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Concentration and Distribution of the Transuranium Radionuclides $^{239+240}$Pu, ^{238}Pu and ^{241}Am in *Mytilus edulis*, *Fucus vesiculosus* and Surface Sediment of Esk Estuary

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ABSTRACT: Concentrations and distributions are reported for $^{239+240}$Pu, ^{238}Pu and ^{241}Am in *Mytilus edulis* L., *Fucus vesiculosus* L. and surface sediment from the Esk estuary Cumbria UK, which is subjected to effluents from the British Nuclear Fuel Ltd uranium reprocessing plant at Windscale, Cumbria. For *M. edulis*, data was obtained on total soft tissues, shell and for 11 organs and tissues. The distribution of alpha particle activity for thin sections of the mussels was obtained by autoradiography using a new thermoset dielectric detector CR-39. Evidence is presented which indicates that uptake of transuranium radionuclides is probably from seawater rather than from ingested sediment. Pu und Am retained within the intestinal tract is excreted in faeces; that which enters the systemic circulation gives rise to a diffuse distribution. No significant enrichment of Pu and Am occurs in kidney granules, but in the pericardial gland as a result of ultrafiltration processes localised enhanced levels of alpha radioactivity were observed. Highest enrichment of Pu and Am occurs in byssal threads and periostracum, lowest in the shell when the periostracum has been removed. Alpha particle distribution for byssal threads and periostracum is diffuse, hot-spots are absent and hence uptake is probably direct form conservative species present in the seawater. In situ dialysis studies in surface silty sediments of the area provide evidence of conservative species for both Pu and Am. Differences in concentration of Pu and Am for 1977, 1978 and 1979 are described; in 1979 there was an increase in levels of Pu in the mussel and sediment. *F. vesiculosus* contained more Pu than Am. However, the Am/Pu ratio for *F. vesiculosus* is similar to that in byssal threads of *M. edulis*.

INTRODUCTION

Published measurements of transuranium radionuclides present in marine biota and associated sediments are usually for total concentrations (Goldberg et al., 1978), very little data exists for distributions; where available it is often derived from laboratory radiotracer experiments which may not be applicable to natural conditions (Fowler et al., 1975). We report data for concentrations and distributions of ^{238}Pu, $^{239+240}$Pu and ^{241}Am in the mussel *Mytilus edulis*, the seaweed *Fucus vesiculosus* and surface sediment associated with the main mussel bed of the Esk Estuary at Ravenglass, Cumbria, UK (Map Ref. 54°20.5′ N, 3°24.3′ W). For the past 30 years this estuary has been subjected to effluents containing Pu and Am discharged from the British Nuclear Fuel Limited (BNFL) nuclear processing plant at Windscale, Cumbria. We also consider the question of bioavailability of Pu and Am to marine biota and the importance of Pu and Am associated with particulate or dissolved species in terms of uptake by the mussel.

MATERIALS AND METHODS

Samples of *Mytilus edulis* L., between 5.0–7.5 cm in length, were collected from a population in the Esk estuary, near the village of Ravenglass, in October 1977 and September 1978 and 1979 when the body flesh weight was near the annual maximum. Samples were immediately cleaned of any epibiotic growth, washed with local filtered seawater and placed in a bed of cleaned seaweed taken from an area adjacent to the mussel bed. Within 2 d, during which time the shells remained closed, the mussels were returned to the Plymouth Laboratory and divided into two groups each containing about 50 individuals. Those of the first group were opened, seawater contained within the shell cavity was drained off and discarded; the total

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Table 1. *Mytilus edulis.* Percentage water content and weight of various organs and tissues

Tissue	Water content (%)	Wet weight (%)
Digestive gland*	76.5	20.3
Kidney	81.5	1.0
Mantle	87.3	29.6
Mantle edge	82.4	12.1
Gill	87.8	10.8
Muscle	80.0	18.0
Foot	82.2	3.9
Byssal threads	85.4	4.3
Total soft tissue**	–	35.4
Shell	–	64.6

* n = 30
** n = 50

Table 2. Concentration (pCi g^{-1} dry wt) of ^{241}Am in sediments determined by gamma and alpha spectrometry

Sample No.	^{241}Am Gamma spectrometry*	^{241}Am Alpha spectrometry**
308	5.2 ± 0.4	5.4 ± 1.3
327	17.6 ± 1.2	18.6 ± 1.3
328	22.0 ± 3.9	24.7 ± 6.0
329	106.4 ± 3.5	108.8 ± 12.1
330	46.6 ± 2.3	45.0 ± 6.3
331	31.4 ± 0.5	31.0 ± 5.2
332	11.1 ± 0.5	10.7 ± 2.6
333	5.6 ± 0.6	5.2 ± 1.4

* 30cc Ge (Li) detector. Internal standard addition calibration using ^{241}Am
** ^{241}Am yield-tracer technique

mass of soft tissues and the separated byssal threads were removed and prepared for analysis. The second group was initially treated in the same manner, but then a variety of organs (Tables 3, 4) were removed by dissection. The internal surfaces of the shell were cleaned to remove any adhering adductor muscle and when practical the periostracum was detached from the external surface by gently scraping with a scalpel. Complete periostracum removal was not always possible, especially where it had become infolded within surface crenulations. All samples for gross analyses were then freeze dried, homogenised by grinding in an agate ball mill, representative aliquots removed and ashed in a low temperature asher by the nascent oxygen technique (Hamilton et al., 1967). The water content of samples, together with the mean values for wet weight of individual mussel organs were determined (Table 1). Approximately 1 kg of *Fucus vesiculosus* L. was collected from the periphery of the mussel bed, epiphytes and residual sedimentary debris removed by shaking the fronds in filtered seawater; the terminal parts of the fronds were then removed, freeze dried and ashed prior to analysis.

The mussel bed at Ravenglass is associated with deposits of fine grained brown-black arenaceous silts. The dominant sediment of the estuary is a coarse grained well sorted sand; particle size of acid insoluble mineral debris: ca 50 × 80 μm mean particle diameter (MPD), acid soluble fraction ~ 10–40 μm MPD. As an aid in representative sampling of sediments in the field the surface gamma activity of the area under investigation was determined using a Nuclear Enterprise, PS R6 portable spectrometer with a 2'' NaI (Tl), detector held 1 m above the surface of the sediment; the total activity, recorded in 10 s, was used to identify spatial variability of gamma emitters in the sediments which originate from BNFL effluents. From the results of the gamma survey we selected eight representative samples of silt which were pooled to form a single sample; this was then freeze dried, ashed, aliquots removed and leached with 6 M HNO_3 at 70 °C for 24 h. The samples were centrifuged, the residue discarded and the supernatant retained for analysis. Preliminary measurements on silts from the Esk had shown that this treatment removed > 95 % of Pu and Am.

Our usual analytical procedures are based upon the use of conventional ion-exchange column chromatography to isolate and separate Pu from Am, spiking with appropriate radiotracers (^{236}Pu, ^{243}Am) in order to determine chemical yields, electrodeposition and final assay by surface barrier alpha spectrometry. Samples containing > 10 pCi ^{241}Am were generally determined by direct gamma spectrometry using a 30 cc Ge (Li) detector; a comparison between data obtained by both techniques is given in Table 2. On occasions, for spiked samples, depending upon the concentration of ^{241}Am and the weight of sample available, ^{241}Am was determined by gamma ray spectrometry using the 74.6 kev. gamma energy of ^{243}Am for yield corrections thus there was no need to purify the Am eluate from the Pu separation stage.

Alpha Particle Distribution Studies

Hamilton (1980) has shown that for practical purposes the major source of alpha emitting radionuclides in the Esk mussels and silts samples originates from Pu and Am. Natural alpha particle activity of the surface sediments arising from U + Th is < 25 pCi g^{-1}, most of which is contained in crystals of zircon and sphene, compared with > 200 pCi g^{-1} from transuranium radionuclides derived from BNFL effluent. We determined the distribution of Pu + Am using a new thermoset

Table 3. Concentration (g dry weight) of plutonium and americium in samples of littoral *Mytilus edulis* and *Fucus vesiculosus* from the Esk Estuary at Ravenglass, Cumbria, UK

Sample	$^{239+240}Pu$[1] pCi g^{-1}*		^{238}Pu[1] pCi g^{-1}		$\frac{^{239+240}Pu}{^{238}Pu}$		^{241}Am[1] pCi g^{-1}		$\frac{^{241}Am}{^{239+240}Pu}$	
	1977[4]	1978[5]	1977	1978	1977	1978	1977	1978	1977	1978
Mytilus edulis										
Total soft tissue	5.4 ±0.4	9.9 ± 0.1	1.3 ±0.1	3.2 ±0.5	4.1±0.8	3.1±0.7	18.2± 2.8	8.3±1.0	3.4 ±0.6	0.84±0.16
Digestive gland	18.5 ±1.0	23.1 ± 3.0	7.4 ±0.5	6.0 ±0.9	2.5±0.2	3.8±0.8	49.0± 5.9	22.0±2.4	2.7 ±0.3	0.95±0.16
Kidney	7.5 ±0.1	5.5 ± 0.6	2.2 ±0.2	4.6 ±0.6	3.5±0.3	1.2±0.2	11.2± 1.1	16.6±1.4	1.5 ±0.1	3.0 ±0.4
Mantle	1.1 ±0.1	3.0 ± 0.3	0.26±0.3	1.0 ±0.1	4.1±0.6	3.0±0.4	5.2± 0.4	3.7±0.3	4.7 ±0.5	1.2
Mantle edge	2.5 ±0.1	5.7 ± 0.6	0.7 ±0.1	2.1 ±0.3	3.7±0.5	2.7±0.5	5.0± 0.4	7.5±0.8	2.0 ±0.2	1.3 ±0.2
Gill	13.1 ±0.1	12.8 ± 1.7	2.2 ±0.2	8.4 ±1.2	5.9±0.5	1.5±0.3	29.5± 6.8	26.1±3.6	2.2 ±0.5	2.04±0.39
Muscle (adductor)	1.2 ±0.1	5.8 ± 1.1	0.5 ±0.03	3.3 ±0.8	2.5±0.2	1.8±0.5	4.9± 0.3	5.8±0.8	4.1 ±0.2	1.0 ±0.2
Foot	3.2 ±0.1	24.0 ± 3.1	0.65±0.27	9.9 ±1.5	4.9±3.9	2.4±0.5	NS[2]	1.2±0.8	NS	0.05±0.03
Periostracum	47.0 ±2.9	31.0 ± 3.0	13.5 ±1.6	12.2 ±1.4	3.5±0.5	3.3±0.5	60.0± 1.2	54.0±1.1	1.3 ±0.4	1.4
Byssal threads	106 ±6.0	80.1 ±11.0	17.8 ±2.2	30.7 ±5.1	6.0±0.4	2.6±0.6	47.0±22.3	36.2±3.4	0.5 ±0.2	0.45±0.28
Hinge	5.3 ±0.4	ND[3]	1.4 ±0.3	ND	3.8±0.9	ND	3.4± 0.3	ND	0.64±0.4	ND
Shell minus periostracum	0.32±0.02	0.28± 0.02	0.09±0.01	0.08±0.01	3.7±0.5	3.5±0.5	2.4± 0.5	2.8±0.5	7.5 ±1.6	10.8 ±2.0
Fucus vesiculosus	16.3 ±0.3	ND	4.4 ±0.2	ND	3.6±0.2	ND	3.3± 0.3	ND	0.2 ±0.02	ND

[1] Chemical separation followed by alpha-spectrometry using surface barrier detectors. Radiotracers used ^{236}Pu, ^{243}Am
[2] Activity not significant above background
[3] Not determined
[4] n = 48
[5] n = 52
* (S.I. Units – ICurie (Ci) = 3.7×10^{10} becquerels (Bq). IBq = 2.7×10^{-11} Ci = 27 picocuries (pCi)

dielectric detector, CR-39, which is a polymer of the monomer oxydi-2 l, ethanedyl di-2-propenyl diester of carbonic acid (allyl diglycol carbonate); a preliminary account of its use in investigations of environmental radioactivity has been described by Hamilton (1978); a more detailed account of its uses and properties will be presented by Hamilton and Clifton (in preparation). In the work reported here we used 1 mm thick sheets of CR-39 which had been cured by the manufacturer for 36 h. The routine counting efficiency of CR-39 for alpha particles between 5–8 MeV for 2 π geometry was > 85 %. Fresh samples of mussel and seaweed were rapidly frozen, 7–15 μm thick serial sections were cut using a freezing microtome and then mounted on 3'' × 1'' glass microscope slides. The tissue sections were then covered with CR-39, placed in sealed plastic boxes containing aged nitrogen to eliminate background events, and then exposed at room temperature for up to 166 d. Aliquots of sediment were pressed into tablets and the thick sources exposed to CR-39 for up to 10 d. After the exposure period, in order to develop the alpha tracks, the detector was removed from the samples and etched for three hours in 6.0 NaOH at 85 °C. On some occasions, after etching, considerable details of tissue structure were also observed on the surface which had been placed against the detector; this mechanochemical damage, when present, was used to identify sites from which the alpha particles in the samples originated; the nature of this type of damage to the surface of the detector is being studied further. After etching, the detector was washed in 0.1 HCl, then deionised water, dried and treated with an antistatic liquid to prevent adherence of particulates through static charge. The etched CR-39 was then repositioned over the sample to an accuracy of about 2 μm and the distribution of alpha particles observed in relation to tissue structure using a conventional microscope with a x5 or x16 objective and x10 oculars. Compared with other alpha sensitive detectors the clarity of tracks in CR-39 was excellent and the signal-to-noise-ratio unprecedented.

Dialysis Studies

In September 1979 we used in situ dialysis (Cellophane bags, Medicell Int. London, average pore radius 24 Å) to separate dissolved from particulate material present in seawater. The site chosen was situated ca 500 m from the main mussel bed and consisted of ca 1 m of soft thixotropic silt deposits resting upon an indurated arenaceous substrate. At the site ten dialysis bags, with an inflated diameter of 139.7 mm, were soaked in deionised water and then filled with 2.0 l of deionised water; the bags were then placed in trenches 0.3 m deep cut into the silt, covered with the silt which had been removed and gently compacted in order to remove air pockets. The bags were deployed at low tide over an area 6 × 6 m and left in position for 60 h, during which they were covered by sea water throughout four periods of high tide. The bags were then recovered, washed in sea water followed by a copious washing with de-ionised water to remove all the adhering silt. Subsequently, they were punctured and the contents transferred to pre-cleaned Teflon bottles containing 2.0 M HNO_3 to prevent adsorption of Pu and Am onto the walls of the bottle. A separate bag deployed at the site contained a MC 5 salinometer to determine saline influx during dialysis. For practical reasons the bags were removed when the salinity of the contents had reached 50 % of that determined at high tide, namely ca 32 ‰. Preliminary measurements had shown that while smaller dialysis bags (ca 10 mm inflated diameter) reached equilibrium with external salinities in about 1 h, because of a need to sample a large volume of water entrained in the silt, and to overcome transient changes in water type during tidal incursions no attempt was made to reach equilibrium conditions for a defined state of the tide. We also determined the concentration of ^{137}Cs (by gamma ray spectrometry) – a major constituent of BNFL effluent, which provided an independent estimate for saltwater transport across the membrane. No ^{137}Cs radioactivity was detected for the emptied dialysis bags, hence no surface retention of this radionuclide occurred.

One litre aliquots of sea water were also sampled through half a tidal cycle near the mussel bed; immediately after collection each aliquot was filtered through a pre-weighed 0.45 μm Millipore membrane filter. Later, in the laboratory, the filters were dried at 110 °C and the particle load determined by weighing. Using the CR-39 method the total alpha particle activity of each dried sample was determined by counting the number of alpha tracks, using a Quantimet, recorded for a known period of exposure.

RESULTS

The concentrations of Pu and Am in organs and tissues of the mussel collected in 1977 and 1978 are given in Table 3; some data for September 1979 are listed in Table 4. For the samples collected in 1977 and 1978 – with the exception of byssal threads, hinge material and foot for 1978 – tissues generally contained more Am than Pu, but for those collected in 1979 there was a significant enrichment in Pu compared with the 1977 and 1978 samples although the levels of Am showed very little change. For all samples the ^{241}Am/

Table 4. *Mytilus edulis*. Concentration (pCi g^{-1} dry wt) of $^{239+240}$Pu, ^{238}Pu and ^{241}Am in samples collected from Esk estuary at Ravenglass, Cumbria, UK, in September 1979

Sample	$^{239+240}$Pu (pCi g^{-1})	^{238}Pu (pCi g^{-1})	$\frac{^{239+240}Pu}{^{238}Pu}$	^{241}Am (pCi g^{-1})	$\frac{^{241}Am}{^{239+240}Pu}$
Total soft tissues minus byssal threads (n = 50)	37.6	8.0	4.7	8.0	0.2
Digestive gland	179.7 ± 122	33.0 ± 7.0	5.5 ± 0.8	13.6 ± 1.3	0.08 ± 0.01
Kidney	77.4 ± 3.1	7.3 ± 0.4	10.6 ± 0.3	6.6 ± 0.4	0.09 ± 0.01
Mantle	11.5 ± 1.1	2.1 ± 0.3	5.5 ± 0.1	4.2 ± 0.4	0.4 ± 0.1
Mantle edge	8.6 ± 0.6	1.3 ± 0.2	6.6 ± 0.1	3.4 ± 0.4	0.4 ± 0.1
Gill	23.2 ± 7.0	3.7 ± 0.2	6.3 ± 0.4	0.6 ± 0.1	0.03 ± 0.02
Muscle (adductor)	7.4 ± 0.4	1.6 ± 0.2	4.6 ± 0.1	4.8 ± 0.4	0.7 ± 0.1
Foot	5.4 ± 0.4	1.4 ± 0.2	3.9 ± 0.1	1.2 ± 0.2	0.2 ± 0.1
Byssal threads	149.1 ± 8	32.0 ± 5.2	4.7 ± 0.4	38.0 ± 0.8	0.3 ± 0.1

Table 5. *Mytilus edulis*. Comparison between measured concentrations of $^{239+240}$ Pu and ^{241}Am in samples of total soft tissue (minus byssal threads) for 1977, 1978 and 1979, with values calculated from assay of levels in individual organs. Consult Table 1 for concentration weight factors

Year	$^{239+240}$ Pu in total soft tissue measured (pCi g^{-1} dry wt)	$^{239+240}$ Pu in total soft tissue calculated (pCi g^{-1} dry wt)	^{241}Am in total soft tissue measured (pCi g^{-1} dry wt)	^{241}Am in total soft tissue-calculated (pCi g^{-1} dry wt)
1977	5.4	6.2	18.2	18.5
1978	9.9	9.7	8.3	10.5
1979	37.6	44.2	10.6	7.1

$^{239+240}$Pu ratio for byssal threads were similar. Tissues directly associated with food had the highest degree of enrichment of Pu while those, with the exception of byssal threads, which represent tissues that obtain their body burden of Pu or Am following transport across biological membranes showed less enrichment in Pu. Data for *Fucus vesiculosus* showed significantly more Pu than Am.

Allowing for analytical errors associated with the small mass available for some tissues (kidney, periostracum, byssal thread, random loss of fluids during dissection and occlusion of sediment debris) Table 5 compares total soft tissue data with that calculated from analyses of individual tissues in terms of total tissue content which show excellent agreement.

The distribution of alpha emitters in tissues and organs of the mussel determined by CR-39 revealed the following order of activity: byssal threads and caps > periostracum > stomach > intestine > pericardial gland > kidney > diverticula of digestive gland tubules > muscle > mantle tissue. Hot* particles were only observed in the intestine and pericardial gland. Within the intestine very little activity was associated with the typhosole or epithelium lining the lumen, but there was a trend towards higher levels of activity associated with the lateral horns of the lumen. The characteristic feature of hot spots in the lumen of the intestine, and an associated low diffuse distribution throughout the rest of the organ is illustrated in Figure 1. With the exception of the kidney which was associated with a higher level diffuse distribution (Fig. 2), elsewhere in the mussel the low activity diffuse pattern of alpha particles was dominant. We examined the histology of tissue adjacent to hot spots but could not observe any effects likely to be attributable to the influence of ionising radiation. A detailed examination of the numbers, size and specific activity of alpha tracks for hot particles with distance along the digestive tract did not appear to change significantly, hence it appears that the particles are not dissolved to any appreciable extent during transfer through the intestinal tract and are likely to be lost in faeces.

In the Esk estuary we recognise two major types of sediment: coarse sands dominate while fine-grained arenaceous silts are found associated with the mussel bed and cloaking the sides of the estuary, especially along its upper reaches. Our measurements of gamma activity (Table 6), using the field probe, clearly show that areas of highest activity were always associated with silts, intermediate levels with silty sands and the lowest levels with coarse-grained sand; the highest specific activity for silts was found in the upper reaches of the estuary which can contain up to ca 800 pCi g^{-1} of transuranium radionuclides. Changes in levels of gamma activity in a transect across the shore are illus-

* Defined as a small area from which several alpha tracks originate

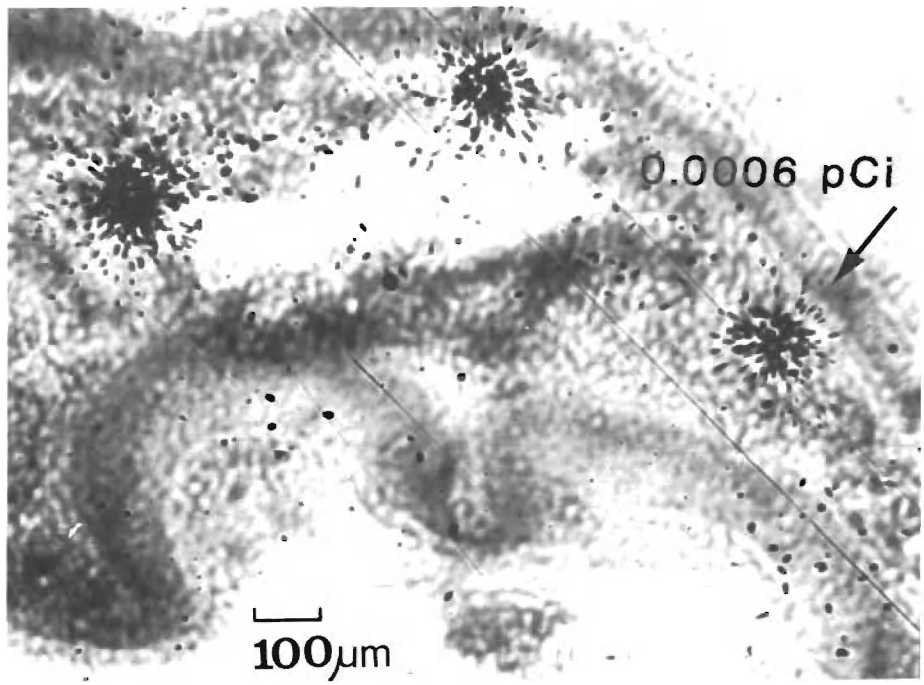

Fig. 1. *Mytilus edulis*. Thin section across the lumen of the intestine of Ravenglass individuals, illustrating the presence of hot particles recorded in CR39 detector superimposed upon the section. Exposure period 166 d

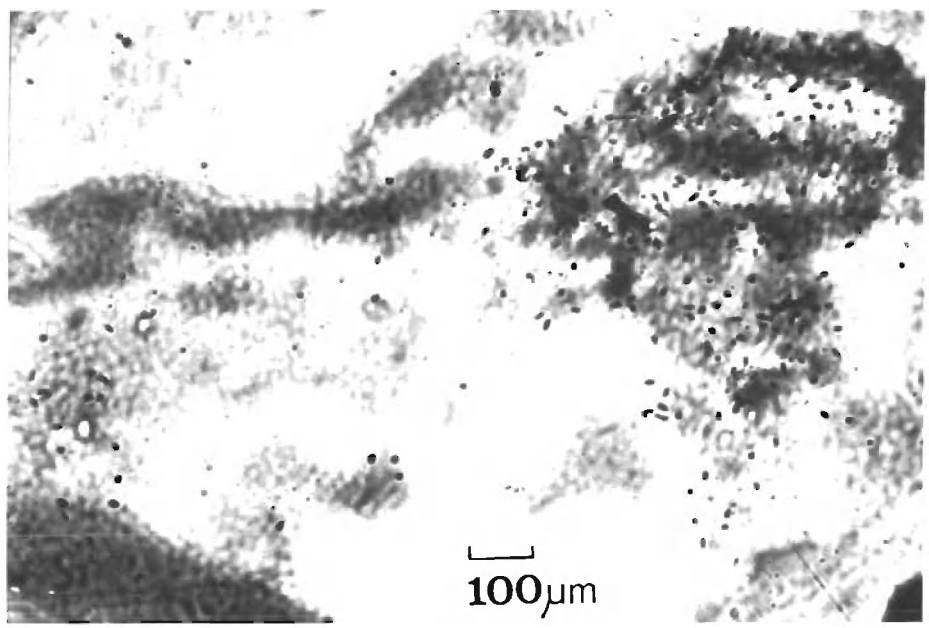

Fig. 2. *Mytilus edulis*. Distribution of α activity in a transverse kidney section of Ravenglass individuals, illustrating localised enriched levels of activity. Exposure period 166 d. Procedures as in Figure 1

trated in Figure 3. Our data for levels of Pu and Am in the mussel and sediments together with various isotope ratios are given in Table 7. An average $^{239+240}Pu/^{238}Pu$ ratio of 4.3 ± 1.0 was obtained for samples of sediment collected in 1977, 1978 and 1979; an average $^{241}Am/^{239+240}Pu$ ratio for samples collected in 1977 and 1978 was 1.6 ± 0.5 compared with a value of 0.4 ± 0.1 for the 1979 samples.

CR-39 studies showed that the alpha particle activity of the sediments associated with the mussel bed had three types of distribution: (i) a general diffuse distribution which accounted for between 20 and 60 % of

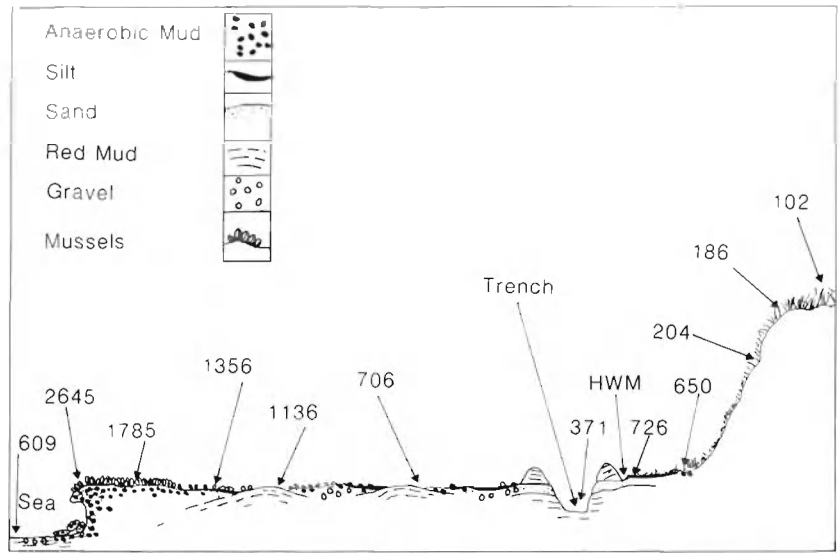

Fig. 3. Diagramatic representation of α activity distribution across the foreshore, 200 m from Ravenglass, Esk Estuary, Cumbria. Numbers indicate γ events s^{-1} obtained with a field single channel sepctrometer, using a 2'' Na I (Tl) crystal, held 1m above the sediment surface

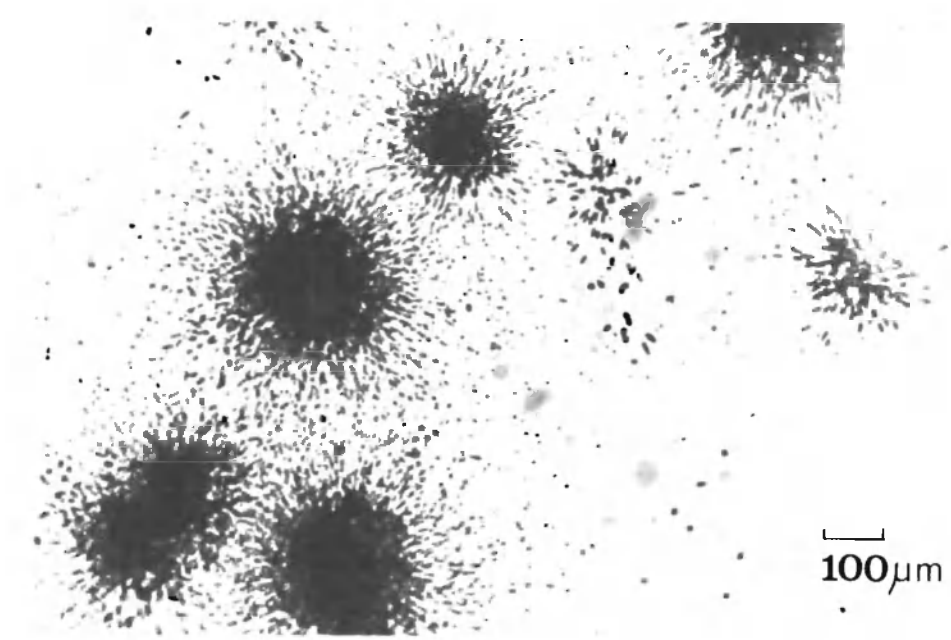

Fig. 4. Hot spots of α activity in silts from the Ravenglass mussel bed. Exposure period 10 d. Procedures as in Figure 1. Because of the high activity originating from these samples the CR39 detector is almost saturated in the central areas

the total alpha particle activity; (ii) activity associated with hot spots with a mean particle diameter of between ca 0.3–30 μm as illustrated in Figure 4 (note that the exposure period was 10 d compared with 166 d for the hot spots from the intestinal tract of the mussel); (iii) an association with well-defined surfaces, for example a diffuse distribution on the surface of sand grains and hot spots associated with 3 × 6 μm particles whose composition so far has not been identified, although we have observed similar particles produced during the corrosion of uranium rods in seawater.

DIALYSIS EXPERIMENTS

On the basis of ^{137}Cs measurements we estimate a concentration of about 450 pCi l^{-1} in local seawater. From data presented by Hunt (1979) we calculate that

Table 6. Relative gamma radioactivity from sediments in the vicinity of Ravenglass, Esk Estuary, Cumbria, UK

Sediment types	Gamma radioactivity* (Cps.)	Number of measurements
Sand dunes	336 ± 48	18
Shingle	418 ± 76	18
Shingle & worm casts	284 ± 14	7
Shingle & seaweed	560 ± 96	7
Sand	292 ± 77	46
Sand & worm casts	284 ± 14	12
Sand & mud	1158 ±380	14
Mud (inner estuary)	3127 ±720	15
Mussel bed		
a) Mud	1642 ±314**	22
b) Sand	896 ± 46	15
c) Sand & sea grass	3590 ±620	8
d) Mud & sand & seaweed	1271 ± 69	10
e) Indurated shingle + 2 cm mud	1194 ± 13	8
f) Shingle	604 ± 52	13

* Assay in field using 2″ NaI(Tl) unshielded detector held 1 m above sediment surface
** Equivalent to a gamma radiation dose of about 120 μ rad h^{-1}

the expected concentration of ^{137}Cs in the Esk estuary would be 450–500 pCi l^{-1}; hence, on this basis, we infer that the dialysis data will provide information for other conservative radionuclides in seawater, for example ^{+6}Pu. From the bulked contents of the dialysis bags we obtained a concentration of 2.0 ± 0.4 pCi $^{239+240}Pu$ l^{-1} (assumed to be ^{+6}Pu see Nelson and Lovett 1978) and 0.6 pCi ± 0.2 of ^{241}Am l^{-1}.

Data illustrated in Figure 5, for particulate matter filtered from the ambient seawater show changes in salinity, temperature, particle load and alpha particle activity through one half of a tidal cycle. As high tide is approached both the particle load and the alpha particle activity of the particulate material suddenly increase. Field observations have shown that after the initial period of silt resuspension, water clearance is fairly rapid, hence for the mussel bed the animals in each tidal cycle are only exposed to high concentrations of silt for short periods of thime.

CONCLUSIONS AND DISCUSSION

In *Mytilus edulis* the tanned proteins of byssal threads and periostracum contain the highest concentrations of Pu and Am; the distribution of alpha particle activity clearly shows that it is evenly distributed on surfaces, hot spots are absent. The lowest concentration of Pu and Am was found in shell when the periostracum had been removed. For a variety of marine molluscs Guary and Fraizier (1977) noted that Pu enrichment is associated with an increase in calcification; they compare this feature with the uptake of Pu in bone of mammals. Our work does not support an association with Ca pathways, but possibly an increase in Ca (shell) in some species may also be associated with a greater abundance of tanned proteins surrounding Ca crystallites of the shell. Guary and Fraizier

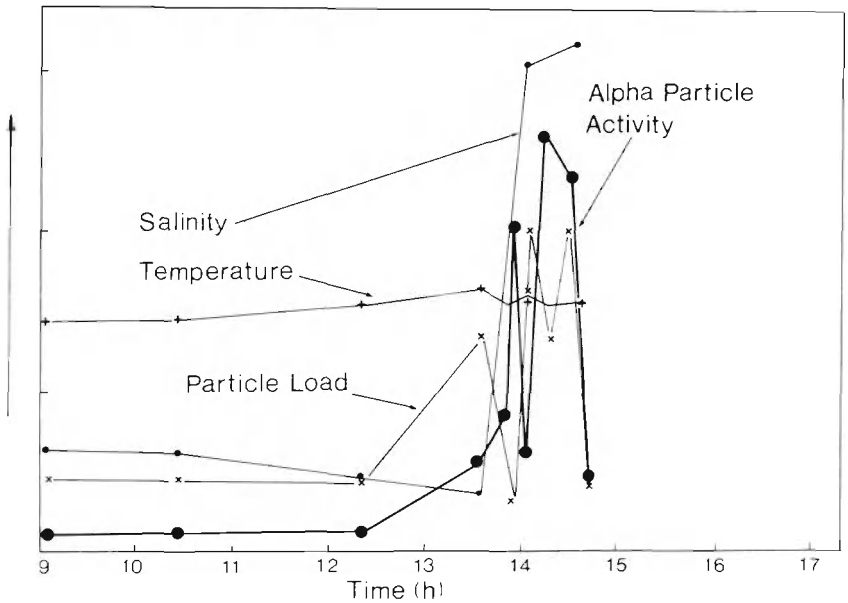

Fig. 5. Variations in total alpha particle activity and particle load for suspended particulates filtered from 1 l of seawater through half a tidal cycle at Newbiggin, Esk Estuary, Cumbria. Range of values: alpha particle activity, 0.3–2.6 c.p.m. cm^{-2}; particle load, 11.72–98.76 mg l^{-1}; salinity, 8.0–31.5 ‰; temperature, 14.1 °–16.0 °C

Table 7. Average values of $^{239+240}Pu/^{238}Pu$ and $^{241}Am/^{239+240}Pu$ isotopic ratios for mussel tissues and sediments 1977–1979; Esk Estuary, Cumbria, UK

Material	Number of samples	Year	$\frac{^{239+240}Pu}{^{238}Pu}$	$\frac{^{241}Am}{^{239+240}Pu}$
Mussel tissues	12	1977	4.0 ± 1.1	2.3 ± 1.4
Mussel tissues	11	1978	2.5 ± 0.8	1.2 ± 0.8
Mussel tissues	11	1979	5.5 ± 1.8	0.2 ± 0.1
Sediment/silt/Newbiggin	8	1977	3.6 ± 2.4	1.4 ± 0.1
Sediment/silt/Newbiggin	3	1979	4.2 ± 2.3	0.5 ± 0.2
Sediment/silt/Ravenglass	4	1979	5.5 ± 2.6	0.4 ± 0.3
Sediment/sand/Ravenglass	2	1979	5.1 ± 2.2	0.4 ± 0.4

(1977) have also noted that in environments only subjected to atmospheric fall-out of Pu, the shell: soft-tissue ratio is always < 1 while the reverse is found for mussels taken near the outfall of nuclear reprocessing plants; the Ravenglass samples support this finding which may reflect differences in the physical and chemical forms of Pu. Goldberg et al. (1978) have shown that for mussels collected distant from sources of nuclear effluents the byssal threads contain the highest concentrations of Pu which Fowler et al. (1975) have also observed from laboratory radiotracer experiments. Goldberg et al. (1978) suggested that the shell of the mussel could be used to record historical levels of the transuranics in the marine environment which would greatly facilitate large-scale monitoring programmes. For littoral mussels, from the Esk estuary at least this is not practical, especially for those aberrant ecotypes with very thick shells and random retention of the periostracum between ridge-like folds of external shell surfaces. However, it is possible to consider thin shell sub-littoral mussels where the periostracum is often intact. For mussel samples collected in 1977 and 1978, and with the exception of the byssal threads hinge and periostracum, the Am/Pu ratio is usually > 1; in the 1979 mussels there was more Pu and slightly less Am which may reflect differences in the mass of Pu and Am released by BNFL between 1978 and 1979.

CR-39 autoradiography has shown that hot spots are restricted to the lumen of the intestine which is believed to represent the presence of sediment debris; the pericardial gland also contains hot spots in accordance with the recent findings of Pirie and George (1979) who have identified this gland as being associated with ultrafiltration processes, the residues of which are excreted in the renopericardial canal to the exterior. No hot spots were found associated with the kidney; this organ contained a much higher diffuse concentration of alpha activity and in spite of the presence of numerous granules they do not appear to concentrate the transuranics. A major role of the kidney is concerned with the removal of waste products from the surrounding blood hence the diffuse distribution arising from Pu and Am may reflect the localised concentration of proteinaceous debris upon which Pu and Am are absorbed (Robinson, 1970). Pu and Am in the gills, together with the distribution of alpha particle activity, was rarely associated with hot spots and presumably reflects uptake of material containing a diffuse distribution of these two radionuclides.

The highest concentrations of Pu, Am and alpha particle activity were found for silts in the vicinity of the mussel beds and for thixotropic silts cloaking the banks of the estuary. As illustrated in Figure 4 the highest levels of radioactivity found in the water occur when the tide changes; under these conditions of maximum turbidity particle loads of about 100 mg l^{-1} are common, dropping to < 10 mg l^{-1} between periods of tidal disturbances; only the fine-grained particles are resuspended and the bulk of the sediment which consists of sands (up to ca 200 μm MPD); these remain on the bottom and are not available for uptake by the mussel. Widdows et al. (1979) have shown that for a 5 cm mussel the onset of pseudofaeces production occurs at a particle concentration in the water of 5 mg l^{-1}, providing a maximum ingestion rate of 11 mg of particulate material h^{-1}; the average water content of the silts is 33 ± 5 % hence, and with a submergence time of ca 4 h/tidal cycle, assuming a maximum concentration of ca 60 pCig $^{239+240}Pu$ wet weight, ca 11 mg of sediment will contain ca. 3 pCi of alpha activity from Pu. Using a measured average value of 1.2 g wet weight for the digestive gland this amounts to a total of about 2.4 pCi of $^{239+240}Pu$ in the lumen of the digestive tract, hence most of the activity present could be accounted for by the presence of sediment. In an alternative calculation – as the total mean water content of mussel tissues, with the exception of the digestive gland is 83.8 + 2.8 %, compared with 76.5 % for the digestive gland – the difference in water content between digestive gland and other tissues is assumed to arise because of the presence of sediment and this would amount to ca 4 pCi of $^{239+240}Pu$ of silt in an average digestive gland.

From calculations based upon alpha particle activity

distributions in the digestive gland we note that the ratios of 'activity of hot spots within the lumen': 'diffuse level in the lumen': 'diffuse levels in the tissues of the digestive gland proper', are 3:1:0.5. We estimate that the intestinal tract accounts for about 18 % by mass of the total digestive gland and therefore ca 53 % of the total activity of the digestive gland is in the lumen, and ca. 47 % in the rest of the gland. Because of the lack of any significant level of activity associated with hot spots as they pass through the lumen, and as the internal pH is 6–7, neither Pu nor Am are likely to be lost from particles unless due to digestive processes which take place in this gland.

The apparent size of a hot particle is calculated from the mean diameter of the alpha particle cluster with which it is associated; however, this need not represent the presence of a single isolated particle, but more likely a hot particle attached to a larger inactive particle. Nevertheless in the mussel there are very precise processes whereby particles enter the digestive gland; discrimination is achieved through a combination of particle size, density and shape. Of the resuspended particulate debris present in the water column, very little is available to the mussel and that which is ingested is mainly excreted in the various types of faeces. Hodge et al. (1979) calculate that the mussel only derives about 11 % of its uranium from solid phases; Hamilton (1980) has shown that the distribution of uranium in the mussel is almost identical to that observed for Pu and Am, hence a direct comparison seems realistic.

Because of the lack of any published data for the composition and form of Pu and Am in the effluent pipe, or storage tanks prior to release, a quantitative evaluation of the bioavailability of Pu and Am from BNFL effluents is not possible. Hetherington et al. (1975) describes the effluent which enters the discharge tanks as being strongly acid (pH 2–3) with Pu at least in solution. However, before discharge the pH is increased by the addition of ammonium hydroxide to neutralise the acid; at this pH the Pu will be predisposed to assume less soluble forms and to reach the sea as a hydrous complex of a colloidal nature. The effluent also contains significant amounts of iron, hence at a pH of 2–3 it will precipitate and contain significant amounts of the transuranics. Following neutralisation of the effluent any transuranics still in solution will then be precipitated and upon exit into the sea flocculation will take place even in the absence of solid surfaces. From this we conclude that a substantial amount of Pu and Am enters the sea as discrete solid phases, or associated with colloids. Observed changes in the concentration of transuranium radionuclides down sediment cores taken for the Ravenglass area (Clifton and Hamilton, in preparation) can be related to changes in the amounts of these radionuclides released by BNFL; with the exception of unusual releases of Pu or Am by BNFL the Pu/Am ratio tends to be constant. Once flocs originating from the BNFL pipeline enter the marine environment they will participate in normal processes of geochemical cycling which will involve changes in redox state. However the Pu-Am pair do not appear to be affected by geochemical processes and retain element and isotope abundance ratios characteristic of the BNFL effluent for defined periods of release. The isotopic composition of hot particles present in Esk sediments will be discussed later by Hamilton (in preparation), but for present purposes, it is worth noting that the particles appear to be the same as those released in BNFL effluent.

So far, our evidence indicates that the mussel lives in an environment where most of the Pu and Am is associated with particulate phase debris, little of which is available to enter organs of the mussel and that which enters the digestive tract is excreted in faeces. Nelson and Lovett (1978) have shown that some of the Pu, at least, which is released in BNFL effluent in seawater behaves in a conservative manner, i.e. as $^{+6}$Pu. Our dialysis measurements confirm their measurements, but also indicate the presence of a mobile form of Am, which passes across the dialysis membrane with the Pu. For the samples collected in 1977 and 1978 the byssal threads, and hinge material were enriched in Pu relative to Am. More significant was the observation that none of these materials were associated with hot spots; instead, the distribution of alpha particle activity was homogenous which would be reconcilable with direct uptake (active or passive), of a conservative species from seawater. Such a conclusion was also reached by Hamilton (1980) for uranium in the same materials. Further The Am/Pu ratio found for *Fucus vesiculosus* sampled at the same time is similar to that found for the byssal threads.

This study has identified some significant differences in the concentration of Pu in samples collected in 1977 and 1978 with those for 1979. At present it is not possible to comment further except to note that they may reflect natural changes in the abundance of Pu and Am in relation to biological and geochemical processes which are characteristic of the area, or alternatively they reflect differences in the amounts, and perhaps chemical form, of Pu and Am present in BNFL effluents for which no detailed information is currently available.

The silts of the Esk estuary contain a historical record for the last 30–50 years for the accumulation of transuranium radionuclides originating from BNFL effluent. These silts, together with the mussels, provide important evidence for the manner in which Pu and

Am become distributed in an estuarine environment. Because of the shallow nature of the estuary, and the thin layers of silt (maximum ca 1m) it has become urgent to study the area in detail with the minimum of delay. It seems inevitable that following one severe storm, or a period of very high freshwater run-off, the silts are likely to be lost, or at the least so disturbed that details of the historical record of transuranium radionuclide deposits will be lost.

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