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Some Observations on the Geochemistry and Isotopic Composition of Uranium in Relation to the Reprocessing of Nuclear Fuels

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ABSTRACT

In order to determine whether or not uranium depleted in ^{235}U and derived from the British Nuclear Fuels Ltd (BNFL) nuclear fuel reprocessing plant at Sellafield, Cumbria, UK can be detected in environmental samples, we have investigated the isotopic composition of uranium in ammonium carbonate leachates from marine and terrestrial samples from near Sellafield. Some show a depletion in ^{235}U and the presence of ^{236}U which unequivocally identifies the presence of uranium derived from BNFL. The $^{234}U/^{238}U$ activity ratio and total uranium content of samples are not significantly different from those of natural uranium abundances. The highest concentrations of uranium are found in anaerobic organic-rich silts and the lowest in sandy silts and coarse-grained sands.

INTRODUCTION

Since the reprocessing of spent Magnox fuel (uranium oxide) rods first started at the BNFL site at Sellafield in Cumbria in the latter part of the 1950s, the factory has discharged ~70 tonnes of uranium in an unknown chemical and physical form into the NE Irish Sea (see Fig. 1). In seawater, uranium exhibits conservative behaviour and, because of its ubiquitous concentration of ~3 μg U per litre, Pentreath *et al.* (1979) noted that in local seawater the discharges of uranium from BNFL would not be detected; this was confirmed by Hamilton (1980) who determined a
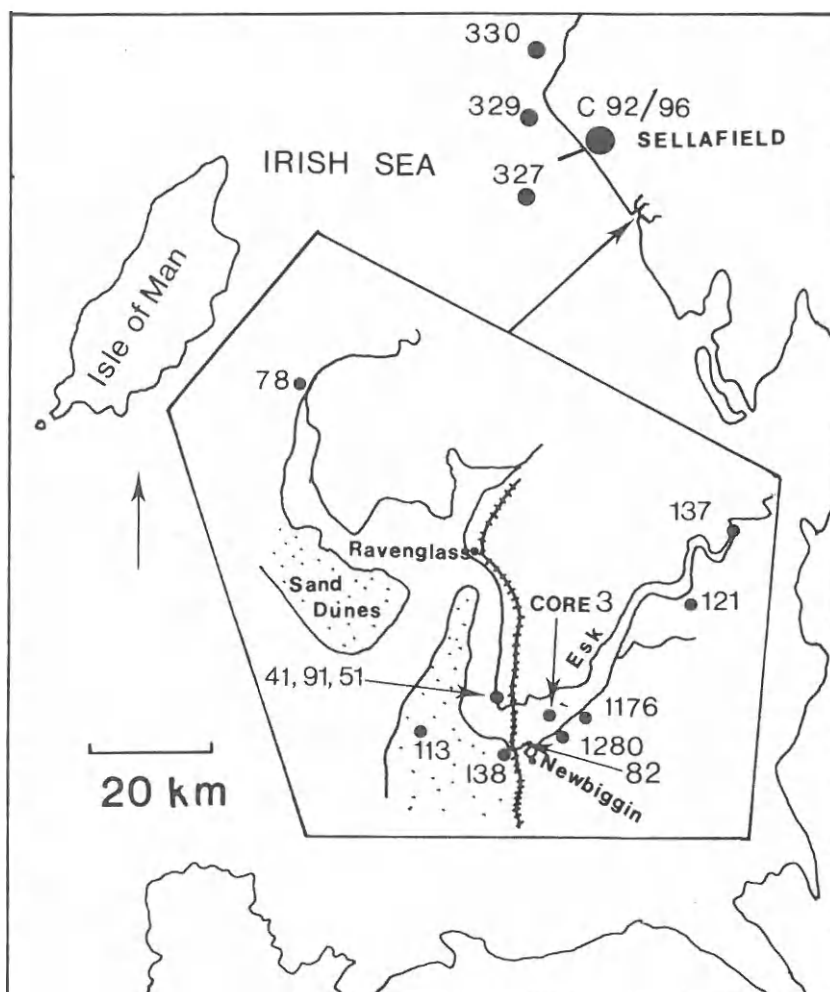
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Fig. 1. Sampling sites.

concentration of 2.8 ± 0.3 μg U per litre in $31\%_{00}$ seawater of the Esk estuary, Cumbria, ~10 km to the south of Sellafield. Later, however, Hamilton (1981) identified the presence of uranium associated with particulate debris originating from BNFL in sediments of the Esk and at the air/seawater interface; hence the sediment (particulate) transport pathway could provide a route for the introduction of BNFL debris into Esk sediments. Because of the similarities in abundances of several

gamma- and alpha-emitting radionuclides in BNFL effluents and in sediments of the Esk, they must represent particulate phases either of spent fuel rod debris (possibly derived from the open spent fuel cooling ponds), a phase which is produced within the confines of the factory and whose composition is retained in the sea (for example flocs of hydrated iron and magnesium oxides), or of solid matter formed by interaction between the effluent and seawater at the discharge site.

MATERIALS AND METHODS

Here we consider the concentration of uranium together with its isotopic composition (α-activity ratios and mass abundance) in representative samples (see Fig. 1) of sediment from the Esk estuary, bottom sediment from the Irish Sea adjacent to Sellafield and, in order to sample any contribution from aerial deposition, in moss and lichen from the littoral zone near Sellafield. The total concentration of uranium in the samples was determined either by the delayed neutron method (140 samples) (Hamilton, 1966) or by instrumental neutron activation analysis (INAA) using the reaction $^{238}U \xrightarrow{n\gamma} {}^{239}U$ (8 samples). Within an analytical error of $\pm 5\%$ and a sampling error of $\sim \pm 10\%$, both methods gave the same results; hence, as the former is based upon the fission of ^{235}U and the latter upon activation of ^{238}U, analysis of bulk samples does not provide any evidence of a depletion in ^{235}U which would be characteristic of spent Magnox fuel. The $^{234}U/^{238}U$ activity ratio and mass isotopic composition were determined on the ammonium carbonate leachates of samples as described by Joshi and Ganguly (1972, 1976). The technique is accepted as one which removes uranium associated with surfaces, rather than that present in accessory minerals. Knowing the total concentration of uranium in the samples and assuming that the fraction of total uranium which is leached is reproducible, the total mass of uranium leached was calculated using the following experimentally determined factors: ion-exchange recovery, $90 \pm 10\%$; electro-plating efficiency, $70 \pm 15\%$; and a 4π silicon surface barrier counting efficiency of $17 \pm 1\%$. Samples, from Core 3 at 5 and 25 cm depth, of Drigg mud (78) and of Irish Sea sediment (330) were subjected to a second leaching with saturated ammonium carbonate to determine the efficiency of the method for removal of leachable uranium; $<5\%$ of the uranium extracted by the initial leach was removed; hence, for samples of sand and silt, most of the uranium which

is leachable is removed by the method. The ^{241}Am content of samples was determined by gamma spectrometry as described by Clifton and Hamilton (1982). In order to evaluate the influence of redox states on the mobility of uranium in sediments, *in-situ* 200 MW cut-off Medicell dialysis tubes containing a mixture of equal volumes of $31\%_{00}$ seawater and deionised water were placed into, and upon, Esk sediments. After two days the tubes were removed and the dialysate aerated to precipitate a hydrated iron-rich floc (i.e. $Fe^{+2} \rightarrow Fe^{+3}$) in which the concentration of uranium was determined by INAA; uranium was not detected (<0.1 μg litre^{-1}) in the supernatant.

RESULTS

The concentrations of uranium associated with silty surface sediments (see Table 1) collected in 1980 were similar; plant material contained less uranium but samples analysed by the CR-39 autoradiographic technique (Hamilton & Clifton, 1981) showed that most of the alpha activity is trapped on external surfaces of foliage. The distribution of uranium in various sediment profiles of the Esk estuary is illustrated in Fig. 2. The highest concentration of uranium is found near the surface of the sediment and is associated with fine grain silts which are usually anaerobic and support a sparse cover of salt marsh vegetation. The concentrations of uranium in arenaceous facies of the sediments tend to be constant and site specific; the lowest concentrations of uranium are found in coarse sands or silts which have been subject to resuspension (Hamilton & Clarke, 1984).

In the Esk, Core 3 has been subjected to intense study; Hamilton and Clarke (1984) have shown that it is representative of a site of continuous accretion over the last ~50 years. Using statistical modelling techniques (Hamilton & Clarke, 1984), a sedimentation rate of ~3·5 cm y^{-1} has been determined and verified by three independent methods. The uranium profile, illustrated in Fig. 3, is similar to those in other silts as illustrated in Fig. 2. In Fig. 3, depth data are presented for the time of deposition of sediment over the past ~20 years. The shape of the uranium-in-sediment profile appears to be unrelated to the rate of release by BNFL of uranium or of total alpha radioactivity; between 0 cm and 10 cm the profile is a reflection of seasonal processes which take place in the estuary and this pattern is characteristic also of many other elements. The gradual increase in total uranium content of the sediment in Core 3, since 1960,

TABLE 1

α Activity Ratios, ^{236}U Activity (Surface Barrier Alpha Spectrometry) and Total Concentration of Uranium together with Leachable Uranium for Samples of Sediments and Moss, from near Sellafield, Cumbria

Material, locality	α Activity ratios		^{236}U $(pCi/g \times 10^{-4})$	Total U $(ppm/dry\ wt)$	Percentage leached U (estimate)
	$^{234}U/^{238}U$	$^{235}U/^{238}U$			
Mud, Tamar Estuary, Devon	$1 \cdot 15 \pm 0 \cdot 01$	$0 \cdot 045 \pm 0 \cdot 002$	0^+	$4 \cdot 2$	$5 \cdot 8$
Sediment, Irish Sea					
Site 329	$1 \cdot 05 \pm 0 \cdot 02$	$0 \cdot 044 \pm 0 \cdot 003$	~ 0	$2 \cdot 0$	$1 \cdot 0$
Site 330	$1 \cdot 10 \pm 0 \cdot 02$	$0 \cdot 043 \pm 0 \cdot 004$	~ 0	$2 \cdot 9$	$0 \cdot 8$
Site 327	$1 \cdot 09 \pm 0 \cdot 03$	$0 \cdot 042 \pm 0 \cdot 004$	~ 0	$2 \cdot 1$	$1 \cdot 3$
Surface muds, Esk					
C113 Eskmeals sand	$1 \cdot 13 \pm 0 \cdot 03$	$0 \cdot 042 \pm 0 \cdot 004$	~ 0	$1 \cdot 2$	$4 \cdot 7$
138 Viaduct mud	$1 \cdot 08 \pm 0 \cdot 02$	$0 \cdot 044 \pm 0 \cdot 004$	0^+	$1 \cdot 8$	$7 \cdot 0$
121 Waberthwaite mud	$1 \cdot 15 \pm 0 \cdot 02$	$0 \cdot 042 \pm 0 \cdot 003$	~ 0	$1 \cdot 6$	$7 \cdot 7$
137 Esk Bridge mud	$1 \cdot 11 \pm 0 \cdot 02$	$0 \cdot 044 \pm 0 \cdot 004$	0	$2 \cdot 6$	$5 \cdot 5$
78 Drigg mud	$1 \cdot 12 \pm 0 \cdot 01$	$0 \cdot 044 \pm 0 \cdot 003$	$1 \cdot 4$	nd	nd
Sediment cores					
(a) Core 3, silt Esk					
Sampling depth (cm)					
5	$1 \cdot 06 \pm 0 \cdot 02$	$0 \cdot 037 \pm 0 \cdot 003$	$3 \cdot 1$	$3 \cdot 4$	$0 \cdot 7$
10	$1 \cdot 03 \pm 0 \cdot 02$	$0 \cdot 044 \pm 0 \cdot 004$	~ 0	$3 \cdot 4$	$0 \cdot 8$
15	$1 \cdot 07 \pm 0 \cdot 02$	$0 \cdot 040 \pm 0 \cdot 004$	~ 0	$3 \cdot 2$	$0 \cdot 9$
20	$1 \cdot 02 \pm 0 \cdot 02$	$0 \cdot 046 \pm 0 \cdot 003$	~ 0	$3 \cdot 1$	$1 \cdot 4$
25	$1 \cdot 07 \pm 0 \cdot 02$	$0 \cdot 037 \pm 0 \cdot 003$	$0 \cdot 9$	$3 \cdot 0$	$1 \cdot 0$
30	$1 \cdot 07 \pm 0 \cdot 02$	$0 \cdot 043 \pm 0 \cdot 004$	0^+	$2 \cdot 9$	$0 \cdot 8$
35	$1 \cdot 07 \pm 0 \cdot 02$	$0 \cdot 045 \pm 0 \cdot 005$	0^+	$2 \cdot 9$	$1 \cdot 0$
40	$1 \cdot 01 \pm 0 \cdot 02$	$0 \cdot 046 \pm 0 \cdot 004$	0^+	$2 \cdot 8$	$0 \cdot 3$
45	$1 \cdot 01 \pm 0 \cdot 03$	$0 \cdot 044 \pm 0 \cdot 003$		$2 \cdot 7$	$0 \cdot 3$
50	$1 \cdot 03 \pm 0 \cdot 02$	$0 \cdot 042 \pm 0 \cdot 004$	$0 \cdot 5$	$2 \cdot 6$	$0 \cdot 2$
55	$1 \cdot 11 \pm 0 \cdot 02$	$0 \cdot 047 \pm 0 \cdot 003$	0^+	$2 \cdot 5$	$0 \cdot 7$
60	$1 \cdot 09 \pm 0 \cdot 02$	$0 \cdot 045 \pm 0 \cdot 003$	0^+	$2 \cdot 5$	$0 \cdot 7$
65	$1 \cdot 00 \pm 0 \cdot 02$	$0 \cdot 037 \pm 0 \cdot 003$	$0 \cdot 9$	$2 \cdot 4$	$0 \cdot 8$
70	$1 \cdot 08 \pm 0 \cdot 02$	$0 \cdot 043 \pm 0 \cdot 003$	$0 \cdot 004$	$2 \cdot 2$	$0 \cdot 9$
75	$1 \cdot 00 \pm 0 \cdot 04$	$0 \cdot 046 \pm 0 \cdot 005$	0^+	$2 \cdot 2$	$0 \cdot 4$
(b) Core 1176, silt Esk					
$\Sigma 2 + 3 + 5$ cm sections	$1 \cdot 17 \pm 0 \cdot 02$	$0 \cdot 043 \pm 0 \cdot 003$	~ 0	$3 \cdot 6$	$15 \cdot 8$
$\Sigma 27 + 29 + 32 + 33$ cm sections	$1 \cdot 15 \pm 0 \cdot 03$	$0 \cdot 047 \pm 0 \cdot 003$	0^+	$2 \cdot 1$	$5 \cdot 7$
(c) Core 1280, silt Esk					
$\Sigma 9 + 10$ cm sections	$1 \cdot 14 \pm 0 \cdot 03$	$0 \cdot 044 \pm 0 \cdot 004$	~ 0	$2 \cdot 0$	$2 \cdot 8$
$\Sigma 33 + 34 + 35$ cm sections	$1 \cdot 15 \pm 0 \cdot 02$	$0 \cdot 046 \pm 0 \cdot 003$	0^+	$2 \cdot 1$	$4 \cdot 4$
Vegetation					
C96 moss, Friar Well near Sellafield	$\begin{cases} 1 \cdot 15 \pm 0 \cdot 03 \\ 1 \cdot 16 \pm 0 \cdot 02 \\ 1 \cdot 24 \pm 0 \cdot 03 \end{cases}$	$\begin{cases} 0 \cdot 035 \pm 0 \cdot 004 \\ 0 \cdot 031 \pm 0 \cdot 004 \\ 0 \cdot 032 \pm 0 \cdot 003 \end{cases}$	$9 \cdot 1$	$0 \cdot 06$	—
C92 moss, St Bridgets Church near Sellafield	$\begin{cases} 1 \cdot 15 \pm 0 \cdot 02 \\ 1 \cdot 14 \pm 0 \cdot 02 \end{cases}$	$\begin{cases} 0 \cdot 037 \pm 0 \cdot 003 \\ 0 \cdot 039 \pm 0 \cdot 003 \end{cases}$	$41 \cdot 0$	$0 \cdot 8$	—
127 Salicornia, Newbiggin Viaduct	$1 \cdot 17 \pm 0 \cdot 03$	—	0^+	$0 \cdot 05$	—
111 lichen, Newbiggin Viaduct	—	—	—	$0 \cdot 01$	—

0^+, not detected
~ 0, trace. present but not measurable
nd. not determined

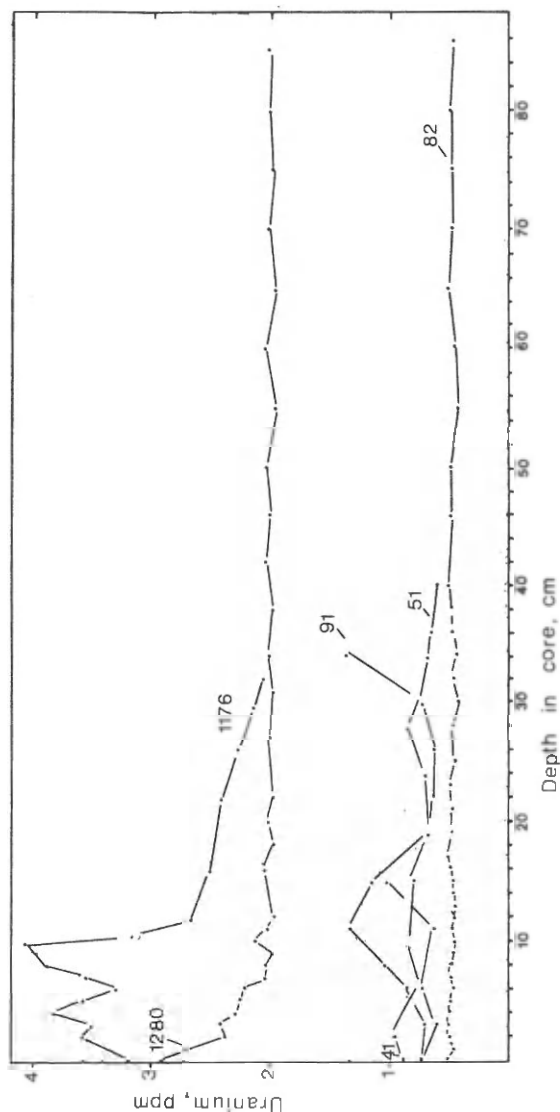*E. I. Hamilton, H. E. Stevens*

Fig. 2. The distribution of uranium in sediments of the Esk, Cumbria.

Core 1176 (September 1978). Mud-silt core from the southern bank of the estuary. The top ~10 cm have been disturbed to give an apparent sedimentation rate of 6·2 cm y^{-1} (see Clifton and Hamilton (1982)), compared with 0·4 cm y^{-1} for the interval 12–32 cm.

Core 1280 (September 1978). On the basis of $^{134}Cs/^{137}Cs$ ratios (see Clifton and Hamilton (1982)) the profile consists of post-1974 sediments, deposited at a rate of ~1 cm y^{-1}, resting on older material which does not contain any BNFL debris and which gives, on the basis of ^{210}Po dating, a deposition rate of 0·4 cm y^{-1}.

Cores 41, 91 and 51 (June 1977). Medium to coarse grained aerobic silts representative of the edge of the developing salt marsh.

Core 82 (August 1979). Silt devoid of any vegetation from an area known to be frequently disturbed to a depth of 6 cm by pedestrian traffic. In the field, the area does not show any unusual features but because of regular reworking of sediment most of the uranium has been lost; the nearly constant concentration which remains reflects the presence of naturally occurring uranium-rich accessory minerals. (NB Anaerobic sediment containing ~8000 ppm acid-released sulphide; aerobic sediment < 10 ppm S^{-2}.)
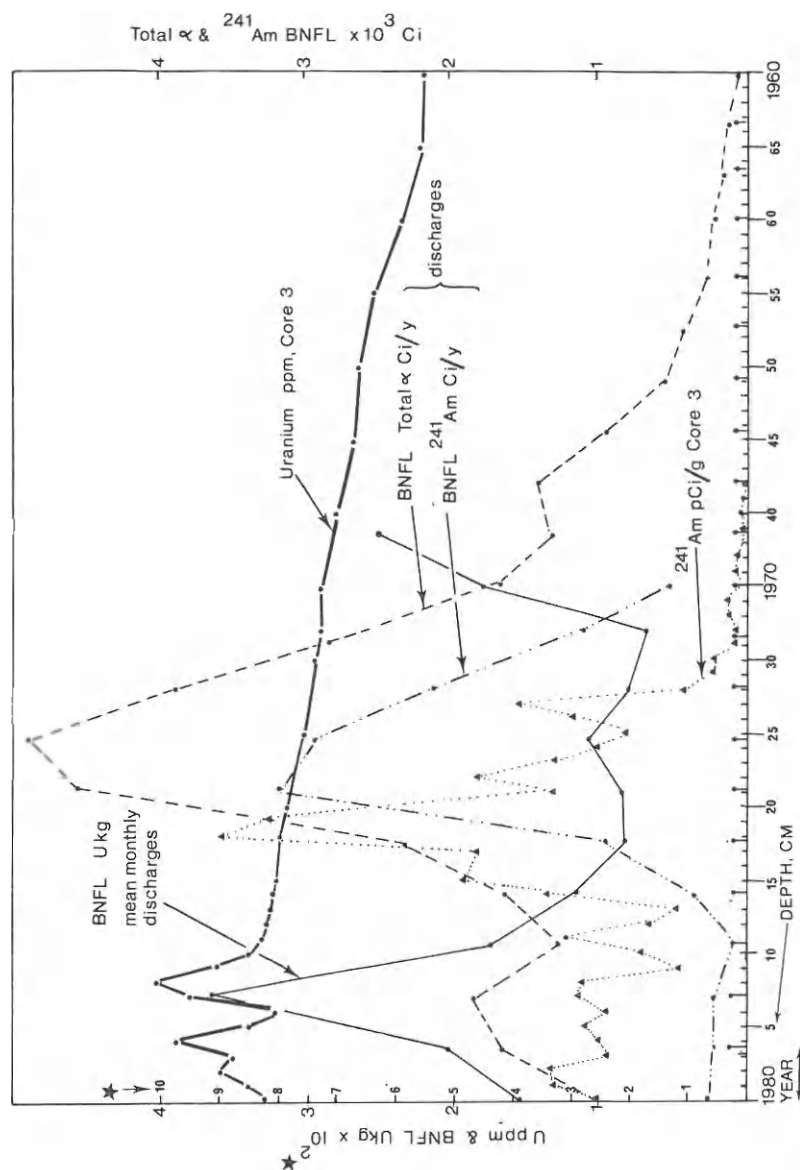
Fig. 3. Relationships between U (ppm dry wt), ^{241}Am (pCi/g dry wt) and total discharges of ^{241}Am (Ci y^{-1}), total alphas (Ci y^{-1}) and mean monthly discharges of U(kg) by BNFL for the period 1960–1980 (Atherton, 1979, 1980, 1981; Hetherington, 1976, 1978; Howells, 1977; Hunt, 1979, 1980, 1981, 1982, 1983; Mitchell, 1967, 1968, 1969, 1971, 1972, 1973, 1975, 1977a, 1977b; Pentreath & Lovett, 1978). The *x*-axis is presented in terms of depth in sediment profile (cm) and time of sediment deposition in the past, based upon radiodating of the core by ^{210}Po, ^{137}Cs, ^{134}Cs and ^{106}Ru methods (Hamilton & Clarke, 1984).

does not appear to be related to the BNFL releases of uranium. In Fig. 2, the increase of uranium at ~34 cm, in a core (91) of constant lithology, may be related to the 1969–70 enhanced levels of uranium released by BNFL. Evidence that the historical pattern of BNFL releases of radio-nuclides is preserved in accreting sediment profiles is also illustrated in Fig. 3; the [241]Am releases by BNFL and concentrations of this radio-nuclide in the sediment profile are matched, but are not coincident, possibly because in the model (Hamilton & Clarke, 1984) a lag time, for transit of BNFL debris from Sellafield to the Esk, of ~1 year has been used. This value does not take account of the relative rates of transport of [241]Am in its conservative and non-conservative forms; better estimates can only be made when more information is forthcoming concerning the composition of the BNFL source term for uranium.

Estimates for the mass of uranium leached by the ammonium carbonate treatment of samples are given in Table 1, and for most samples amount to <5% of the total uranium content. Samples were analysed in a random manner but it soon became apparent for some samples that the $^{235}U/^{238}U$ activity ratio of the electroplated uranium indicated a depletion in ^{235}U and these samples also contained an alpha particle emitter with an alpha energy of 4·49 MeV which, together with a consideration of chemical and electroplating characteristics, was identified as ^{236}U; these features were subsequently confirmed by solid state source mass-spectrometry on the separated uranium. In several of the samples, as illustrated in Fig. 4, ^{236}U could only just be measured because of the small amounts present.

The $^{234}U/^{238}U$ activity ratio of seawater is constant, i.e. Pacific Ocean, 1·14 ± 0·04 (Sugimura & Mayeda, 1980) and Atlantic and Pacific Oceans and the Mediterranean Sea, 1·14 ± 0·014 (Koide & Goldberg, 1965). The $^{234}U/^{238}U$ activity ratios of uranium leached from samples are shown in Table 1; as the ratio is >1·0, according to Hodge *et al.* (1979), a significant absorption of dissolved uranium from seawater is indicated. Measure-ment of ^{235}U in the presence of ^{236}U is difficult, but is possible, as illustrated in Fig. 5, by selecting those samples with identifiable ^{236}U alpha energy peaks, which are related to the degree of apparent depletion in ^{235}U. However, the $^{234}U/^{238}U$ activity ratio will be dominated by natural uranium leached from samples; hence once more the influence of BNFL debris is considerably diluted, even although the total amount of uranium leached from the samples is small compared with the total concentration of uranium.
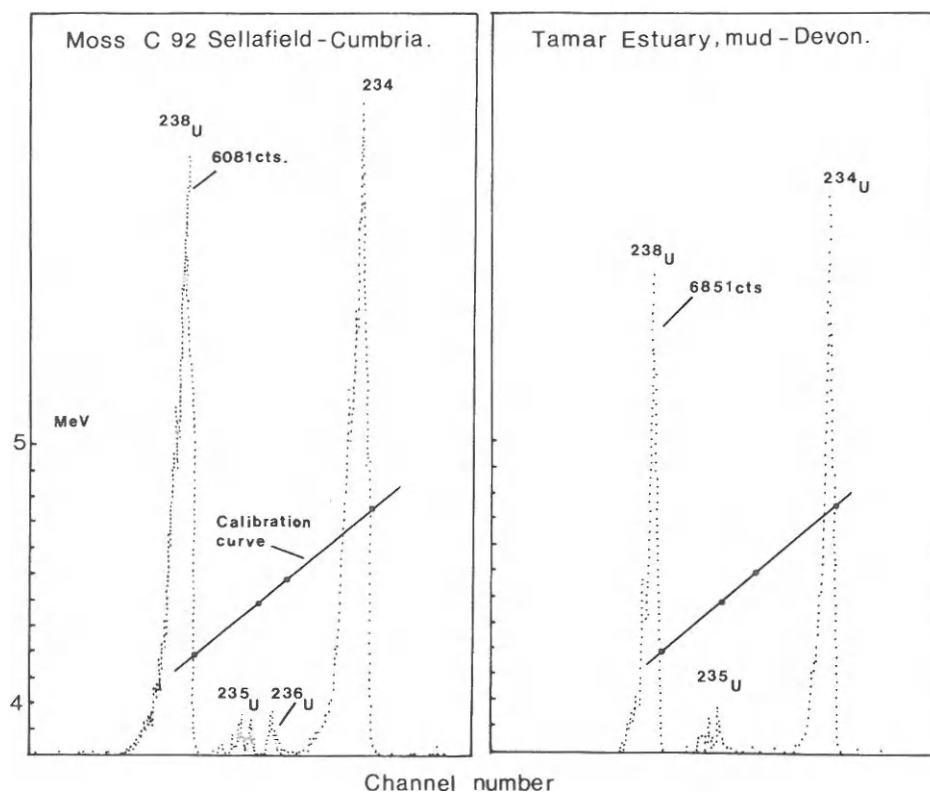
Fig. 4. Uranium spectra for moss C92, which contains ^{236}U, compared with uranium from an estuarine sediment site distant from any influence of BNFL effluent.

After ~6 years of irradiation in a Magnox reactor the ^{234}U/^{238}U alpha particle activity ratio would be ~0·8. However, it is likely that the irradiation times for average processed uranium fuel released by BNFL during the 5–10 years prior to sample collection would have been appreciably shorter. It is most unlikely that sources of highly depleted uranium derived from activities other than the reprocessing of Magnox fuel would contribute to the total uranium in the effluent from the BNFL site.

The isotopic composition of uranium determined by mass-spectrometry on leachates from samples is presented in Table 2; the data confirm the presence both of some depletion in ^{235}U and of ^{236}U in sample C92. The ratios ^{235}U/^{238}U (α-activity)/^{235}U/^{238}U (mass-spectrometry data converted to units of α-activity) for C92, Drigg mud and Core 3 (0–15 cm) are 0·94, 1·04 and 1·1 respectively; for Core 3 the U-activity ratio was first deter-
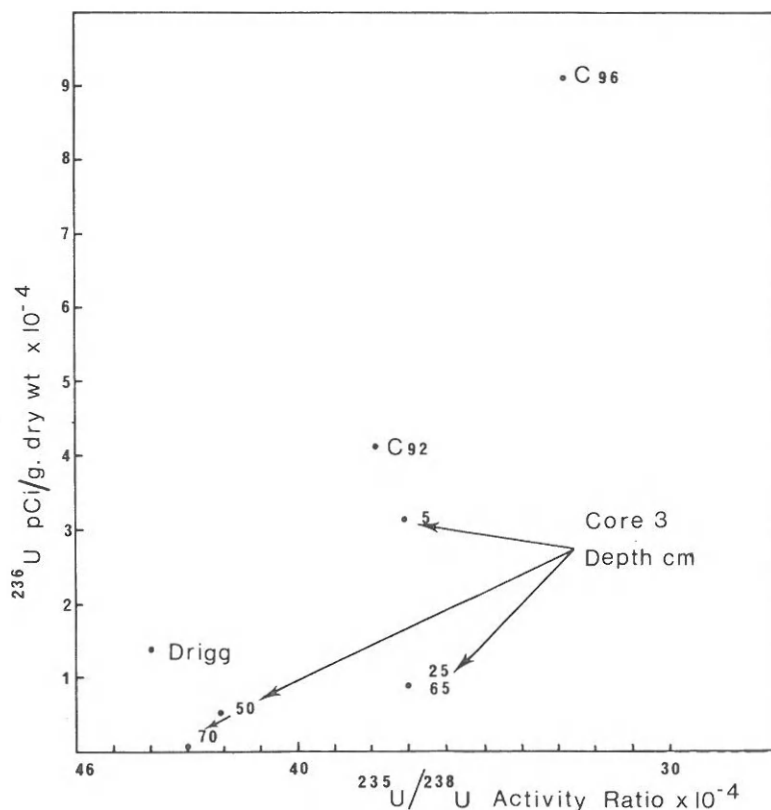
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Fig. 5. Relationships between the concentration of ^{236}U (pCi/g U) and the ^{235}U/^{238}U activity ratio for some samples of sediment and moss (C96, C92) from the vicinity of Sellafield, Cumbria.

mined, then the uranium was removed from the counting planchet and used for the mass isotopic analysis. A ^{236}U/^{238}U activity ratio of 0·83 was calculated for the moss sample, C92, based upon the mean mass isotopic data and those obtained by alpha spectrometry; this is considered to be acceptable because of the low abundance of ^{236}U in the sample.

DISCUSSION

For a conservative species of radionuclide, in seawater, such as uranium, Hamilton and Clarke (1984) estimate a transit time of <1 year from

TABLE 2

Isotopic Composition of Uranium in Samples of Moss and Estuarine Sediment Determined by Solid Source Mass Spectrometry

Material	$^{235}U/^{238}U$	$^{234}U/^{238}U$	$^{236}U/^{238}U$
Natural uranium[a]	0·007 26	0·000 055 4	0·0
C92 moss, St Bridgets	0·006 46 ± 0·000 03	0·000 057 3 ± 0·000 000 5	0·000 046 9 ± 0·000 000 6
Church near Sellafield[b]	0·006 44 ± 0·000 02	0·000 056 8 ± 0·000 000 5	0·000 146 5 ± 0·000 001 0
Drigg mud, Esk[c]	0·007 12 ± 0·000 04	0·000 059 ± 0·000 004	—
Core 3 E, 1–15 cm depth[c]	0·006 94 ± 0·000 05	0·000 063 ± 0·000 004	—

[a] Hyde, E. K. *et al.* (1964)
[b] Anonymous source (3-stage instrument)
[c] Kindly provided by J. W. Arden (single stage instrument)

Sellafield to the Esk. If the *total mass* of uranium which has been released into the Irish Sea from the reprocessing of uranium fuel rods has been retained in an off-shore parcel of water (see Box 1, 26·5 km^3, in Jefferies *et al.*, 1982), this would only increase the normal levels by *c*. 30%. However, assuming normal conservative transport of uranium based upon the dispersion of ^{137}Cs in the Irish Sea (as described by Jefferies *et al.*, 1982), the contribution from BNFL would not be detected.

A study of surface sediment from the Esk shows an association between uranium and the presence of anaerobic conditions which are associated with decaying organic matter; with an increase in depth in sediments the anaerobic zone is lost (see Fig. 2, Core 1176 at ~12 cm and Core 1280 at ~10 cm in depth) with an associated significant reduction in the concentration of uranium. We interpret this feature as illustrating an active association between uranium and the organic-rich anaerobic facies; once this phase is lost by depletion of organic matter, the structure of the sediment is lost and the anaerobic thixotropic state gives way to coarse aerobic sands which contain the lowest concentrations of uranium, e.g. Cores 41, 51, 82 and 91. The anaerobic fine-grained silts contain between 1 and 3% organic carbon (Hamilton, 1984) but, in relation to the thixotropic nature of these sediments, this is enough to impart a dark brown to black colour to the fresh material and also to provide an inter-grain matrix which is sufficient to account for the coherence of the sediment as a whole. As Core 3 (Fig. 3) is accreting at a rate of ~3·5 cm y^{-1} (Hamilton & Clarke, 1984), the lower parts will have been deposited before BNFL operations had started; the uranium present is mainly contained in common accessory minerals such as sphene, zircon and fluorite.

The samples of flocculated dialysate liquid from the aerobic sediment contained between 1·8 and 2·0 ppm U (in dialysate residues), compared with <0·2 ppm U for anaerobic silts and indicating a greater mobility of uranium in aerobic facies.

The samples of moss, C92 and C96, were collected from the top of a 2 m high wall in an open situation; hence they are not likely to receive any significant contribution from soil-splash. There is no information available to indicate whether or not any uranium is currently lost through the BNFL high stacks but the consensus of opinion (Atherton, 1983) is that this does not occur, although very small losses by this route may be accumulated by mosses. Within the region, the source of depleted uranium is from BNFL; the extent of depletion will depend upon the

burn-up time of the fuel which is unknown in relation to the BNFL discharges, but the maximum time is likely to be ~2000 days. Using data obtained from the RICE CODE (see Mairs & Nair, 1979) together with data in Flowers (1976), we calculate that, after 2000 days of burn-up, Magnox fuel will contain ~580 ppm ^{236}U/gU. If sample C92 contained ~1 ppm U, then a concentration of 40×10^{-4} pCi ^{236}U/g sample is equivalent to a burn-up time of 218 days and a 10·8% depletion of ^{235}U; this may be compared with a value of 11·0% depletion which was obtained by mass-spectrometry. However, it should be noted that the BNFL uranium effluent can contain uranium from many diverse sources which have been exposed to a variety of burn-up times.

The highest ^{234}U/^{238}U activity ratios are found in the samples of moss (C92 and C96) which were collected near the coast in a region which is subjected to direct aerial deposition of marine particulate debris as a result of the penetration of sea spray inland, as described by Eakins & Lally (1984).

In Japan, Sugiyama & Takagi (1977) were unable to detect any unusual levels of uranium in bulk samples of river water and marine sediments in the vicinity of a nuclear fuel factory. Joshi & Mishra (1981) report a mean ^{235}U/^{238}U activity ratio of $0·046 \pm 0·001$ for coastal sediments from the East coast of India, which is the same as that for natural uranium. For our samples which contain some ^{236}U ($n = 12$), we calculate a ^{235}U/^{238}U activity ratio of $0·043 \pm 0·001$, and, for those which did not, $0·045 \pm 0·001$. Gorham (1958) and Cambray & Eakins (1982) have described the transport of marine aerosols and some radionuclides from the littoral region of the NE Irish Sea across Cumbria. In sediments of the Esk, hot particles containing alpha emitters (U, Pu, Am, Cm) are found on the sea-surface and in the upper layers of sediment (Hamilton, 1981); away from the coast, hot particles are also found at some sites, but the distribution appears to be of a random nature. There are several possible sources for the hot particles; for example, marine aerosol debris, especially from the sea-surface in the vicinity of the BNFL outfall, general wind-blown debris from the BNFL site, especially from the surface microlayer of the open cooling ponds in which spent uranium fuel rods are stored prior to reprocessing, and an unknown, but probably insignificant, contribution from stack releases. During the Windscale accident in October 1957, which involved overheating of uranium fuel elements in a reactor, Dunster *et al.* (1958) and Ellis *et al.* (1960) noted the release of small quantities of uranium in particulate form which penetrated the filters in

the reactor stacks. Since then the filtration efficiency for retention of particulate debris from stacks has been improved considerably. By selection of dated undisturbed soil profiles in the vicinity of BNFL, the presence of particulate forms of uranium released during the accident should be easily measured and, from an examination of the post-1957 soil horizons, any subsequent deposition could be determined.

The ^{234}U/^{238}U activity ratios of the samples we have examined indicate a mixture of marine and terrestrial sources and in some areas a slight contribution from BNFL debris which is of no significance in relation to risks to man from ionising radiation. The ^{234}U/^{238}U activity ratios we observe are similar to those reported by Borole *et al*. (1982) ($1 \cdot 05 \pm 0 \cdot 03$) for marine sediments from two estuaries in India and those by Church *et al*. (1981) ($1 \cdot 03$ to $1 \cdot 14$) for a salt marsh in USA. Matsunami & Mamuro (1968) determined a ^{234}U/^{238}U activity ratio of ~1 for uranium particles in nuclear fallout debris. Hodge *et al*. (1979) have shown that continental debris tends to have a ^{234}U/^{238}U activity ratio of <1 compared with the characteristic seawater value of $1 \cdot 14$. The hinterland of the Esk region is associated with slight uranium mineralisation which could give rise to an enhanced loss of ^{234}U. However, the Esk sediments also receive a significant input of groundwater; Asikainen (1981) records ^{234}U/^{238}U activity ratios of between $0 \cdot 76$ and $4 \cdot 75$ with the most frequent values showing a 60% excess of ^{234}U. Finkel (1981) records ^{234}U/^{238}U ratios of between $0 \cdot 88$ and $5 \cdot 4$ in groundwater and Cowart & Osmond (1974) values of between $0 \cdot 5$ and 12 for natural waters. Further work is in progress to evaluate the significance of the ^{234}U/^{238}U activity ratios and the abundance of ^{236}U in the NE Irish Sea and coastal ecosystems in relation to the transport and deposition of uranium.

ACKNOWLEDGEMENTS

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