proportional to the square root of the number of samples).

3.3 RADIUM

3.3.1 Occurrence and controls

Radioactive decay of U produces a number of daughter products, including radium (^{226}Ra). Radium comprises the naturally-occurring isotopes ^{223}Ra, ^{224}Ra, ^{226}Ra and ^{228}Ra, the most significant of which is ^{226}Ra. The half-life of ^{226}Ra is 1622 years.

Radium is an alkaline earth metal, behaving in the environment in a similar way to barium and strontium. It may be present in clay minerals, micas and metal oxides as well as barite and carbonate minerals. Greater Ra contents have been found in sediments with fine grainsizes than sand grade, suggesting the importance of clay-size minerals (Cuttell et al., 1988).

Radium has only one oxidation state, Ra(II), in natural systems. Radium compounds are relativity insoluble in water and so concentrations are usually very low, rarely exceeding a few Bq/L (Young et al., 2015). The element occurs in solution dominantly as free Ra^{2+} or as $RaSO_4^0$ and also forms complexes with carbonate (Wanty and Nordstrom, 1993). Mobility may be enhanced by alpha recoil but is also strongly limited by co-precipitation with barite or calcite, as well as by sorption reactions and ion exchange. Radium is known to be present in the mineral scales (calcite, barite) of groundwater systems with elevated uranium contents (Talbot et al., 2000). Sorption of Ra to metal oxides and clays is pH-dependent, being less significant under acidic conditions (e.g. Almeida et al., 2004). Higher concentrations of Ra have been found in acidic and anoxic groundwater conditions (USGS, 2016). Radium is also relatively mobile in saline groundwaters (Cuttell et al., 1988; Tomita et al., 2014). The mobility of ^{226}Ra influences the mobility of dissolved Rn.

^{226}Ra/^{238}U activity ratios of rock samples can be less than unity, indicating ^{226}Ra mobilisation relative to the ultimate parent ^{238}U (Cuttell et al., 1988).

3.3.2 Activity concentrations in groundwater

Very few data exist for radium activities in British groundwater. Cuttell et al (1988) reported activities of ^{226}Ra of 0.07–24 dpm/kg in groundwaters from the Permo-Triassic Sandstone of

Merseyside (0.001–0.4 Bq/L). Talbot et al. (2000) analysed groundwater samples from Devon (Dartmoor Granite, Silurian–Carboniferous sedimentary rock aquifers) but reported all analyses below the analytical detection limit of 0.1 Bq/L.

3.4 RADON

3.4.1 Occurrence and controls

Radon is a radioactive noble gas that exists naturally as three isotopes (^{222}Rn, ^{220}Rn, ^{219}Rn), derived from three radioactive decay chains. The most stable and environmentally relevant isotope of Rn, ^{222}Rn, forms from the alpha decay of ^{226}Ra, and ultimately from ^{238}U. ^{222}Rn is a short-lived isotope with a half-life of 3.8 days. During decay, an alpha particle is ejected, emitting radon in the process. This alpha recoil can alter crystal lattices and increase the leaching potential of Rn from the crystal surfaces (Wanty and Nordstrom, 1993). By the recoil process, Rn may be transported as a dissolved gas in porewater or retained in the mineral structure. Alpha recoil is likely an important mechanism for transferring Rn to groundwater and has been cited as a cause of radioactive disequilibrium in a number of groundwater studies (Wanty and Nordstrom, 1993).

As an inert gas, the mobility of radon in water is controlled by physical rather than chemical processes. Radon does not precipitate in mineral phases nor participate significantly in sorption reactions. Radon decays rapidly and does not accumulate in groundwater along flow paths because decay rates are typically faster than rates of groundwater flow. Hence, high Rn concentrations in groundwater are usually indicative of local parent (U, Ra) sources. Dissolved radon is lost from groundwater via release to the atmosphere as well as by radioactive decay.

The emanation efficiency of Rn (proportion of Rn released to groundwater compared to the total Rn produced) is a function of recoil and diffusion processes and is affected by Ra distribution in the host rock, surface geometry (e.g. rock specific surface area and roughness), surface wetness and rock porosity. The emanation efficiency in saturated aquifers is typically lower than 30% (Wanty et al., 1992). For a given U content of an aquifer host, Rn concentrations in groundwater are expected to be greater in aquifers of lower porosity, higher density or higher emanating efficiency (Wanty et al., 1992). The extent of transport from a Ra decay site is also determined by the permeability of the host rocks. In crystalline rocks, this is influenced by the extent and connectivity of fractures.

High Rn concentrations are typically not found in zones of high aquifer transmissivity as a result of lower rock/water ratios and dilution of emanating Rn (Lawrence et al., 1991). Inverse relationships have been found between ^{222}Rn concentration and well yield (Hall et al., 1987).

The solubility of Rn in water is temperature dependent, decreasing by about 3% per °C as temperature decreases from 20°C to 10°C. Barometric pressure and rainfall also have an influence, though less than other physical processes (Lindsey and Ator, 1996).

Temporal variations in Rn concentration have been observed in association with fluctuations in water level and groundwater pumping rates. The variation may be attributed to changing relative influences of different water-producing horizons (Lawrence et al., 1991).

In groundwater, although associated, the properties of Rn and U differ significantly. Radon is a dissolved inert gas and uranium a redox-sensitive metal with strong adsorption and complexation controls. Hence, although the two elements can be derived from a common geogenic source and can occur together in local groundwaters, they have very differing transport behaviour (Veeger and Ruderman, 1998) and may therefore become separated (Dowdall et al., 2013). The concentrations of uranium in groundwater are therefore not a reliable indicator of the concentrations of dissolved radon gas.

High Rn concentrations in groundwater are typically associated with U-rich rocks such as granite, granite gneiss and pegmatite (Banks et al., 1998a; Przylibski et al., 2004; Skeppström and Olofsson, 2007; Veeger and Ruderman, 1998; Vinson et al., 2009). In Britain, highest concentrations of Rn in the environment are associated with the Cornubian granite batholith of south-west England (Talbot et al., 2001) and the Grampian and Helmsdale areas of Scotland. High levels are also associated with the Carboniferous Limestone, Carboniferous shales of northern England, ironstone deposits (e.g. the Jurassic Northampton Sand), Palaeozoic mudrocks, and the Middle Old Red Sandstone of north-east Scotland (Appleton, 2005).

3.4.2 Activity concentrations in groundwater

The concentrations of Rn in groundwater typically vary over a large range, from around 3 Bq/L to 80,000 Bq/L (Appleton, 2005). Data for Rn in British groundwater are sparse. The most comprehensive recent review of available information is that carried out by Young et al. (2015). They concluded that air radon was likely a good indicator of dissolved radon in groundwater. Mean values for dissolved Rn in groundwater from Denbighshire, Ceredigion and Anglesey in Wales were recorded as 30.2 Bq/L, 47.1 Bq/L and 24.8 Bq/L respectively, the former two designated as Radon Affected Areas in terms of atmospheric concentrations.

In areas of granitic rocks, ^{222}Rn activities greater than around 50 Bq/L are not uncommon. Activities up 5300 Bq/L have been found in granitic groundwater from south-west England (Young et al., 2015). In a Devon groundwater study, 9% of groundwater samples analysed for Rn were found to contain more than 1000 Bq/L (n=105) (Talbot et al., 2000). Mean activity for groundwater from the Dartmoor Granite was >700 Bq/L. Banks et al. (1998b) reported values in the range 44–200 Bq/L (median 140 Bq/L) from groundwaters in the granite of the Isles of Scilly. Activities of 40–76 Bq/L (mean 61 Bq/L) have also been reported in areas of granite and granite pegmatite in Aberdeenshire, Scotland. The same study found lower activities of 3–35 Bq/L (mean 23 Bq/L) in areas of metasedimentary rock (Al-Doorie, 1993).

In the Permo-Triassic Sandstone aquifer, Rn activities are also relatively high, though lower than in groundwater from granitic rocks. A range of 7.1–35.4 Bq/L was found in groundwaters from Merseyside (Cuttell et al., 1988), while activities of 5.8–36.6 Bq/L were found in the equivalent lithologies of Northern Ireland (Gibbons and Kalin, 1997). Values up to 50 Bq/L have also been found for Triassic sandstone groundwater from Lancashire (BGS, unpublished data, 2016). Young et al. (2015) reported activities up to 1350 Bq/L in undifferentiated Upper Devonian rocks from Great Britain, presumably including the red-bed Old Red Sandstone aquifer.

In Chalk groundwater, activities <10 Bq/L are more typical. In the Chalk aquifer of south-east England, radon activities in the range 3.5–9 Bq/L were found in public-supply boreholes and 3.8–10.5 Bq/L in groundwater from springs (Low, 1996).

The investigation by Young et al. (2015) summarised groundwater data from databases held by BGS and Public Health England. A number of aquifers were represented, providing maximum observations of: Teign Valley Group (657 Bq/L), Hawick Group (57 Bq/L), Holsworthy Group (353 Bq/L), Dinantian volcanics (103 Bq/L), Ordovician volcanics (43 Bq/L), Palaeogene intrusions (64 Bq/L), Gala Group (35 Bq/L), Bridport Sand (10 Bq/L) and Gault (10 Bq/L) (Young et al., 2015). Ranges of ^{222}Rn activity reported for groundwater (wells, boreholes) from local authorities/water companies were in the range 0.01–382 Bq/L (mean 9.9 Bq/L, n=1561, England & Wales only). Highest values were from igneous intrusions and Caradoc, Pridoli and Triassic aquifers (Young et al., 2015).

3.5 THORIUM

3.5.1 Occurrence and controls

The principal isotope of thorium is ^{232}Th, with a half-life of 1.39 x 10^{10} years. Thorium is around three times more abundant in the earth's crust than uranium, but it is much less soluble in water and its concentrations are therefore usually low. It is commonly undetectable and so data for thorium in groundwater are limited.

Thorium occurs in the tetravalent (Th(IV)) state (Hem, 1992). The element's occurrence as a major constituent in minerals is restricted to thorianite and thorite (Langmuir and Herman, 1980). Thorium also occurs in the zircon, monazite and uraninite. The low solubility of these minerals is a major factor in the low abundance of Th in groundwater. It is present as a trace constituent in phosphate, oxide and silicate minerals and sorbs to clays. Thorium tends to be more concentrated in sediments with fine grain sizes (Cuttell et al., 1988).

Thorium in solution is invariably complexed, dominant ions being $Th(SO_4)_2^0$, ThF_2^{2+} and $Th(HPO_4)_2^0$. Complexation can increase the mobility of Th by some orders of magnitude (Langmuir and Herman, 1980). Complexing is more important at pH<7. Thorium mobility is likely most strongly controlled by slow mineral dissolution kinetics and by sorption (Langmuir and Herman, 1980). Sorption of thorium to clays, metal oxides and organic matter increases with increasing pH, and is practically complete at pH 6.5 (Langmuir and Herman, 1980).

3.5.2 Concentrations in groundwater

Available BGS data for thorium concentrations in British groundwater are in the range <0.001–1.85 µg/L (Table 3, Figure 35). The highest recorded observations occur in groundwater from the Permo-Triassic Sandstone and Chalk aquifers. These also had the largest ranges (and numbers of samples). Median and mean values (where calculable) across the aquifers are <0.03 µg/L.

Few other data are available for thorium in the literature. A range of 0.4–0.5 µg/L was determined in groundwater from granite in Altnabreac, Caithness (Ivanovich and Kay, 1983). Talbot et al. (2000) reported Th concentrations in the range 0.02–0.066 µg/L in groundwater from Dartmoor Granite of Devon.

$^{230}Th/^{234}U$ ratios of 0–0.037 were reported by Cuttell et al. (1988) from the Permo-Triassic Sandstone aquifer of Merseyside.

Table 3. Statistical summary data for thorium (Th) in groundwater from various aquifers in Great Britain (BGS databases).

Stratigraphy	N	ncens	min	mean	max	P5	P10	P25	P50	P75	P90	P95
Ashdown & Hastings Beds	8	8	<0.005		<0.005							
Bridport Sands	52	48	<0.016		0.0789							
Carboniferous	78	55	<0.001	0.0238	0.979	0.00016	0.00030	0.000844	0.003	0.00995	0.027	0.083
Carboniferous Limestone	100	91	<0.005		0.23							
Chalk	305	269	<0.001		1.47							
Coal Measures	12	8	<0.005	0.0114	0.07	0.00036	0.00051	0.00113	0.00319	0.0138	0.0199	0.0425
Corallian	53	52	<0.005		0.026							
Crag	18	18	<0.05		<0.05							
Fell Sandstone	3	3	<0.005		<0.005							
Granite	25	24	<0.05		0.28							
Igneous extrusive	13	12	<0.005		0.006							
Igneous intrusive	18	18	<0.05		<0.05							
Lincolnshire Limestone	19	19	<0.05		<0.05							
Lower Greensand	62	60	<0.005		0.006							
Lower Palaeozoic	104	93	<0.05		0.27							
Magnesian Limestone	48	46	<0.005		0.0309							
Millstone Grit	27	26	<0.005		0.008							
Old Red Sandstone	141	99	<0.02	0.0291	0.13	0.0157	0.0179	0.0229	0.025	0.0312	0.0397	0.05
Oolite	58	55	<0.005		0.11							
Ordovician	8	8	<0.05		<0.05							
Palaeogene	62	59	<0.005		0.08							
Permo-Triassic Sandstone	265	246	<0.005		1.85							
Precambrian	37	34	<0.005		0.02							
Sand & gravel	18	14	<0.005	0.013	0.029	0.003	0.00332	0.00434	0.00697	0.025	0.0262	0.0276
Silurian	40	40	<0.05		<0.05							
Tunbridge Wells Sand	6	3	<0.005	0.0085	0.014					0.013		
Wealden Group	2	0	0.016	0.047	0.078	0.016	0.016	0.016				

ncens: number of censored points (non-detects); P5–95: percentiles

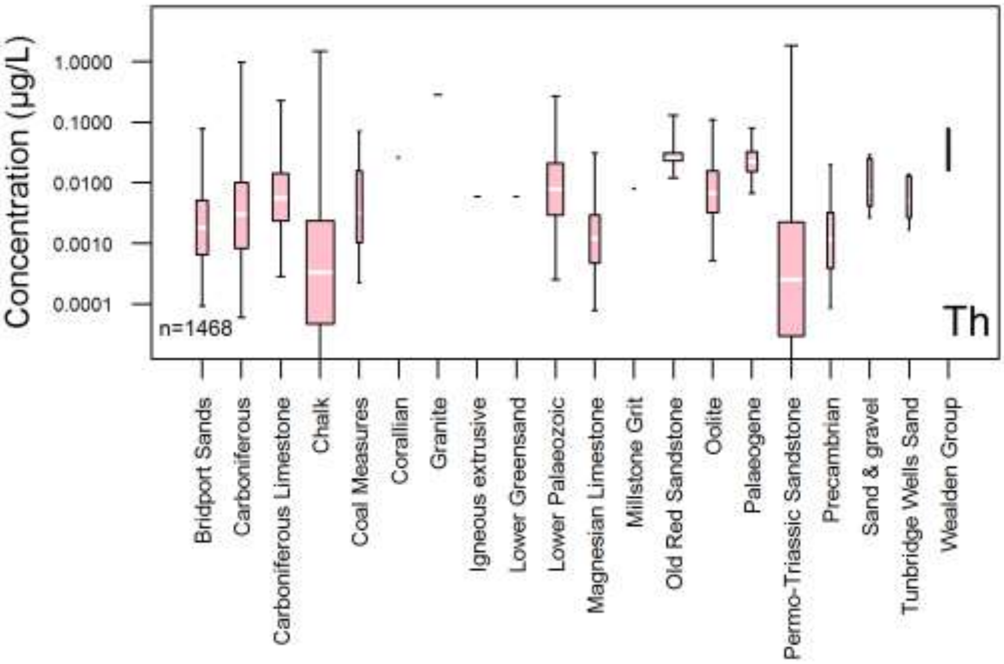

Figure 35. Boxplots showing thorium concentrations in groundwater from British aquifers; whiskers show the range of concentrations (box widths are proportional to the square root of the number of samples).

3.6 URANIUM

3.6.1 Occurrence and controls

Natural uranium comprises three radioactive isotopes: ^{234}U, ^{235}U and ^{238}U, by weight constituting respectively about 0.0054%, 0.72% and 99.27%. Natural waters often display secular equilibrium between these isotopes but can depart from these mass proportions as a result of natural nuclear and chemical processes, leading to either enrichment or depletion of ^{234}U relative to ^{238}U. The theoretical mass ratio of ^{234}U/^{238}U (0.0000554) has been observed to vary from 0.00003 to 0.0014 in natural waters, with activity ratios in the range 0.5 to 40 relative to the secular equilibrium ratio of unity (Ivanovich and Harmon, 1982). High ^{234}U/^{238}U activity ratios (greater than unity) have been linked to preferential leaching of ^{234}U from minerals as a result of alpha decay causing recoil of ^{234}U and ^{234}Th (Andrews and Kay, 1982), in turn causing damage to the crystal lattice (Gascoyne, 1992). High ^{234}U/^{238}U ratios have also been found in reducing aquifers close to redox boundaries, linked to redox transformations of uranium (Andrews and Kay, 1982; Bonotto and Andrews, 2000).

Uranium occurs in nature in two main oxidation states: the hexavalent form, U(VI), and the tetravalent form, U(IV). Uranium forms a major constituent of minerals such as uraninite, coffinite and autunite. These can be significant localised sources of uranium in some groundwaters, especially in ore mineralised areas and some granitic terrains. In Britain, occurrences of uranium mineralisation are relatively rare and usually below economic grade. Pitchblende-bearing mineral veins occur alongside Cu-Sn and Pb-Zn-Ni mineralisation around the Cornubian granite of south-west England. In Scotland, U mineralisation occurs in U-Pb mineral veins as well as phosphatic and carbonaceous horizons of the middle Devonian (Old Red Sandstone) of Caithness and Orkney. It also occurs in veins associated with granitic rocks (Helmsdale granite of Ousdale; Criffel-Dalbeattie granodiorite). Other occurrences in England & Wales are mainly associated with black shale deposits.

Uranium is also closely associated with the more common iron oxides, phosphates, clays and organic matter, and these minerals can be important sources, as well as sinks, of uranium. Iron oxides and clays are rock-forming minerals and are particularly important in iron-rich and argillaceous sediments and metasediments. Phosphate minerals, especially apatite and hydroxyapatite, are accessories in granitic and sedimentary rocks. The concentrations of uranium in rock-forming silicate minerals such as quartz and feldspar and carbonate minerals are usually low.

Iron oxides, including goethite, haematite, ferrihydrite and magnetite, have a strong affinity for uranium (Bianconi and Kögler, 1992; Casas et al., 1994; Duff et al., 2002; Scott et al., 2005). This is either attached via surface adsorption of the $U(VI)O_2^{2+}$ uranyl ion, or incorporation of U(VI) within the structure of haematite and other iron oxides (Duff et al., 2002).

Additional anthropogenic sources of uranium in the environment can derive from industry (e.g. ceramics, chemicals, photographics and lighting industries) and agriculture. Uranium can be present (abundance around 20–200 mg/kg) in phosphate fertilisers (Zielinski et al., 2000) and may therefore be introduced to soils by agricultural activities. Enriched uranium (enriched in ^{235}U) is used in nuclear power plants and nuclear weapons, and its by-product, depleted uranium (relatively enriched in ^{238}U), has been used in military operations and the aircraft industry.

The mobility of U in water is controlled substantially by pH, redox status and concentrations of other coexisting solutes. Uranium is a redox-sensitive heavy metal that occurs in water principally under oxic conditions in its hexavalent (U(VI)) state. It is usually complexed in solution, especially with carbonate ligands (Kohler et al., 2004; Villalobos et al., 2001). At alkaline pH, the uranyl ion forms stable complexes with carbonate ions, notably $UO_2(CO_3)_2^{2-}$ and at higher pH, $UO_2(CO_3)_3^{4-}$. Uranium complexes less significantly with phosphate, fluoride or sulphate, depending on their respective concentrations and ambient pH (Drever, 1997; Sandino and Bruno, 1992). Chloride and sulphate may become important ligands in saline waters (Porcelli and Swarzenski, 2003) ; U(VI) also forms stable complexes with dissolved organic carbon (Arey et al., 1999; Cothern and Lappenbusch, 1983; Higgo et al., 1993).

Despite the relative mobility of U(VI) in the aqueous environment, the concentrations of U under oxidising conditions can be limited by adsorption onto phosphate minerals and iron oxides, as well as organic matter and clay minerals (Ivanovich, 1994). These minerals can therefore act as important sinks as well as potential sources. As many of the uranyl-carbonate complexes are anionic, sorption is generally less strong at alkaline pH (>7). Sorption of U onto minerals is enhanced under pH-neutral conditions (Langmuir, 1978; Prikryl et al., 2001). Pabalan and Turner (1997) observed maximum sorption of U(VI) onto montmorillonite at pH 6.0–6.5.

Under anoxic conditions, U is reduced to its tetravalent U(IV) state and its concentration in water is low as a result of stabilisation of the sparingly soluble uraninite (UO_2), or adsorption to mineral surfaces such as iron oxides and clays. Equilibrium with uraninite limits uranium concentrations to less than 0.06 µg/L (Gascoyne, 1992; Langmuir, 1978). The reduction of U(VI) is facilitated by microbial activity (Davis et al., 2006; Fox et al., 2006; Lovley et al., 1991).

3.6.2 Concentrations in groundwater

Observed baseline concentrations of uranium in British groundwater span some four orders of magnitude, from <0.002 to 67 µg/L in the BGS databases. The observed maximum equates to 1.7 Bq/L assuming secular equilibrium. Median values are almost invariably 1 µg/L or less (up to around 0.026 Bq/L, same assumption; Table 4, Figure 36). Highest concentrations are observed in groundwater from red-bed sandstone aquifers (Old Red Sandstone; Permo-Triassic Sandstone). These high values occur in oxic groundwater conditions, the sources of uranium likely being iron oxides and/or phosphate minerals (Read et al., 1993) in the sandstone matrices. A similarly large range of concentrations was found in Permo-Triassic Sandstone groundwater from Merseyside. Ivanovich et al. (1992) reported concentrations of 0.3–13.6 µg/L ($^{234}U/^{238}U$ activity ratios of 1.6–13.8). Cuttell et al. (1988) recorded ^{238}U concentrations up to 42 µg/L in this aquifer. Fresh oxic groundwaters had ^{234}U/^{238}U activity ratios of around 1–5, as did fresh estuarine and saline groundwaters; flushed brackish groundwaters by contrast had activity ratios up to around 14.8, potentially linked to ion-exchange and desorption of U from iron oxides. Talbot et al. (2000) reported concentrations of uranium up to 11.6 µg/L in groundwater from Devon, the highest concentrations being form the Dartmoor Granite. Such high concentrations for the granite of south-west England were not recorded in the BGS database (Table 4). Relatively high U concentrations are also observed in the Carboniferous Limestone and igneous rock types, likely linked to the presence of authigenic phosphate minerals and uranium mineralisation. Lowest baseline concentrations are observed in the Lincolnshire Limestone (Jurassic) and Palaeogene. These groupings contain a high proportion of anoxic groundwaters from confined aquifers.

Table 4. Statistical summary data for uranium (U) in groundwater from various aquifers in Great Britain (BGS databases).

Stratigraphy	**n**	**ncens**	**Min**	**mean**	**max**	**P5**	**P10**	**P25**	**P50**	**P75**	**P90**	**P95**
Ashdown & Hastings Beds	8	3	<0.002	0.0135	0.061				0.003	0.011		
Bridport Sands	52	7	<0.05	0.608	5.47			0.16	0.5	0.808	0.97	1.06
Carboniferous	78	8	<0.02	0.862	9.96	0.003	0.009	0.03	0.19	0.727	3.16	4.74
Carboniferous Limestone	100	7	<0.02	1.10	7.84	0.005	0.05	0.3	0.69	1.57	2.61	3.44
Chalk	446	50	<0.002	0.368	7.63	0.002	0.018	0.11	0.23	0.41	0.77	1.29
Coal Measures	12	2	<0.002	0.132	0.417			0.005	0.05	0.249	0.335	
Corallian	53	8	<0.02	0.43	7.46	0.006	0.006	0.07	0.21	0.4	0.89	1.22
Crag	18	5	<0.02	0.123	0.37				0.04	0.24	0.33	
Fell Sandstone	3	0	0.052	0.168	0.4	0.052	0.052	0.052	0.053			
Granite	25	0	0.02	0.983	3.57	0.04	0.2	0.29	0.55	0.88	2.97	3.56
Igneous extrusive	13	1	<0.2	1.42	13.3	0.02	0.03	0.04	0.23	0.84	1.94	
Igneous intrusive	18	1	<0.02	0.933	12.0		0.02	0.04	0.14	0.46	1.07	
Lincolnshire Limestone	19	13	<0.02	0.0753	0.4	0.0002	0.00033	0.0012	0.00635	0.03	0.374	0.391
Lower Greensand	99	70	<0.02	0.0688	0.81	0.0013	0.00213	0.0053	0.0172	0.0442	0.181	0.363
Lower Palaeozoic	115	56	<0.02	0.162	7.93	0.017	0.017	0.017	0.02	0.07	0.23	0.76
Magnesian Limestone	48	0	0.0211	1.65	8.08	0.373	0.833	1.13	1.53	1.86	2.45	2.59
Millstone Grit	27	9	<0.02	0.191	1.87	0.008	0.008	0.008	0.04	0.29	0.49	0.69
Old Red Sandstone	141	6	<0.005	2.71	48.0	0.033	0.11	0.29	1.01	2.29	5.36	8.4
Oolite	58	10	<0.02	0.506	3.7			0.17	0.29	0.51	1.19	2.3
Ordovician	8	1	<0.02	0.286	1.3			0.03	0.04	0.13		
Palaeogene	62	28	<0.005	0.306	4.65			0.005	0.02	0.09	0.495	2.38
Permo-Triassic Sandstone	327	11	<0.02	1.94	67.2	0.04	0.18	0.392	0.9	1.93	4.38	6.86
Precambrian	37	10	<0.02	0.806	6.19				0.09	0.9	3.03	4.98
Sand & gravel	18	1	<0.005	1.29	6.11		0.009	0.027	0.342	1.07		
Silurian	40	5	<0.02	0.729	4.14		0.03	0.17	0.4	1.14	1.66	2.15
Tunbridge Wells Sand	6	0	0.013	0.0408	0.155	0.013	0.013	0.013	0.014	0.026		
Wealden Group	2	0	0.037	0.05	0.063	0.037	0.037	0.037				

ncens: number of censored points (non-detects); P5–95: percentiles

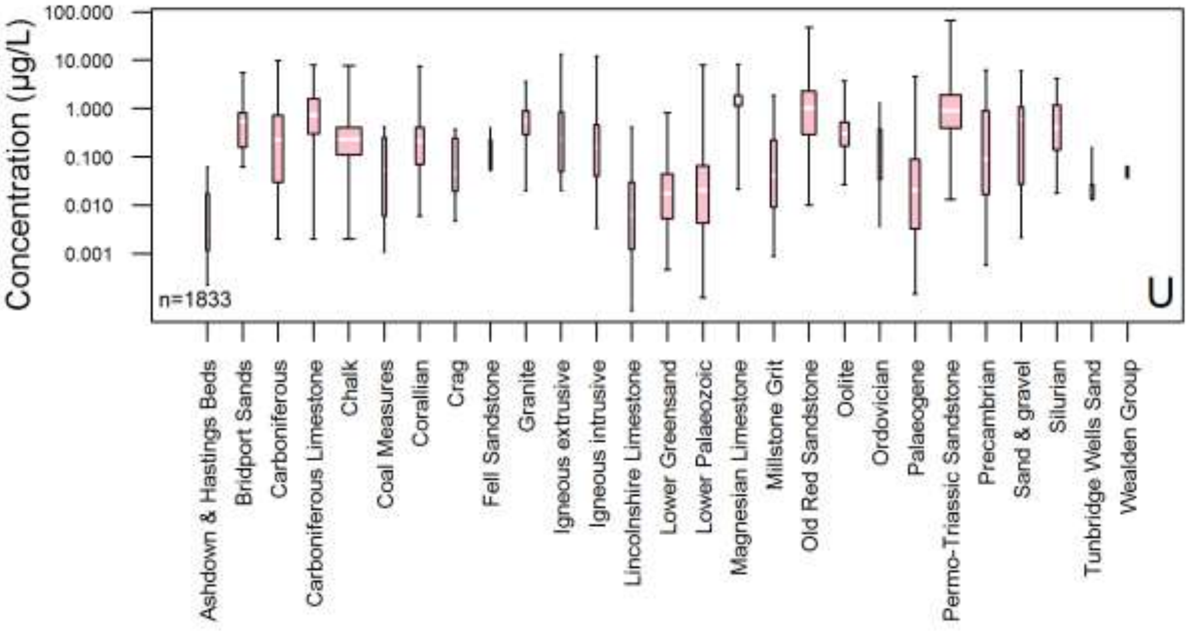

Figure 36. Boxplots showing uranium concentrations in groundwater from British aquifers; whiskers show the range of concentrations (box widths are proportional to the square root of the number of samples).

4 Background natural radioactivity in Soils

The use of total element concentrations for radiological assessments of environmental media has been undertaken previously (EA, 2007). This was undertaken on a UK regional basis by combining the specific activities of ^{40}K, ^{232}Th and $^{238\text{Th}}$, these being 31.6 Bq g^{-1} K, 4.1 Bq mg^{-1} Th and 12.2 Bq mg^{-1} for U respectively, with total element concentrations.

4.1 AVAILABILITY OF DATA

Data concerning the National datasets for background radioactivity (U, Th, K) in soils include the G-BASE datasets, which only have partial coverage for UK soils. This relates to how the geochemical survey evolved over 30 years. However, G-BASE sediment and soil data were previously used in an assessment of radioactivity in environmental media (EA, 2007). However, a re-analysis of the National Soil Resource Institute Geochemical Atlas (originally published by McGrath & Loveland (1992) with a sampling resolution of one sample per 5 km^2 grid) by BGS provides national coverage but at a slightly lower sampling density than G-BASE for England and Wales. This is known as the Advanced Soil Geochemistry Atlas and contains data and maps for total soil concentrations of U, Th, and K and is available on-line at:

http://www.bgs.ac.uk/GBASE/advSoilAtlasEW.html

G-BASE soil geochemistry data and maps been obtained for Topsoils <2mm and subsoils (<250 µm) can be can be found at:

http://www.bgs.ac.uk/products/geochemistry/home.html?src=topNav

A recently completed high resolution survey of the South West of England, a major area of England with high natural background radioactivity, has top soil and sediments data and maps for U, Th and K can be found at:

http://www.bgs.ac.uk/gbase/gBaseSW.html

At present Scotland has limited National coverage of Soil Geochemistry. The Geochemical Atlas for Scottish Topsoils (Paterson, 2011) has information regarding Potassium. However, proxies of soil parent materials through the use of stream sediment will give an indication of those geological formations that may result in high background radioactivity concentrations. Regional G-BASE data for stream sediments can be found at:

http://www.bgs.ac.uk/data/maps/maps.cfc?method=listResults&mapName=&series=RGA&scale=&pageSize=100&

However, there are strong similarities between the geology of Scotland and Northern Ireland where a recent geochemical survey (TELLUS) has been undertaken with soil geochemistry being included. This can be used as proxy data. Datasets can be found at:

https://www.gsi.ie/Tellus/

4.1.1 Uranium

The mean and median values of Uranium in soils from England and Wales using data from the Advanced Soil Geochemistry Atlas are 2.4 and 2.3 mg kg^{-1} respectively. In soils, it occurs in common minerals such as Zircons, Apatite, monazite and carbonates but also binds strongly to humus and peat (Read et al. 1993). Soils formed from geological parent materials with high U, typically show the highest U concentrations. Within England and Wales, 90 % of the data from the Advanced Soil Chemistry atlas was below 3.3 mg kg^{-1}. Geological formations where elevated concentrations occurred include the (a) lower cretaceous non-marine sandstones and clays of the Weald, (b) the Devonian and Carboniferous terrane of Cornwall, including the Granites, (c) the Holocene peats of the Fen Basin, (d) the marine alluvium of the Lincolnshire coast, e) the soils above the Carboniferous and Permian limestone outcrop stretching from the Peak District to Newcastle and the (f) Silurian strata between Welshpool and Hereford. Typically concentrations of U in the upper 10th percentile have concentrations ranging from 3.3 to ~90 mg kg^{-1}. In Scotland, concentrations of U in Caithness are considered to be 3.5 times greater than the UK average (Nicholson et al. 1990). Using TELLUS data from Northern Ireland as a proxy for Scotland because of the close similarity in geology, concentrations of U in soils derived from granites can exceed 100 mg kg^{-1}, but the median concentration is 10 mg kg^{-1} and the 75th percentile value is <30 mg kg^{-1}. However, for other geological formations found in NI that are similar to Scottish formations, the soils typically have a 95th percentile which is < 5 mg kg^{-1}. These include soils formed on Gabbro, Lithic Arenites (sandstones), Basalts, Andesites, Acid Volcanics, Psammite and Semi-pelites, conglomerates, sandstone, mudstone and limestone. In Scotland, concentrations of U in soils from Sutherland associated with the Helmsdale granite had concentrations of U between 1.1 and 16 mg kg^{-1} (Nicholson et al. 1990).

Enhanced concentrations of Uranium may occur not only as a result of contamination from industrial processes and mining activites, but through the widespread application of Fertiliser P. Recent work by Ahmed *et al*. (2014) demonstrated the effects of P fertilisation using paired depth profiles of arable and woodland soils in Nottinghamshire. In arable soils there was good agreement between Total P and Uranium to depths of about 50 cm, with U concentrations in the top soil of being ~ 1.6mg kg^{-1} compared to 1.2 mg kg^{-1} in the adjoining woodland soils. Uranium in the arable soils was strongly correlated (r=-0.94) with Ca, suggesting that co-precipitation of U with poorly soluble Ca-Phosphates occurred (maybe because of liming). Sequential extractions were undertaken to understand the binding phases of U in the non-residual fraction of a sandy loam soil and showed that over 50% was bound to organic matter, sulphides or Fe/Mn oxides.

A more famous example of enhanced U concentrations in soils occurs at Broubster, Caithness in Scotland, and demonstrates the potential of peat to bind U. This occurs through the release of U from the Ciathness flag sequence of sandstone where the U resides in diagenetic apatiotes and U-Si-Ti phases. Weathering processes have released the U, with the 4000 yr old peat being the sink. The maximum concentration of U found in the peat has been recorded as 1200 ppm (Read et al. 1993).

4.1.2 Thorium:

Thorium is naturally associated with K, U and some rare earth elements such as Ce. It is similar to Uranium, as it is found in minerals such as thorite and monazite, is also present in Zircon, sphene and epidote. From the advanced soil atlas of E&W, the mean and median concentrations of Th in soils of England and Wales are 8 mg kg^{-1}. The upper 10th percentile has a concentration range of 11-51 mg kg^{-1} and soils associated with the following geology fall within this range: soils associated with (a) the Silurian of mid and SW Wales, (b) the old red sandstone of the Welsh Borders, (c) the Devonian – Carboniferous sedimentary terrane in the south West but excluding the granite outcrops, and the (d) Jurassic outcrop of central England extending from Somerset to Lincolnshire with the ironstones and ferruginous sandstones having the highest concentrations and lastly e) the non-marine Lower Cretaceous sedimentary strata of the Weald. Soils with the lowest concentrations include those associated with Chalk on the downs of southern England and East Anglia – these soils typically have concentrations < 6mg kg^{-1}. In Scotland, concentrations of Th in soils from Sutherland associated with the Helmsdale granite had concentrations of Th between 2.3 and 32.4 mg kg-1 (Nicholson et al. 1990).

With the exception of industry, the distribution of Th within P fertilisers is considered to be the major route through which background concentrations of Th in soils may be enhanced. Ahmed et al. (2014) examined Th along with U in adjoining arable and woodland soils and found that Th distribution was similar in arable and woodland soils, although slight enrichment was found with depth. This was largely considered to be because Th in P fertilisers is often less than the concentrations found in soils whilst U is concentrations in fertilisers can be several hundred times higher than is found in soils. However, the majority of the non-residual fraction of Th in both the woodland and arable soil was held in the organic matter / sulphide fraction of a sequential extraction.

4.1.3 Potassium

Potassium in the soils of England and Wales are in the range 0.03 to 1.9 % up to the 90th percentile. The upper 10th percentile covers the range of 1.9 – 4.17 % based on data from the Advanced Soil Geochemistry Atlas. The median concentration is 1.2 %. Despite the ubiquitous use of K as a fertiliser on agricultural land, geological formations rich in clay minerals still notably possess identifiable elevations in K concentrations. Soils with K concentrations above 1.9 % largely include those based on parent materials consisting of undifferentiated mudstones and siltstones such as (i) the Devonian strata in the south west of England, (ii) the Triassic age Mercia Mudstone group that extends from Somerset to Nottinghamshire, (iii) the lower Palaeozoic aged sediments of Mid Wales and (iv) Carboniferous sediment rocks in Northumberland and Berwick.

4.2 ESTIMATES OF BACKGROUND U, TH AND K CONCENTRATIONS OF SOILS ASSOCIATED WITH GEOLOGY AT UK NUCLEAR SITES

Using information from the different Geochemistry databases we compiled information from soils or sediments associated with the geology on which the UK nuclear establishments are built. These can be seen in Table 1. Different databases needed to be used, particularly for Scotland where a lack of soils data is available, for different parts of the country as a consequence of how the G-BASE sampling program developed over 30 years. .

Table 5. Estimates of likely background concentrations of U, Th and K in soils or sediments associated with rock types found at UK Nuclear sites. The data is collated from G-BASE Topsoil, G-BASE Subsoil, G-BASE sediment and the Advanced Geochemical Atlas for England and Wales.

Location	U (mg kg^{-1})	Th (mg kg^{-1})	K (%)	Source
Dounrey	4	-	2.26	G-BASE Sediment
Clyde	2.8	-	2.81	G-BASE Sediment
Hunterston	2.2	-	2.63	G-BASE Sediment
Rosyth	2.7	-	1.50	G-BASE Sediment
Torness	3.4	-	1.5	G-BASE Sediment
Chapelcross	2.5	-	2.0	G-BASE Sediment
Sellafield	2.5	<8	1.6	G-BASE Sediment
Eskmeals	2.6	<8	2.0	G-BASE Sediment
Hartlepool	2.8	<9	1.7	G-BASE Sub soil
Heysham	2.8	<6	1.4	G-BASE Sub soil
Springfields	2.5	<6	1.5	G-BASE Sub soil
Capenhurst	2	7	2.2	G-BASE Sub soil
Wylfa	2	9	1.7	G-BASE Sediment
Trawsfynydd	1-10	<8	1.7	G-BASE Sediment
Donnington	2	8.4	1.7	G-BASE Top soil
Sizewell	1.2	2.2	0.71	G-BASE Top soil
Bradwell	2.8	7.6	1.6	G-BASE Top soil
Amersham	1.6	4	0.55	G-BASE Top soil
Culham	1	2.6	0.41	G-BASE Top soil
Harwell	1.5	8	1.0	G-BASE Top soil
Aldermaston	1.7	6.8	1.1	G-BASE Top soil
Berkley and Oldbury	3.1	12.4	2.3	G-BASE Top soil
Cardiff	2.4	6.5	1.1	G-BASE Top soil
Hinkley Point	<4	11	1.9-4.0	Advanced Geochem Atlas
Winfrith	<2	<6	<0.9	Advanced Geochem Atlas
Portsmouth	<3	<8	<1.5	Advanced Geochem Atlas
Dungeness	<3	<10	<1.5	Advanced Geochem Atlas
Devonport	4.1	15	3.2	Advanced Geochem Atlas

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