The Presence of ^{237}Np in the Irish Sea

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ABSTRACT: Concentrations of ^{237}Np, a long-lived radionuclide discharged under authorization from the British Nuclear Fuels Ltd. reprocessing plant at Windscale, UK, have been measured in samples of sea water, sediment and biological materials collected from the Irish Sea. The data suggest that this nuclide is concentrated by sedimentary materials in suspension to give a K_d in the region of 10^3 to 10^4, lower than those of the other transuranium nuclides previously recorded in the area. It is also accumulated by marine biological materials, occurring in internal organs such as the gonad of echinoderms, but the concentrations are relatively low compared to those of ^{239,240}Pu and the ^{239,240}Pu/^{237}Np quotients are higher than those of recent discharges from Windscale. From the radiological aspect, initial calculations suggest that the presence of ^{237}Np in fish and shellfish of the Irish Sea is of little significance, but further data are required to estimate its long-term impact.

INTRODUCTION

Transuranium nuclides are present generally in marine surface waters as a result of the atmospheric testing of nuclear weapons, but concentrations over and above fall-out levels do occur in a few coastal marine environments as a result of waste-management practices associated with the nuclear industries. Such an environment is that of the Irish Sea which receives low-level liquid effluent discharged, under authorization, from the British Nuclear Fuels Ltd. reprocessing plant at Windscale, Cumbria, UK. As a result of these discharges enhanced levels of plutonium, americium and curium nuclides have been detected in a wide range of materials. The occurrence of these nuclides in this area is closely monitored and the results reported annually, most recently for 1978 (Anonymous, 1979; Hunt, 1980) and 1979 (Anonymous, 1980a). In addition to these reports more detailed studies have been made on various transuranium nuclides in biological materials: for example Pentreath and Lovett (1976, 1978), Pentreath et al. (1980), Hamilton and Clifton (1980). None of these reports contain measurements of neptunium nuclides. Indeed the only references to the occurrence of neptunium in the marine environment appear to be those of Freiling and Ballou (1962), and Ballou (1963), who reported the short-lived ^{239}Np isotope ($t_{1/2}$ 2.35 d) in sea water as the result of underwater tests in the Pacific; that of Lowman (1960) who

detected ^{239}Np in plankton from the Enewetak test site in 1956 and 1958; and that of Noshkin et al. (1974) who detected the long-lived ^{237}Np isotope ($t_{1/2}$ 2.14 × 10^6 y) in lagoon water from Enewetak atoll.

The short-lived ^{239}Np isotope was also produced by neutron bombardment of one of the natural uranium isotopes (^{238}U) in Columbia River water used in the one-pass coolant of the Hanford reactors in the USA. In a review article, Foster (1963) reported that ^{239}Np had been recorded in freshwater biological samples, and in river water as far as the Pacific coast, but no data were reported for marine organisms or marine sediments.

Of greater interest is the long-lived ^{237}Np isotope. This isotope occurs in irradiated nuclear fuel (predominantly as a result of ^{238}U (n, 2n) $\rightarrow$ ^{237}U (β^-) $\rightarrow$ ^{237}Np reactions), and it has now been detected in biological and non-biological samples from the Irish Sea.

MATERIALS AND METHODS

Samples of sea water (25 to 100 l) were collected from a number of locations within the Irish Sea (Fig. 1) in April 1980, and from off the Scottish coast. These were filtered (0.22 μm) on board ship and both filtrate and particulate fractions retained for analysis. Various biological samples were collected from the Cumbrian coast in May and August 1978, some of which were bulked in order to provide sufficient material for analy-

sis. Some sea bed sediment (mud) samples were also taken.

Sample Treatment

The yield tracer used was ^{239}Np, prepared from ^{243}Am by the method of Sill (1966) as required, and added to the samples in the pentavalent state. Filtered sea water was spiked with ^{239}Np, treated with sodium sulphite, and left to stand for about 16 h in the presence of 0.1 M hydrochloric acid to reduce Np to the tetravalent state. The Np was then co-precipitated with iron (1 mg l^{-1}), along with other transuranium nuclides, by adjusting the pH to about 9 by the addition of ammonia solution. The Fe(OH)$_3$ was filtered off by pumping the sample through a 0.22 µm filter paper. Filter papers were subsequently digested in concentrated nitric acid and then adjusted to 3 to 4 M before subsequent analysis. Particulate samples were treated in a similar manner, having been spiked with ^{239}Np.

Sediment samples were ashed (500 °C) and exhaustively leached with nitric acid, followed by filtration and the addition of ^{239}Np. Again the nitric acid concentration was adjusted to 3 to 4 M before subsequent analysis.

Biological samples were ashed at 500 °C, dissolved in nitric acid with the addition of ^{239}Np, and after completing the wet-ashing procedure adjusted to 3 to 4 M nitric.

Radioanalysis

The analytical method was based on procedures discussed by Moore (1957) and in Mikhailov (1973). It was designed to provide the necessary high degree of decontamination from the major interfering alpha-emitting contaminants known to be present in the samples (^{234}U, ^{231}Pa and ^{230}Th) as well as from $^{239/240}$Pu whose alpha-spectrum can cause interference if the electrodeposited source is of relatively poor quality. To each sample (typically 100 to 200 ml) 100 mg of Nd carrier and 10 ml of 1 M hydrazine nitrate were added, and the sample then heated to 60° for 10 min to reduce Np to the tetravalent state. When cool, ammonium fluoride was added as a 12 % solution to precipitate the Nd as NdF$_3$. This precipitate was centrifuged off, dissolved in concentrated nitric acid, and then boiled with boric acid to remove as much fluoride as possible. Neodymium hydroxide was then precipitated by the addition of ammonia solution, separated by centrifugation, and dissolved in hydrochloric acid. After adjusting to 1 M, and adding ferrous sulphamate to reduce the Np to the tetravalent state, the Np was extracted
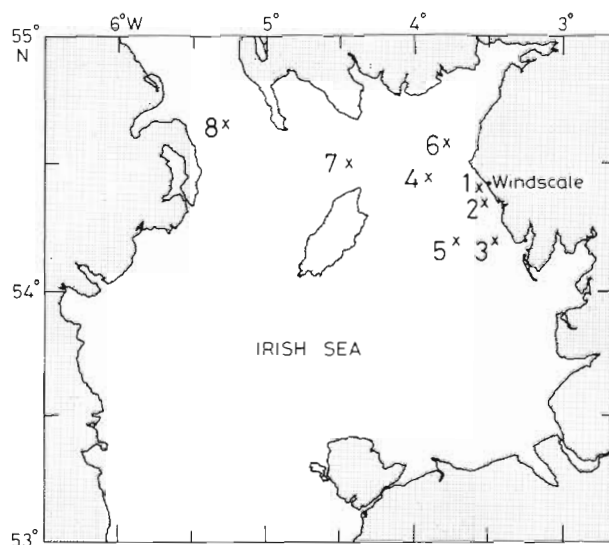

Fig. 1. Location of sea water sampling stations listed in Table 1

into a mixture of 0.5 M 2-thenoyltrifluoroacetone in xylene in the presence of aluminium nitrate to complex any remaining fluoride. The Np was then back extracted into 8 M nitric acid and further purified by passing the extract through a column of Biorad AG 1 × 4 ion exchange resin in the nitrate form. After washing the column with 8 M nitric acid, 12 M hydrochloric acid was passed through the column before the elution of Pu with 12 M hydrochloric acid/0.1 M ammonium iodide. Finally, Np was eluted with 5 column volumes of 4 M hydrochloric acid. Samples were electrodeposited from a solution containing potassium sulphate and ammonium oxalate, made slightly acid with hydrochloric acid, onto 2.4 cm diameter stainless steel discs. The chemical yield, based on the gamma spectrometric analysis of the ^{239}Np tracer present on the electrodeposited source, was typically between 50 and 80 %: the lower yields occurred in samples which had a relatively high phosphate content. Standards of ^{239}Np, prepared on similar discs, were counted for each batch of ^{239}Np obtained from the ^{243}Am parent solution. The ^{237}Np content of each sample was determined by alpha spectrometry using very low background silicon surface barrier detectors which had been calibrated using sources prepared from known amounts of a standardized ^{237}Np solution supplied by Amersham International Ltd.

Despite the elaborate purification process used, samples were occasionally found to be contaminated by small amounts of uranium. This contaminant occurred in some bottles of even the highest quality hydrochloric acid. The alpha particle energies of ^{234}U (4.72 and 4.77 MeV) cannot be resolved from those of ^{237}Np (4.77 and 4.79 MeV), but their presence can be inferred, assuming a normal ^{234}U/^{238}U ratio, by including the

Table 1 ^{237}Np in samples of sea water taken from the Irish Sea in April 1980. Errors are based on $\pm$ 1σ propagated counting errors

Station	Location	^{237}Np on particulate matter (Bq kg^{-1}dry)*	^{237}Np in filtrate water (mBq kg^{-1})	K_d $\dfrac{\text{Bq kg}^{-1} \text{ particulate}}{\text{Bq kg}^{-1} \text{ filtrate}}$
1	54°25'N 3°33'W	19.9 $\pm$ 0.3	1.44 $\pm$ 0.04	1.4 $\pm$ 0.04 $\times$ 10^4
2	54°22'N 3°32'W	38.9 $\pm$ 2.2	1.18 $\pm$ 0.04	3.3 $\pm$ 0.2 $\times$ 10^4
3	54°12'N 3°27'W	3.1 $\pm$ 0.3	0.76 $\pm$ 0.01	4.1 $\pm$ 0.4 $\times$ 10^3
4	54°27'N 3°54'W	1.6 $\pm$ 0.2	0.13 $\pm$ 0.01	1.2 $\pm$ 0.2 $\times$ 10^4
5	54°12'N 3°42'W	4.4 $\pm$ 0.7	1.04 $\pm$ 0.04	4.2 $\pm$ 0.7 $\times$ 10^3
6	54°35'N 3°46'W	2.8 $\pm$ 0.3	0.46 $\pm$ 0.01	6.1 $\pm$ 0.7 $\times$ 10^3
7	54°30'N 4°25'W	3.4 $\pm$ 0.4	0.37 $\pm$ 0.04	9.2 $\pm$ 1.5 $\times$ 10^3
8	54°40'N 5°16'W	0.19 $\pm$ 0.07	0.08 $\pm$ 0.02	2.4 $\pm$ 1.1 $\times$ 10^3

* 1 Bq = 27 pCi

^{238}U peak, at 4.19 MeV, in the alpha spectrum. It has therefore become a standard procedure to check for the absence of uranium in the hydrochloric acid used, and to ensure that the alpha spectrum covers the ^{238}U peak in order to confirm that uranium was absent from the final electrodeposited source.

All of the analytical results quoted in the text are given together with $\pm$ 1 σ propagated counting errors.

RESULTS

The concentrations of ^{237}Np in sea water samples taken at the locations shown in Fig. 1, at a depth of 3 m, are given in Table 1 for both filtrate and particulate fractions. It is to be expected that such sea water concentrations would vary both in space and time because of the variable nature of the discharge and the changeable dispersion characteristics obtaining in the Irish Sea. The total quantity of ^{237}Np discharged during 1978 was 592 GBq (Anonymous, 1979), and 333 GBq were discharged in 1979 (Anonymous, 1980a); but these quantities were not discharged at a constant rate. It can be seen that the concentration in filtrate sea water, in April 1980, was more than one order of magnitude lower at the North Channel (Station 8) than those measured close to the Cumbrian coast. In addition to the data shown in Table 1, a filtrate water sample taken close to the Cumbrian shore in February 1980 contained 3.8 $\pm$ 0.9 mBq l^{-1} of ^{237}Np, whereas a sample taken in November 1979 only contained 0.48 $\pm$ 0.1 mBq l^{-1}. Further afield, in April 1980, a filtrate sample taken from the eastern Scottish coast (58°00'N, 2°11'W), at a depth of 3 m, contained 0.01 $\pm$ 0.002 mBq l^{-1} of ^{237}Np.

By dividing the particulate fraction ^{237}Np concentrations by their respective filtrate concentrations, estimates of the distribution coefficient (K_d) can be obtained. These estimates are also given in Table 1. It must be noted that these values relate only to the very

Table 2. ^{237}Np in biological samples taken near Windscale. *Asterias rubens* were collected in August 1978, all of the other samples in May 1978. Errors are based on $\pm$ 1σ propagated counting errors

Sample description	^{237}Np (mBq kg^{-1} wet)*	$\dfrac{^{239,240}\text{Pu}}{^{237}\text{Np}}$
ALGAE		
Fucus serratus	26 $\pm$ 2	2127 $\pm$ 173
MOLLUSCA		
Patella vulgata		
Total soft parts	278 $\pm$ 11	406 $\pm$ 19
Neptunea antiqua		
Total soft parts	14 $\pm$ 2	712 $\pm$ 103
ARTHROPODA		
Eupagurus bernhardus		
Head and thorax	133 $\pm$ 12	328 $\pm$ 31
Abdomen minus muscle	163 $\pm$ 15	187 $\pm$ 18
ECHINODERMATA		
Asterias rubens		
Aboral body wall	96 $\pm$ 5	365 $\pm$ 20
Digestive gland	67 $\pm$ 6	397 $\pm$ 36
Gonad	9 $\pm$ 2	378 $\pm$ 85
Echinus esculentus		
Aboral test	52 $\pm$ 11	354 $\pm$ 75
Gonad	3 $\pm$ 0.5	1500 $\pm$ 261

* 1 mBq = 0.027 pCi

fine materials held in suspension in the surface waters. Six sea bed sediment samples have also been analysed. These were grab samples obtained in an area of muddy sand approximately 2.5 km away from the discharge pipe in November 1979 and February 1980. The samples had a dry particle size distribution of about 60 % > 63 μm, 10 % in the range 15 to 63 μm and 30 % < 15 μm. Loss on ignition at 450 °C was approximately 1 %, indicating that little organic material was present. The concentrations of ^{237}Np ranged from 1.7 $\pm$ 0.1 Bq kg^{-1} dry to 2.4 $\pm$ 0.1 Bq kg^{-1} dry, with a mean and standard deviation of 2.1 $\pm$ 0.3 Bq kg^{-1} dry.

The results obtained from analyses of a range of

biological samples taken along the Cumbrian coast in 1978, north of the Windscale pipeline around St. Bees Head, are given in Table 2. *Fucus serratus* and *Patella vulgata* are intertidal species, the remainder being sub-littoral. The highest concentration of ^{237}Np was that of the soft parts of the limpet *Patella vulgata*. This concentration was considerably greater than that of the soft parts of the much larger, neogastropod *Neptunea antiqua*. The lowest concentrations were those observed in the gonads of echinoderms (*Asterias rubens* and *Echinus esculentus*), samples which were the least likely to be contaminated by extraneous materials, and which were the most likely to represent ^{237}Np which had been biologically assimilated by the animals. The sample of alga, *Fucus serratus*, consisted only of newly-grown fronds which had been thoroughly rinsed before analysis.

These biological samples were also analysed for $^{239/240}$Pu by alpha spectrometry, using methods discussed elsewhere (Pentreath and Lovett, 1978); the $^{239/240}$Pu/^{237}Np quotients are also given in Table 2. The quotient of the Windscale discharges from January to April 1978 was about 80, and from May to July 1978 it was about 40. It is evident that the quotients in Table 2 are considerably greater than those in the discharges during the months immediately preceding sample collection.

In addition to the samples listed in Table 2, samples of edible biological materials were also analysed. Two large samples were available from previous sampling programmes: one of commercial plaice *(Pleuronectes platessa)* fillets landed at a local fishing port, Whitehaven, in 1976, and one of scallops *(Chlamys opercularis)* landed in the same year. The plaice fillets contained only 0.4 ± 0.02 mBq kg^{-1} wet ^{237}Np, and the scallops 2.6 ± 0.6 mBq kg^{-1} wet.

DISCUSSION

In a well oxidised aqueous environment neptunium would be expected to occur, in a free state, as the soluble pentavalent species NpO_2^+; although the presence of the tetravalent oxidation state cannot be excluded. As such, the affinity of neptunium for inorganic particles in suspension would be expected to be less than the affinity exhibited by other transuranium nuclides present in oxidation states other than (V) (Bondietti and Tamura, 1980). The K_d for ^{241}Am in the Irish Sea has been estimated as being in the region of 2.3×10^6, that for $^{243/244}$Cm about 1.5×10^6, and that for $^{239/240}$Pu about 3.0×10^5 (Pentreath et al., 1980). The plutonium estimates are complicated by the existence of more than one oxidation state being present in the Irish Sea (Nelson and Lovett, 1978), the lower

oxidation pair (III + IV) having a higher K_d than the upper pair (V + VI). It also appears that the average K_d outside the Irish Sea is significantly higher than the average inside (Pentreath et al., 1980), suggesting that a change in oxidation state, and hence K_d, may occur as a function of time or as a result of transfer to a slightly different environment.

With regard to the data in Table 1, the derived K_d values range from 2.4×10^3 to 3.3×10^4, and of particular interest is the tendency for the K_d to decrease with increasing distance away from the discharge pipe. It is tempting to attribute this tendency to a change in the oxidation state of the neptunium, the ^{237}Np being presumably discharged as Np (IV) and subsequently being oxidised to Np (V). There are, however, other possibilities, such as differences in the size of the particles in suspension, or differences in their mineralogical composition. Nevertheless, the first possibility should not be discounted. It should also be noted that the surface bottom sediments close to the pipe contained ^{237}Np concentrations which were an order of magnitude lower than the particulate fractions of Stations 1 and 2 in Table 1.

The data in Table 2 indicate that ^{237}Np is clearly accumulated by biological materials. Such accumulation is not merely the result of adsorption to external surfaces, as evidenced by its occurrence in the gonad tissues of both species of echinoderm. All of the $^{239/240}$Pu/^{237}Np quotients are greater than those of the discharges for the months immediately preceding sample collection. It would, however, be presumptuous at this stage to conclude that ^{237}Np is generally less available than plutonium because nothing is known about the relative rates of uptake and loss of either element by any of the organisms analysed. Laboratory experiments made with shrimp *(Lysmata sedicaudata)*, mussel *(Mytilus galloprovincialis)* and crab *(Cancer pagurus)* by Guary and Fowler (1977, 1978) have indicated that the accumulation of ^{237}Np is generally similar to that of plutonium. More data are clearly required.

From the radiological aspect it has been evident, by routinely comparing the total alpha concentrations in edible materials with specific analyses for ^{238}Pu, $^{239/240}$Pu, ^{241}Am, ^{242}Cm and $^{243/244}$Cm, that the importance of ^{237}Np has been extremely small. Using the ^{237}Np data obtained from the commercial plaice and scallop samples it is possible to make more detailed estimates. The annual limit of intake (ALI) for ^{237}Np for exposed workers, as recommended by the International Commission on Radiological Protection (Anonymous, 1980b), is 3 k Bq and one tenth of this (300 Bq) may be taken as the appropriate level for members of the public in line with the general recommendations of the ICRP. The consumption rate of commercial fish for the critical group at Whitehaven is currently estimated

as 0.36 kg per day (Hunt, 1980). Thus at a concentration of 0.04 mBq kg^{-1} the annual intake from commercial plaice fillets would be 5.3 m Bq, less than 0.002 % of the ALI appropriate to members of the public. Similarly a concentration of 2.6 mBq kg^{-1} in the scallops, and a molluscan shellfish consumption rate of 0.05 kg d^{-1} (Hunt, 1980) would result in an annual intake of 47.5 mBq, less than 0.02 % of the ALI appropriate to members of the public. In view of the long halflife of ^{237}Np, however, this nuclide is likely to remain in the biosphere for a considerable time. Estimating the dose commitment arising from its presence in the marine environment will require a more detailed study of its general behaviour.

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