THE UPTAKE AND DISTRIBUTION OF RADIONUCLIDES IN MARINE ORGANISMS

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CONTENTS

ABSTRACT

The behaviour and distribution of α-emitting radionuclides in the mussel (Mytilus edulis), winkle (Littorina littorea) and Dublin Bay prawn (Nephrops norvegicus) have been investigated under both environmental and laboratory conditions using α-autoradiography in conjunction with conventional radioanalytical techniques. Of the samples exposed to environmental levels of radioactivity, Ravenglass mussels, collected between 1983 and 1984, exhibited $^{239+240}Pu$ concentrations ranging from 43Bqkg^{-1} (dry) in muscle tissue to 1658Bqkg^{-1} in byssal threads, the corresponding ^{137}Cs range being 131Bqkg^{-1} to 1340Bqkg^{-1}. Although ^{210}Po concentrations were not determined in byssal threads, muscle tissue still displayed the lowest nuclide concentration (124Bqkg^{-1}), whilst the viscera (containing digestive gland, stomach and kidneys) contained the highest (596Bqkg^{-1}). Subsequent concentration factor calculations for ^{137}Cs, ^{210}Po and $^{239+240}Pu$ in the total soft parts of Ravenglass mussels were, respectively, 9, 25800 and 1400.

In Cumbrian winkles, nuclide concentrations ranged a) for ^{239}Pu, from 18.5Bqkg^{-1} (muscle tissue) to 457Bqkg^{-1} (pallial complex), b) for ^{137}Cs, from 103Bqkg^{-1} (foot tissue) to 1495Bqkg^{-1} (pallial complex) and c) for ^{210}Po, from 12.2Bqkg^{-1} (muscle tissue) to 145Bqkg^{-1} (digestive gland). Total soft parts CFs were calculated at 16 for ^{137}Cs, 5500 for ^{210}Po and 5700 for $^{239+240}Pu$. The magnitude of these CFs, as for those of the mussel is consistent with the respective CF values recommended by IAEA (IAEA, 1985) for molluscs.

Radionuclide concentrations in Whitehaven-landed prawns were much lower than those observed in mussels or winkles; no artificial γ-emitter activities were present above detection limits and the highest $^{239+240}Pu$ concentration was 5.96Bqkg^{-1} in the carapace. ^{210}Po activities, however, were more readily detectable throughout the prawn's tissues, concentrations ranging from 2.7Bqkg^{-1} (abdomen muscle) to 144Bqkg^{-1} (cardiac

fore-gut), producing CFs of the order of $2x10^4$ in tissues associated with feeding and digestion.

Previous studies have attempted to determine the principal nuclide source to marine organisms by comparing nuclide activity quotients in their tissues, sea water and particulate material. From the environmental samples here, no single transport medium appears to dominate such uptake.

Under laboratory conditions, mussels, winkles and prawns all exhibited the ability to accumulate ^{237}Np, ^{239}Pu and ^{241}Am from both sea water and food media. Up to 90% of the accumulated activity was located in the hard protective shells of the organisms. In general, of the soft tissues studied, those associated with feeding and digestion accumulated radionuclides most effectively. In digestive glands/hepatopancreas, the site of nuclide uptake was in the digestive tubules. Other active tissues were the gill and heart of the Dublin Bay prawn and the pallial complex and operculum of the winkle. The prawn's gill was the only tissue to exhibit a clear preference between food and sea water labelling media - with higher accumulation via sea water. Heart tissue contained enhanced levels of ^{239}Pu relative to ^{237}Np and ^{241}Am. This unusual observation may be associated with metal-detoxification processes.

The various glandular and secretory functions of the winkle's pallial complex may account for the comparable magnitude of nuclide activities in this tissue and of those in the digestive gland. Other mucous secretions, on the external layers of the winkle's head and foot tissues, have been observed to accumulate radionuclides but not as efficiently as the pallial complex. The most intense α-track distributions encountered in the project were found in the winkle's operculum. These observations can be attributed to the chitinous nature of the tissue. Laboratory experiments therefore have shown that the accumulation and distribution of transuranic nuclides in marine invertebrates are highly influenced by the presence of scleroproteins, chitinous material and mucous secretions.

Despite the relatively low activities present in Ravenglass mussels and winkles, their α-autoradiographs exhibited tissue activity trends in general accordance with those obtained experimentally. This finding provides some support for the validity of laboratory-derived information and for its extrapolation to environmental conditions. From radiochemical analysis, it is apparent that the ^{210}Po contributes significantly to the total α-activity of the environmental marine organisms. Because of the decreasing concentrations of α-emitting transuranic nuclides (mainly ^{238}Pu, $^{239+240}Pu$ and ^{241}Am) in the Ravenglass environment, the influence of natural ^{210}Po in any future α-autoradiographic studies will become increasingly dominant.

The primary radiological implication of the observed radionuclide concentrations in Ravenglass mussels and winkles is that, from seafood ingestion, the critical group receives only a small percentage of the ICRP-recommended dose limit. Dose contributions from ^{210}Po are higher than those from $^{239+240}Pu$ in mussels but are less than those from $^{239+240}Pu$ in winkles.

CHAPTER 1 : INTRODUCTION

1.1 INITIAL DISCUSSION

The quantities of transuranic and other long-lived radionuclides introduced to the oceans could, in the future, increase through disposal of wastes from an expanding nuclear power industry within both the developed and developing nations (NEA, 1981). The marine discharge of low-level liquid effluents into coastal waters has been supplemented by the practice of dumping packaged low-level solid waste onto the deep ocean floor (Holliday, 1984; NEA, 1985). For the future, the marine option for disposal of high-level wastes continues to remain open. Certainly, the controlled introduction of long-lived radionuclides of whatever origin, to the marine environment is a subject of considerable scientific interest and some public concern.

Extremely little direct knowledge is available to demonstrate conclusively how high-level radioactive wastes would behave once disposed of to the oceans (Baxter, 1983). Theoretical model systems of the oceans have therefore been developed to help quantify the physical, geochemical and biological transport processes which determine the fates and activities of discharged radionuclides, with particular emphasis on quantifying the potential routes exposing man to these nuclides (NEA, 1985). Meanwhile, medium- and high-level radioactive wastes are stored on site at nuclear establishments until a predictably reliable and safe disposal method and site are identified. Marine disposal of wastes remains one of several options, on-land disposal in geological repositories being perhaps the foremost competitor. This study focusses solely on the marine option and indeed on one aspect of it. To generate the comprehensive database necessary to evaluate disposal methods and sites, all the potentially relevant nuclide transfer and exposure pathways must be thoroughly researched.

It is recognised that, in the context of existing coastal discharges of low-level effluents, ingestion of seafood, especially molluscs, provides a significant critical group dose commitment, e.g. as in the vicinity of the British Nuclear Fuels plc

reprocessing plant at Sellafield, Cumbria (Hunt, 1979-1987). In this research project, the behaviour and uptake of transuranic elements in marine organisms are studied to provide further data towards improving the assessment of transfer pathways for transuranic nuclides from nuclear wastes (past, current or future) to marine organisms (seafood) and ultimately to man.

This introductory chapter outlines the detailed aims of the project and provides background information on the abundance of radioactivity in the environment from both natural and anthropogenic sources. The chapter also includes an account of previous research on transuranic nuclides in marine biota, with reference to work carried out both in the field and in the laboratory and, finally, it provides data for phytoplankton and zooplankton, through molluscs and crustaceans, to fish.

1.2 RADIOACTIVITY IN THE ENVIRONMENT

1.2.1 Natural radioactivity

Radioactivity and radiation have been present on earth since genesis - for the earth is perpetually bathed in a sea of ionizing radiation and its lithosphere, oceans, atmosphere and biosphere contain many different naturally occurring radioactive nuclides. Everything - earth, air, water, plants and animals - contains radioactivity from both natural and latterly anthropogenic sources.

The major naturally occurring alpha-radioactive nuclides found in environmental materials belong to the three radioactive decay series of uranium and thorium; these owe their continued existence to the occurrence of a long-lived parent nuclide at the head of each series. Following decay, through many intermediate daughters, all three series terminate in a stable lead isotope, i.e. $^{238}U(t_{1/2} = 4.51 \times 10^{9}yr) \xrightarrow{8\alpha,\ 6\beta} {}^{206}Pb$, $^{232}Th(t_{1/2} = 1.41 \times 10^{9}yr) \xrightarrow{6\alpha,\ 4\beta} {}^{208}Pb$, $^{235}U(t_{1/2} = 7.1 \times 10^{8}yr) \xrightarrow{7\alpha,\ 4\beta} {}^{207}Pb$ (Friedlander *et al.*, 1964).

A sample containing, for example, ^{238}U and its daughters is said to be in secular equilibrium when the activities of all nuclides in the chain are equal. Such a situation occurs if the sample has remained a closed system for a time equivalent to many half-lives of the longest-lived daughter nuclide. In the uranium series, this time interval is 10^6 years (in the thorium series ~34 years; in the actinium series ~1.6×10^5 years) (Cherry and Shannon, 1974). Such an equilibrium situation is not generally found in environmental samples, however, and, in the marine environment, disequilibrium between various members of the series is the rule rather than the exception. In the context of the present study, the most relevant example of disequilibrium involves ^{222}Rn, a member of the ^{238}U decay series. In uranium-bearing rocks and minerals, ^{226}Ra decays to ^{222}Rn and some of this gaseous radon daughter is continually leaked from land surfaces to atmosphere (Hill, 1965; Folsom and Beasley, 1973). Radon decays rapidly to ^{210}Pb which has a half-life of 22 years, much longer than its mean residence time in the troposphere. A natural fall-out and scavenging of ^{210}Pb and its daughters, ^{210}Bi and ^{210}Po, then results and these nuclides are subsequently incorporated into the biosphere, hydrosphere and geosphere (Figure 1.1, Tables 1.1 - 1.3) (Folsom and Beasley, 1973; Baxter, 1983; Woodhead, 1984). Tables 1.2 and 1.3, which summarise the radionuclide composition of sea water and marine sediments, include other major natural β and γ emitters besides the uranium and thorium decay series. Radiocarbon (^{14}C), tritium (^{3}H) and ^{10}Be are all products of neutron capture in the atmosphere from cosmic rays (Pentreath, 1980), whilst ^{40}K and ^{87}Rb owe their terrestrial occurrence to primordial production and relatively long half-lives (1.27×10^9 years and 4.8×10^{10} years respectively). These Tables highlight the fact that, in terms of natural radioactivity, sea water is dominated by β and γ activity, whereas ocean sediments have more equal contributions from β/γ emitters and α emitters.

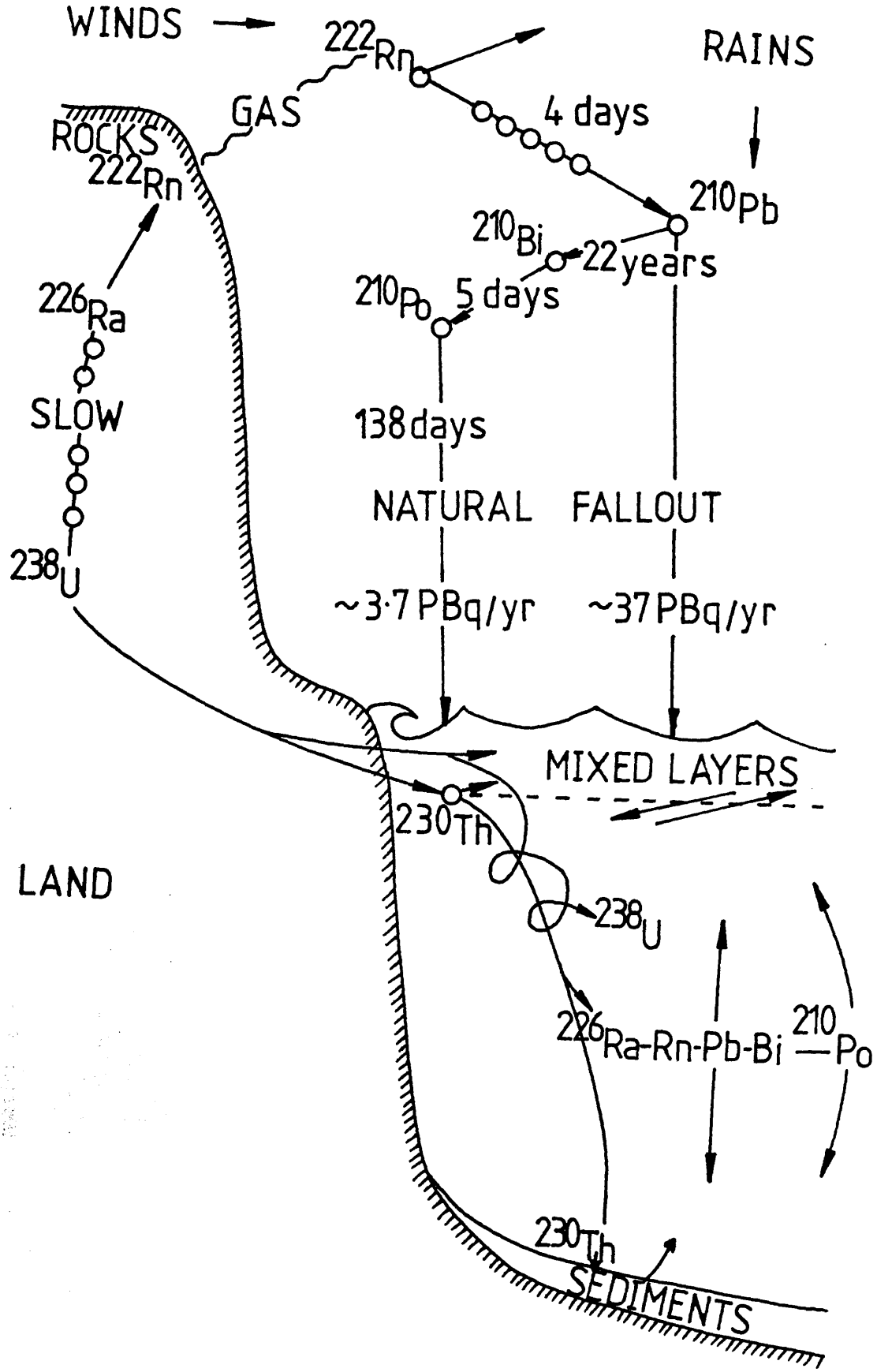


Figure 1.1. Suggested routes by which ^{238}U decay series may enter the marine biosphere (Based on Folsom and Beasley, 1973).

TABLE 1.1

Concentration of natural radionuclides in environmental samples (Based on Woodhead, 1984).

Radionuclide	Half Life	Granite	Limestone	Bqkg^{-1} wet				
	y	Bqkg^{-1}	Bqkg^{-1}	Phytoplankton	Zooplankton	Molluscs	Crustaceans	Fish (Muscle)
^{238}U	4.47×10^{9}	63	16	1.5-1.9	0.37-0.74			0.003-1.1
^{234}U	2.45×10^{5}			1.5-1.9	0.37-0.74			0.003-1.3
^{230}Th	8.00×10^{4}							
^{226}Ra	1.6×10^{3}			0.74	0.74			$0.74\text{-}19 \times 10^{-2}$
^{222}Rn	1.05×10^{-2}							
^{210}Pb	22.3			3.7-26	0.37-9.3	0.19-0.37	1.5-2.6	$0.7\text{-}8.5 \times 10^{-2}$
^{210}Po	3.79×10^{-1}			15-63	1.9-84	12-52	8.5-230	0.015-6.3
^{232}Th	1.4×10^{10}	74	4.4					
^{228}Ra	5.76							
^{228}Th	1.91			0.26-2.0	$7.4\text{-}81 \times 10^{-2}$			$0.1\text{-}52 \times 10^{-3}$
^{235}U	2.45×10^{5}	3.0	0.4	7.4×10^{-1}	2.2×10^{-2}			$0.4\text{-}14 \times 10^{-2}$

TABLE 1.2

Major natural radionuclides in sea water (Based on Baxter, 1983).

	Nuclide	Activity ($mBql^{-1}$)
β, γ emitters	^{40}K	12247
	^{87}Rb	107
	U/Th daughters	85
	^{14}C	5.2
	^{3}H	2.96
Total		12447
α-emitters	^{234}U	46
	^{238}U	41
	^{218}Po	7.4
	^{214}Po	7.4
	^{226}Ra	3.7
	^{222}Rn	7.4
	^{235}U	1.85
	^{210}Po	1.11
Total		116

Total activity of natural sea water 12563 $mBql^{-1}$

Ocean inventory of natural radioactivity = 1.72×10^{28} Bq

TABLE 1.3

Major natural radionuclides in ocean sediments
(Based on Baxter, 1983).

β , γ emitters		α-emitters	
Nuclide	Activity $Bqkg^{-1}$ dry	Nuclide	Activity $Bqkg^{-1}$ dry
^{40}K	1850	^{230}Th	1110
^{210}Pb	740	^{210}Po	740
^{210}Bi	740	^{214}Po	740
^{214}Pb	740	^{218}Po	740
^{214}Bi	740	^{222}Rn	740
^{207}Tl	148	^{226}Ra	740
^{211}Pb	148	^{211}Bi	148
^{227}Ac	148	^{215}Po	148
^{87}Rb	111	^{219}Rn	148
^{234}Th	74	^{223}Ra	148
^{234}Pa	74	^{227}Th	148
^{212}Pb	18.5	^{231}Pa	148
^{228}Ra	18.5	^{238}U	74
^{228}Ac	18.5	^{234}U	37
^{231}Th	18.5	^{216}Po	18.5
^{212}Bi	11.1	^{220}Rn	18.5
^{14}C	7.4	^{224}Ra	18.5
^{208}Tl	7.4	^{228}Th	18.5
^{10}Be	0.07	^{232}Th	18.5
Total	5612	^{235}U	18.5
		^{212}Po	11.1
		^{212}Bi	7.4
		Total	5939

Total activity of natural sediment = 11551 $Bqkg^{-1}$ dry

0-10 metre sediment inventory = 3.2×10^{22} Bq

0-200 metre sediment inventory = 6.3×10^{23} Bq

1.2.2 Production of transuranic elements

The first transuranic elements, neptunium and plutonium, were produced in tracer amounts in 1940 by bombardment of uranium with slow neutrons (McMillan and Abelson, 1940; Seaborg et al., 1946). Transuranic elements with atomic numbers up to 103 have been synthesised since that time, largely by Seaborg and co-workers (Seaborg, 1963), through nuclear reactions of various types with lighter transuranic elements.

The accumulation of transuranic elements in a nuclear reactor follows a fixed pattern because of the restrictions imposed by decay and fission half-lives and neutron reaction cross sections (Figure 1.2) (Bagnall, 1972). Progressive neutron captures on the first-appearing nuclide of a new element forms a longer- or lesser-length series of long-lived α-emitters until a β-emitting isotope is produced. The β-decay yields a nuclide of the next highest element and the capture process then continues. In most cases, the 'crossover' β-emitter has a relatively short half-life, so there is no further significant build-up of even heavier isotopes of the parent element beyond that point. ^{241}Pu is an exception to this as it has a sufficiently long half-life (14.2 years) to allow a sufficient number of atoms to accumulate and thus to permit production of ^{242}Pu and ^{243}Pu and hence maintenance of the primary production chain. Beta-decay of ^{241}Pu yields ^{241}Am, which, after neutron capture and β-decay, yields ^{242}Cm. The latter is relatively short-lived (163 days) for a major α-emitter and it is therefore intensely radioactive and represents a potential problem in fresh wastes. It also acts as a significant producer of ^{238}Pu. ^{241}Am is longer lived (432 years) but, because of its mode of generation, it continues to be produced in the fuel long after reactor discharge and in any plutonium residues in derived wastes, depending on the ^{241}Pu content of the fuel at the time of reactor shutdown (Stewart, 1985).

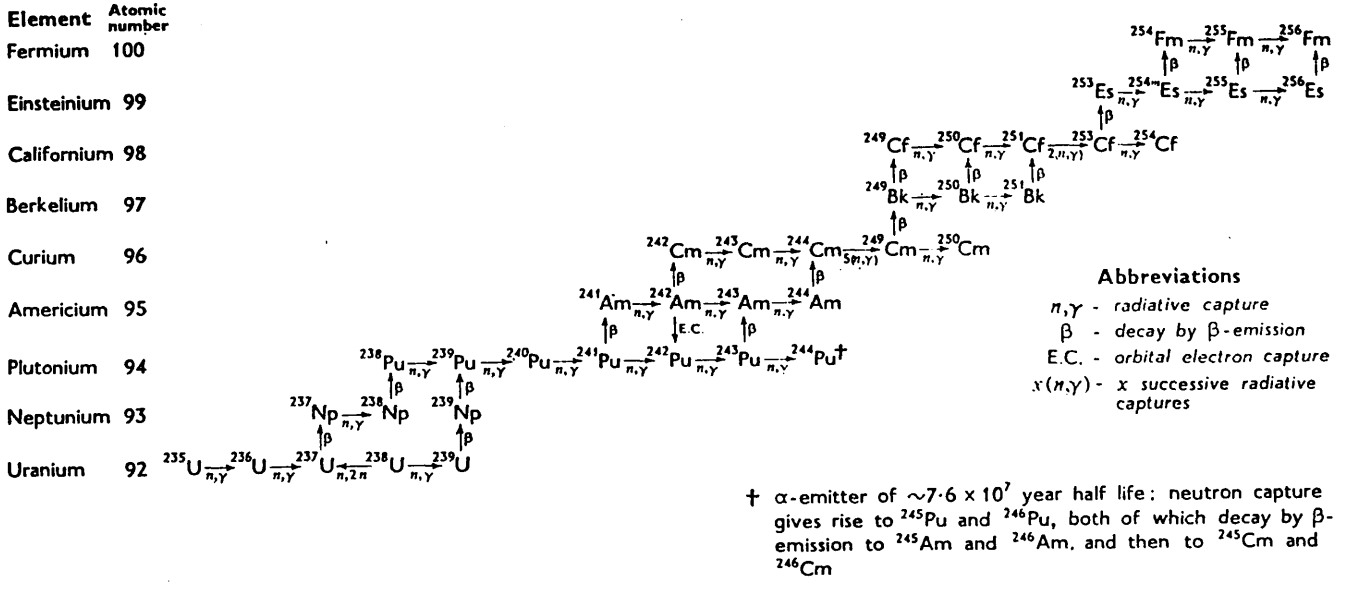


Figure 1.2. The formation of the transuranium elements in a nuclear reactor (Bagnall, 1972).

Milligram or even gram amounts of ^{252}Cf can be produced in special high-flux reactors with appropriate targets but yields drop quickly along the build-up chain and half-lives typically become much shorter past curium. Reactor production of even trace inventories of elements above californium is very difficult (Bagnall, 1972).

On the other hand, surprisingly large quantities of two nuclides, ^{237}Np and ^{238}Pu, are produced in reactor fuels. ^{237}Np has a very long half-life (2.2×10^6 years) and accordingly accumulates during irradiation to the point where, in terms of mass (but not activity), it becomes the major transuranic nuclide next to ^{239}Pu in the fuel (Stewart, 1985).

Transuranic elements are also produced by nuclear explosions by the neutron-capture and β-decay sequence displayed in nuclear reactors (Figure 1.2) The main transuranic α-emitters produced by nuclear explosions are $^{239 + 240}Pu$ and ^{241}Am whilst those produced from nuclear operations are principally ^{238}Pu, ^{241}Am and the curium isotopes (Perkins and Thomas, 1980).

1.2.3 Release of transuranic elements to the environment

1.2.3.1 From the nuclear weapons industry

The principal source of anthropogenic radioactivity is atmospheric fallout from nuclear weapons testing (Cherry and Shannon, 1974; Harley, 1980). Considerable quantities have also been discharged directly into the coastal zone via nuclear waste releases by the nuclear industry (NEA, 1981). Another source, highlighted by the Chernobyl event in 1986, is accidental release from nuclear installations.

The first significant injection of transuranic nuclides into the atmosphere occurred as the result of nuclear weapons testing in New Mexico in 1945. Between then and 1952, most of the debris from further nuclear detonations was, because of their relatively low yield, restricted to the troposphere (NEA, 1981). In 1952

the first thermonuclear device was detonated and production of the transuranic elements increased because of the coupling of the high energy yield of the fusion device with the large increase in neutron flux, resulting in radioactive debris being injected into the stratosphere (10km-50km) (Perkins and Thomas, 1980).

The quantity of transuranic elements released to the environment by atmospheric weapons testing is not known with certainty since the quantity left after an explosion varies according to the incompleteness of the fission chain-reaction (NEA, 1981). This problem is highlighted by the range of values reported for the $^{239+240}Pu$ inventory present in atmospheric fallout: 12000 TBq (Hardy et al., 1973), 13300 TBq (Perkins and Thomas, 1980) and 17000 TBq (Wrenn, 1974).

World-wide fallout derives from the proportion of the debris which is injected into the stratosphere and occurs over a period of many years after detonation. The main transfer of debris from the stratosphere to the troposphere occurs in winter, through the tropopause at temperate latitudes, and results in the observed spring maximum deposition rate in middle latitudes (Perkins and Thomas, 1980; Pentreath, 1980). The limited test ban treaty in 1963, between USA, USSR and UK, was preceded by intensive testing in 1961 and 1962 leading to a maximum annual deposition in 1963 in the northern hemisphere (NEA, 1981; UNEP, 1986). The People's Republic of China began atmospheric nuclear testing in late 1964 and in mid-1966 France began their atmospheric testing programme (Perkins and Thomas, 1980). Both countries have continued weapons testing above ground at smaller yields and with declining frequency. These post-1963 atmospheric tests have resulted in injection of relatively little additional transuranic material into the atmosphere (Stewart, 1985). As a result of the 1963 test ban agreement, the US, USSR and UK have continued their nuclear test programmes underground resulting in a cumulative yield of ~366 megatons between the detonation of the first nuclear weapon in 1945

and June 1978 (Carter and Moghissi, 1977: Carter, 1979). In studying the inventory of the transuranic elements present in the atmosphere from nuclear weapons testing (Table 1.4), the total α-activity of all the transuranic elements of mass greater than 241 is only ~1% of the $^{239+240}Pu$ inventory (Perkins and Thomas, 1980).

A major injection of the isotope ^{238}Pu into the atmosphere occurred in 1964 when a navigational satellite, 'Transit 5-BN-3' failed to achieve stable orbit and disintegrated on re-entry, dispersing 630TBq of ^{238}Pu, contained in the System for Nuclear Auxiliary Power generator (SNAP-9A) in the form of plutonium metal, into the atmosphere (Hardy et al., 1973).

Two accidents involving B-52 bombers carrying plutonium-bearing nuclear weapons have resulted in localised contamination of the environment. In 1966 at Palomares, Spain, radioactive debris was dispersed over about 500 hectares but the amounts released remain classified (NEA, 1981). In 1968, at Thule, Greenland, about 10^{12}Bq were deposited on the shore and bottom sediments, with debris scattered over about 12 hectares (Aarkrog, 1971; 1977). In both instances, intensive clean-up operations involved removing the surface radioactivity to the USA (NEA, 1981).

Other accidental releases of transuranic elements have occurred at laboratories and plants manufacturing nuclear weapons; thus about 5×10^{11}Bq were released into the soil at Rocky Flats, Colorado, USA; about 2×10^{11}Bq of ^{238}Pu were introduced into the site drainage water at the Mound Laboratory, Ohio, USA and about 10^{10}Bq of ^{238}Pu leaked to the atmosphere (NEA, 1981).

1.2.3.2 From the nuclear energy industry

As the operation of nuclear reactors produces transuranic elements, the potential exists for release of some of these to the environment during reactor operation and subsequent fuel reprocessing.

TABLE 1.4

Relative abundances* and estimated amounts of transuranic elements injected into the atmosphere (Perkins and Thomas, 1980).

Radionuclide	Activity abundance*	Total injection** Bq
^{239}Pu	1	5.7×10^{15}
^{240}Pu	1.35	7.7×10^{15}
^{241}Pu	63	3.6×10^{17}
^{241}Am	-	1.2×10^{16}***
^{242}Pu	1.2×10^{-3}	1.0×10^{12}
^{243}Am	6.9×10^{-3}	4.0×10^{13}
^{244}Pu	3.5×10^{-7}	1.9×10^{9}
^{245}Cm	3.6×10^{-4}	2.1×10^{12}
^{246}Cm	2.4×10^{-4}	1.4×10^{12}
^{247}Cm	6.2×10^{-9}	3.3×10^{7}
^{248}Cm	8.4×10^{-8}	4.8×10^{8}
^{249}Bk	3.2×10^{-3}	1.8×10^{13}
^{250}Cm	6.5×10^{-8}	3.3×10^{8}
^{251}Cf	3.8×10^{-7}	2.1×10^{9}
^{252}Cf	9.3×10^{-6}	5.8×10^{8}
^{253}Cf	2.5×10^{-4}	1.4×10^{12}
^{254}Cf	7.4×10^{-6}	4.1×10^{11}
^{255}Es	9.1×10^{-6}	5.2×10^{10}

* Values normalised to ^{239}Pu.

** Assumes 1.3×10^{16} Bq $^{239+240}Pu$ atmospheric injection from weapons testing.

*** ^{241}Am formed on total decay of ^{241}Pu

Controlled discharges of transuranic elements from the nuclear industry are globally and quantitatively less important than those from weapons test fallout but those from the British Nuclear Fuels plc reprocessing plant at Sellafield, Cumbria, England, have constituted the bulk of releases in the former category (NEA, 1981). Annual quantities of Pu and Am discharged from Sellafield into the Irish Sea from the early 1970's to 1986 are depicted in Figure 1.3 (Pentreath et al., 1984; BNF, 1983-87). Further transuranic discharge data from Sellafield are provided in Table 1.5 (Cambray, 1982; BNF, 1983-87). Since 1978, discrete data sets for the activities of ^{238}Pu and $^{239+240}Pu$ discharged are available, the $^{239+240}Pu/^{238}Pu$ quotients varying monthly from 5.5 to 5.2 (Pentreath et al., 1984). ^{237}Np, ^{242}Cm and $^{243+244}Cm$ are also discharged but their total activity is less than 1 TBq per year (BNF, 1983-1987).

Two other commercial reprocessing plants at Marcoule and Cap de la Hague in France are in operation. Since the Marcoule plant discharges directly into the Rhone, the levels of radioactive waste released to the environment are relatively small (UNEP, 1986).

At Cap de la Hague, radioactive waste effluent is discharged into the coastal regions of northern France resulting in the presence of radionuclides in the English Channel and surrounding seas. The levels of α-emitters discharged, however, were ~ 100 times lower than the quantities released from Sellafield between 1974 to 1980 (Table 1.6, UNSCEAR, 1982; NEA, 1985). The catastrophic nuclear reactor accident at Chernobyl, Russia in 1986 released a total of 2000 PBq (2×10^6 TBq) of radioactivity to the environment of Europe, principally to the eastern states. Although the nuclides of most radiological significance to the bulk of Europeans were the γ-emitters ^{134}Cs, ^{137}Cs and ^{131}I, ~ 70TBq of $^{239+240}Pu$ was lost from the reactor core (O'Riordan and Fry, 1986), a quantity comparable to the maximum annual discharge of $^{239+240}Pu$ into the Irish Sea from Sellafield (1973).

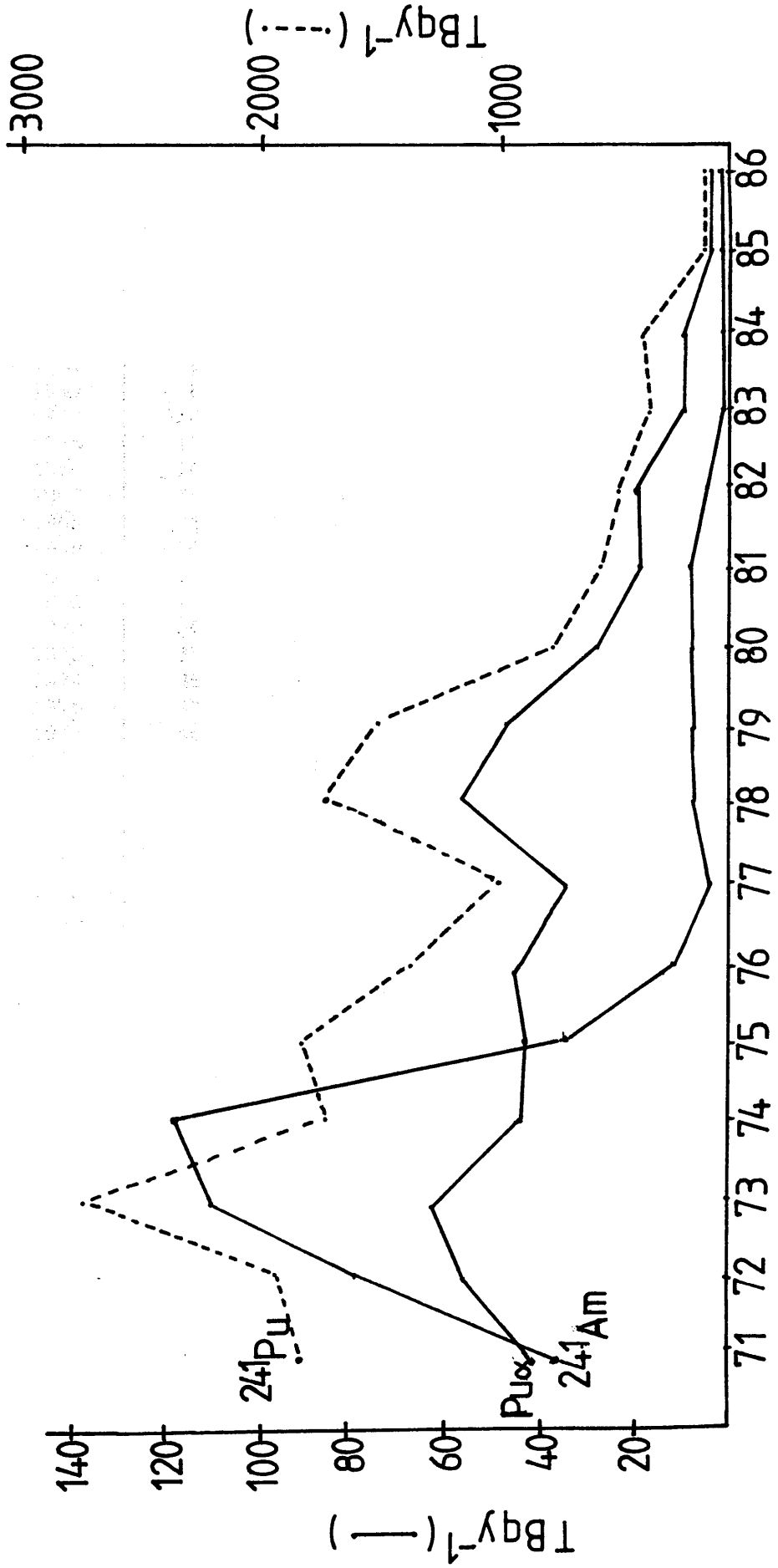


Figure 1.3. Annual discharge rates of Pu and Am into the Irish Sea from Sellafield since 1971.

TABLE 1.5

Discharges to the Irish Sea of plutonium and americium from Sellafield (TBq yr^{-1}) (Based on Cambray (1982) and BNF (1983-87)).

Year	Pu α	$^{239+240}Pu$	^{238}Pu	^{241}Pu	^{241}Am
1960	2.9				
1961	3.8				
1962	6.9				
1963	8.6				
1964	10.5				
1965	10.8				
1966	10.8				
1967	18.5	18.2			
1968	30.6	30.6			
1969	30.2	30.2			
1970	34.6	34.6			19.1
1971	41.7	41.7			37.7
1972	57.2	57.3		1902	79.5
1973	65.6	65.7		2755	109.2
1974	46.2	46.2		1709	118.2
1975	44.2	44.4		1817	36.3
1976	46.8			1297	11.9
1977	36.3	36.3		981	3.7
1978	58.0	45.6	12.4	1773	7.9
1979	49.4	37.4	11.9	1494	7.8
1980	27.2	20.3	6.9	728	8.3
1981	20.3	15.3	5.0	596	8.8
1982	20.7	16.1	4.7	485	6.4
1983	11.6	8.7	2.9	331	2.2
1984	10.9	8.3	2.6	345	2.3
1985	3.4	2.6	0.8	81	1.6
1986	2.7			63	1.3

TABLE 1.6

Total-α releases to the aquatic environment from fuel reprocessing (UNSCEAR, 1982; NEA, 1985).

YEAR	TBq		
	SELLAFIELD	LA HAGUE	MARCOULE
1974	170	1.0	-
1975	85	0.49	0.019
1976	60	0.37	0.011
1977	46	0.67	0.013
1978	68	0.51	0.013
1979	62	0.69	-
1980	39	0.51	-

By the end of 1984, 13% of the world's electricity was generated by 345 nuclear power reactors in operation in 26 countries. This proportion is expected to increase in the near future (UNEP, 1986).

The reprocessing of irradiated fuel is performed to recover the valuable fissile materials, ^{239}Pu and ^{235}U, from the accumulated fission products which act as poisons to the fuel (Woodhead, 1984). The reprocessing waste effluent is produced from two sources. Newly-arrived spent Magnox fuel elements are retained in cooling ponds which are maintained at an alkaline pH to reduce corrosion of the fuel cans. Despite this, considerable quantities of caesium isotopes are still released into the pond water (Woodhead, 1984). These ponds are constantly flushed with water and the purged water is continuously discharged. Other effluent derives from the reprocessing waste streams, the major source of transuranic nuclides, which are held in a separate waste system in sea tanks (Pentreath et al., 1984). These release waste effluent twice daily (along with the pond water) to the sea at high tide (NEA, 1981; Pentreath et al., 1984).

After initial cooling in storage ponds, the alloy cladding of fuel elements is mechanically stripped and stored under water in a shielded silo (Pentreath, 1980). The naked uranium fuel rod is dissolved in nitric acid, from which uranyl and plutonium nitrate are selectively extracted using the complexing agent tributyl phosphate (TBP) in odourless kerosene (OK) (Pentreath, 1980; Woodhead, 1984). Following separation, the organic phase, containing the uranium and plutonium, is back-extracted using ferrous sulphamate as reducing agent, separating plutonium (in the aqueous phase) from the uranium (in the organic phase) (Pentreath, 1980; Livens, 1985). Eventually the plutonium is converted to the dioxide and stored in stainless steel containers (Pentreath, 1980).

At the first separation stage, ~ 99% of the fission and activation radionuclides remain in the aqueous phase, constituting a highly active waste (Woodhead, 1984), which is allowed to boil to reduce the volume of waste, thus producing a high-level concentrate which is stored on site (Pentreath, 1980). Medium-level waste, produced after successive back extractions, is stored to allow decay of short-lived radionuclides before being discharged to the Irish Sea (the effluent is neutralised from its acidic conditions prior to discharge) (Woodhead, 1984).

The disposal of solid waste in the north-east Atlantic has been practised by many European countries, particularly UK and Netherlands, between 1949 and 1982 (Holliday, 1984). Details of this marine disposal option are presented in Section 1.3.3.

1.2.4 Future accumulation of high-activity waste arisings.

Predictions of nuclear capacity, and hence of nuclear waste inventories, at the end of this century have been steadily falling in recent years as the projected expansion of nuclear power slows under the impact of economic recession, energy conservation and public opposition. Predicted values have decreased from 4300 GW (UNSCEAR, 1973) to 500 - 1000 GW of installed nuclear energy capacity by 2000 A.D. (Table 1.7, 1.8). The uncertainty in predicting future quantities of high-activity waste does not influence the range of nuclides which will have particular significance with regard to waste disposal. Baxter (1983), in reviewing the high-activity waste arisings once global nuclear capacity had reached 2500 GW, listed the isotopes of the following elements to be of primary importance: Cs, Sr, Pm, Eu, Sm, Sb, Am, Pu, Cm, Np, Tc, Zr, Sn, Se, Pa, Pd, Ac. Activities of the ten principal nuclides were presented at timepoints 0, 10^2, 10^4 and 10^6 years after disposal, with appropriate consideration of the ingrowth of daughters and decay of parent nuclides. At zero time (early 21st century), Baxter (1983) calculated that ~4 x 10^6 PBq of high-activity waste would have accumulated, virtually all of it being due

TABLE 1.7

Installed nuclear energy capacity 1955-1983 (IAEA, 1984).

Year	Installed Capacity (GW(e)a)
1955	0.005
1960	1.1
1965	5.3
1970	16.6
1975	72.3
1980	135.3
1983	190.8

TABLE 1.8

Predicted installed nuclear energy capacity (GW(e)a)

1985	1990	2000	2025	2050	Reference
		4300			UNSCEAR, 1973
		2000			UNSCEAR, 1977
		1000			UNSCEAR, 1982
292	367-422	576-851			IAEA, 1983
		741	2926	6722	Edmonds and Reilly, 1983
		500			NEA, 1982

to the short-lived fission-product pairs $^{137}Cs/^{137m}Ba$ and $^{90}Sr/^{90}Y$, with ~ 1% attributable to the actinides of which ^{244}Cm and ^{241}Pu are the major species. As post-disposal times increase, the actinide activity contribution increases to 56% of total after 10^4 years and 29% after 10^6 years, with ^{243}Am, ^{237}Np, ^{239}Np and ^{240}Pu delivering the most significant actinide activities. Since the major activities in fresh wastes are associated with the short-lived nuclides, a pre-disposal storage period of 10^2 years would reduce the radioactive waste inventory by ~ 90%. In comparing the levels of high-activity waste arisings with other inventories of marine radioactivity (Table 1.9), Baxter (1983) demonstrated that the high-level waste radioactivity was less than the natural oceanic inventory. Although the former may be insignificant in comparison, care is required in calculating radiological effects on the marine ecosystem and man since localised enrichments of radioactivity may occur, resulting in transfer of enhanced levels through the food chain to man.

The list of important nuclides present in high-level waste not only serves as a reminder of these pathways but identifies those nuclides whose environmental behaviour has been insufficiently studied with regard to waste disposal programmes.

1.2.5 Behaviour of transuranic elements in the marine environment

The five transuranic elements of principal environmental interest are neptunium, plutonium, americium, curium and californium. Of these, plutonium has been the most widely studied because of its world-wide presence in weapons fallout. Americium, although not produced directly in weapon tests, does appear in world-wide fallout because of its production by decay of ^{241}Pu. (The half-life of ^{241}Am (432 years) is rather short to be considered 'long-lived' but ^{243}Am ($t_{1/2}$ = 7.4 x 10^3 years) produced in reactor fuels is 'long-lived'). Because of their widespread distributions, plutonium and americium behaviour in the marine environment has been studied in many different

TABLE 1.9

Present inventories of marine radioactivity. (Baxter, 1983)

Natural sea water	1.7×10^{7} PBq
Natural sediments (top 200m)	6.3×10^{8} PBq
Nuclear weapons fallout (maximum)	7.4×10^{4} PBq
Nuclear industry discharges	$n \times 10^{3}$ PBq
Potential input from high-activity waste arisings	4.4×10^{6} PBq

locations. Curium and neptunium have not been investigated in as much detail because their concentrations in marine materials generally fall below practicable detection limits. Although curium and neptunium are present in world-wide fallout (at much lower activities than plutonium or americium), it is their presence in low-level liquid waste, discharged under controlled conditions from reprocessing plants, which enables some direct environmental study. Research to date has been restricted to localised enhanced (near-site) areas (Pentreath and Harvey, 1981; Hunt, 1985b, 1986).

The isotopes of curium (^{242}Cm, ^{243}Cm, ^{244}Cm) (BNF, 1986) are all short-lived but their study serves to illustrate the expected behaviour of ^{245}Cm ($t_{1/2}$ = 8.5 x 10^3 years) and ^{246}Cm ($t_{1/2}$ = 4.7 x 10^3 years) which are present in high-level wastes. As mentioned earlier, the major neptunium nuclide discharged is ^{237}Np ($t_{1/2}$ = 2.1 x 10^6 years).

Although environmental inventories of californium are expected to be less than those of the other transuranic elements, it should be borne in mind that recent reviews dealing with assessment of the marine disposal option for radioactive wastes have assumed 'calculated guesswork only' when predicting the importance of californium in critical pathway analysis (NEA, 1980). No environmental studies have been reported for californium, although laboratory experiments have recently been performed (Aston and Fowler, 1983; Fowler et al., 1986). In general, then, data from environmental and laboratory studies of these elements are required to fill substantial gaps in knowledge and to improve assessments of current fuel reprocessing, reactor waste management and deep sea disposal options for high-level radioactive wastes.

The biological availability of transuranic nuclides discharged to the marine environment is of considerable interest, particularly with regard to those marine organisms which form a direct pathway back to man. An immediate factor influencing the degree of biological availability of any transuranic nuclide is its interaction with the physical environment and this, in turn, is dependent upon its chemical state.

The transuranic elements form part of a series of the actinide elements which are similar to the lanthanide elements in that electrons are successively being added to the outer 5f (rather than 4f) orbitals. Since the actinides' 5f electrons are less effectively shielded than the 4f valence electrons of the lanthanides and, as the differences in energy between adjacent orbitals are correspondingly smaller, the transuranic elements have more complex chemical properties than the lanthanides, particularly in relation to their oxidation - reduction behaviour (Cotton and Wilkinson, 1980). Both neptunium and plutonium can co-exist under certain circumstances (e.g. in acid solution) in four oxidation states because of the complex relationships between the equilibria and kinetics of conversion from one oxidation state to another. In general, the reactions between M^{3+} and M^{4+}, MO_2^{+} and MO_2^{2+} are rapid and those between M^{n+} and MO_2^{n+} are slow (Edgington and Nelson, 1984). Very different equilibria and kinetics probably exist at the nearer-neutral pH of sea water. Americium and curium apparently occur in a single oxidation state as Am^{3+} and Cm^{3+} (Edgington and Nelson, 1984).

Any transuranic element which has strongly reactive properties will, because of its adsorption onto fine particulate material, be present in particulate-feeding organisms (Pentreath, 1981). Such an element might also be expected to be adsorbed by benthic algae and by small planktonic organisms with relatively large surface areas. In contrast, elements which are largely soluble will be not only more widely dispersed but also less readily adsorbed on biological materials; they may, however, be expected to be more readily absorbed - particularly across gills and gut epithelia.

Plutonium is found to be largely adsorbed onto particulate matter and thus rapidly removed from the water column to the sediment (Hetherington *et al.*, 1976). The small proportion which remains in the aqueous phase behaves more or less conservatively. Nelson and Lovett (1978) have demonstrated that the higher oxidation states of plutonium, Pu (V + VI), are predominant

in the soluble fraction, whilst the lower oxidation states, Pu (III + IV), are primarily associated with particulate material. The significance of this complex distribution is that the distribution coefficients for adsorption onto particulate material or K_d ($Bqkg^{-1}$ particulate material/$Bqkg^{-1}$ filtrate sea water) differ considerably from one oxidation state to another. Thus, for example, the K_d for $^{239+240}Pu$ (V + VI) is estimated at 10^3 to 10^4, whereas, for $^{239+240}Pu$ (III + IV), it is in the range 10^5 and 10^6 (Nelson and Lovett, 1978; Pentreath et al., 1980). The existence of plutonium in its higher oxidation states has also been observed in filtered seawater from the nuclear weapon test sites at Enewetak and Bikini lagoons, ~90% of the $^{239+240}Pu$ being present as Pu (V + VI) (Noshkin and Wong, 1980).

The oxidation states of other transuranic nuclides in seawater have not been studied in detail but americium and curium are generally considered to be present in trivalent form (NEA, 1981). Pentreath (1980) determined K_d values of $\sim 10^6$ for both ^{241}Am and $^{243+244}Cm$, with the mean of the ^{241}Am values being higher than that for curium but both elements being clearly more particle-reactive than plutonium. By contrast to the above transuranic elements, neptunium, which exists in sea water as Np (V), has a much lower K_d value, estimated at $10^2 - 10^3$ for Irish Sea conditions (Harvey, 1981), making it the most conservative of the transuranic elements discussed here. No information on the aquatic behaviour of californium is available. Laboratory-derived K_d values have, however, been obtained by Aston and Fowler (1983) using ^{252}Cf (III), giving a range 1.4×10^4 to 1×10^5 and demonstrating that ^{252}Cf possesses similar adsorptive capacities to plutonium (Table 1.10).

Comparatively few data are available on the chemical behaviour of these elements in undisturbed sediments. Transuranic elements generally tend to form complexes as a function of their oxidation states, the trend being IV> III> VI> V (Pentreath, 1981). The manner of complexation will directly influence the availability, favourably or adversely, for bioaccumulation. In the interstitial

TABLE 1.10

Distribution of transuranic nuclides between suspended particulate matter and sea water (Based on Harvey and Kershaw, 1984).

Element	Range of K_d values	Location	Additional details + Sources
Np	2.4×10^{2}–3.3×10^{3}	Irish Sea	98% Np(V) (Pentreath and Harvey, 1981)
Pu	6×10^{3}–1.4×10^{4}	Irish Sea	Pu(V+VI) (Nelson and Lovett, 1978)
	4×10^{5}–6×10^{6}	Irish Sea	Pu(III+IV) (Nelson and Lovett, 1978)
	4×10^{4}–6×10^{5}	Enewetak Lagoon	(Edgington, 1981)
	3×10^{5}	Lake Michigan	(Edgington, 1981)
Am	2.2×10^{6}–2.4×10^{6}	Irish Sea	(Pentreath et al., 1980)
Cm	1.2×10^{6}–1.6×10^{6}	Irish Sea	(Pentreath et al., 1980)
Cf	1.4×10^{4}– 1×10^{5}	Laboratory	(Aston and Fowler, 1983)

waters of Irish Sea sediments, plutonium is predominantly in the higher oxidation states just below the sediment surface but is predominantly in the lower oxidation states below 5 to 10cm depth (Pentreath et al., 1980). Americium, curium and californium are likely to remain trivalent (Pentreath, 1981; Fowler et al., 1986) but neptunium could be reduced to Np(IV) in interstitial waters (Pentreath, 1981).

As with many contaminants released into the marine environment, transuranic nuclides tend mostly to be removed from the water column by fine-grained particulate matter and the resulting distribution of activity on the sea bed serves as an approximate guide to the variations in grain-size of the bottom sediments (Hetherington et al., 1976; Pentreath et al., 1984). The influence of the varying mineralogies of the particles is largely lost because of the widespread occurrence of hydrous oxide and organic coatings on the marine particulate matter. These coatings, along with variations in redox conditions, appear to be the primary factors in determining the adsorption of radionuclides by the solid phase (Harvey and Kershaw, 1984).

The partitioning of sediment-bound radionuclides between the solid and liquid phases is controlled by many factors, including bioturbation of the sea bed, the porosity and permeability of the sediment and the in-situ chemical changes, largely induced by microbial activity (Harvey and Kershaw, 1984).

1.3 RADIOLOGICAL SIGNIFICANCE OF MARINE TRANSURANICS

1.3.1 Radiation Protection

The practice of radiation protection throughout the world is greatly influenced by the advice and recommendations of the International Commission on Radiological Protection (ICRP). Their policy is to consider the basic principles upon which appropriate radiation protection measures can be based with emphasis on "the protection of individuals, their progeny

and mankind as a whole, while still allowing necessary activities from which radiation exposures might result" (ICRP, 1977). It is to be remembered that the ICRP publications are recommendations only and therefore their interpretation at a national level differs in some respects from country to country. The ICRP philosophy of radiation protection is based on the following main principles (ICRP, 1977):

1. No practice shall be adopted unless its introduction produces a positive net benefit.

2. All exposures shall be kept as low as reasonably achievable (ALARA), economic and social factors being taken into account.

3. The dose equivalent to individuals shall not exceed the limits recommended for the appropriate circumstances by the Commission.

These three requirements apply in theory to all sources of radiation but, in practice, unavoidable exposure to radiation occurs from natural sources and from fallout from previous weapons tests. Medical irradiation is a matter of clinical judgement and, since the collective dose from medical procedures is high, clinicians must take into consideration the other ICRP requirements. In practice, the requirements apply fully to the exposure of

i radiation workers
ii the public, from industrial and other practices involving radiation
iii the public, from miscellaneous artificial sources (NRPB, 1986).

Justification of practices which may result in radiation exposure emphasises the obvious need to consider harmful effects when deciding whether the proposed practice or operation

is acceptable. The ICRP recommends that the acceptability of such a practice or operation should be determined by cost-benefit analysis (ICRP, 1977). The term 'cost' is not taken literally in this context as it refers to the sum total of all the negative aspects of the practice. Similarly 'benefit' includes all the advantages to society as a whole.

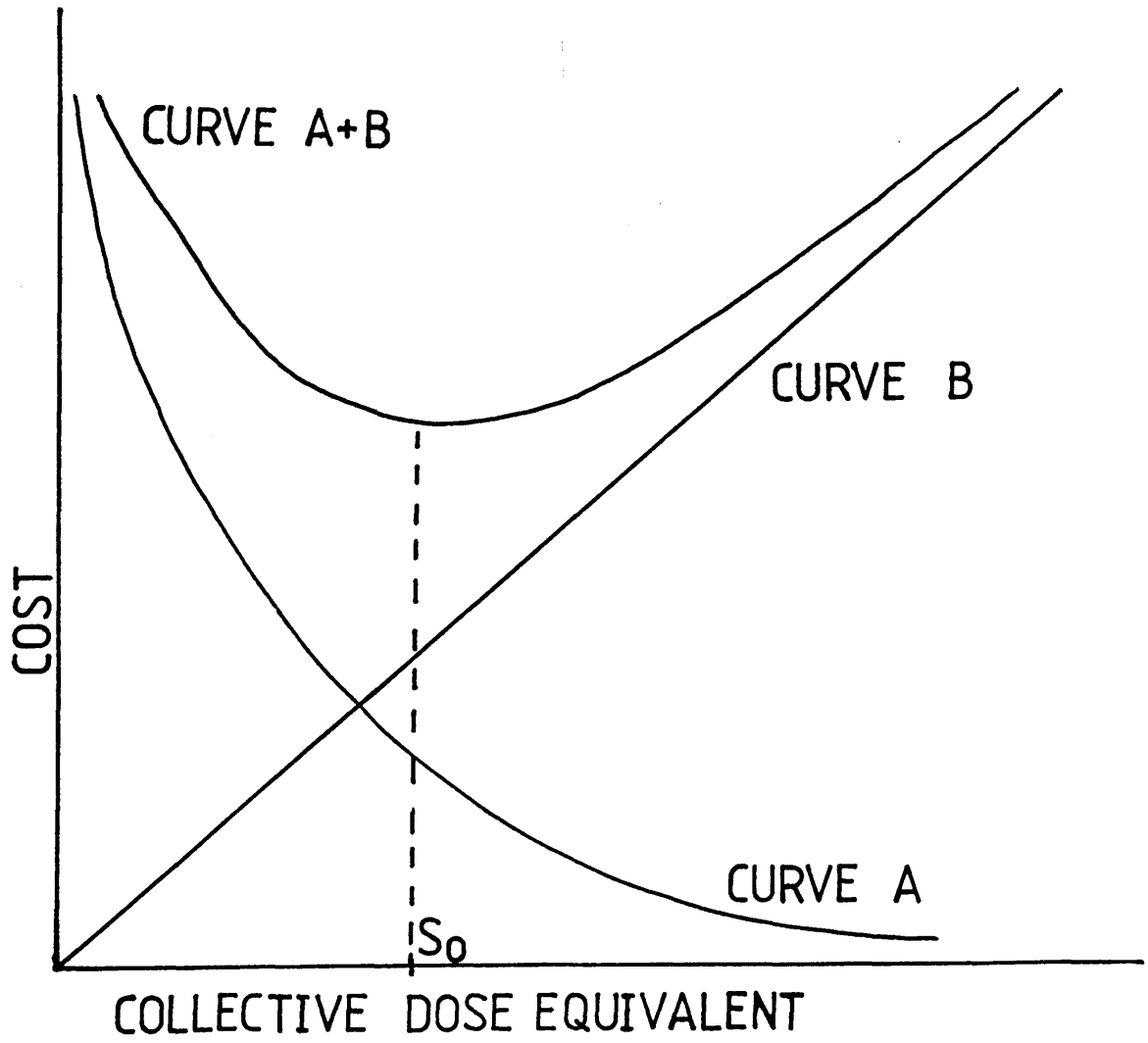
In the case of nuclear power, comparison must be made with the consequences of alternative methods of producing power, for example from coal burning. In such comparisons, all health risks, not only radiation, need to be considered, besides strategic, economic and social factors, to be able to justify the acceptability of the favoured practice.

In employing the ALARA principle the ICRP introduces the concept of 'optimization'. In determining what is reasonably achievable, the benefits gained in reducing doses below the recommended limits must be weighed against the increased costs of achieving the reduction.

The total cost may be considered as the addition of two curves (Figure 1.4, based on ICRP, 1973). Curve A is the direct cost of reducing the radiation exposure. Curve B is the cost of the radiological detriment which can be converted to a monetary equivalent by assessing the resultant health effects. If the idealized curves in Figure 1.4 are related to the dose, it can be seen that low protection costs correspond to high exposures (Curve A) and vice versa (Curve B).

The optimization technique attempts to achieve the level of expenditure at which the combined costs are at the minimum value, (S_o in Figure 1.4) i.e. to maximize the net benefit in relation to the collective dose.

(A brief summary of dose terms is given in Figure 1.5, UNEP, 1986).

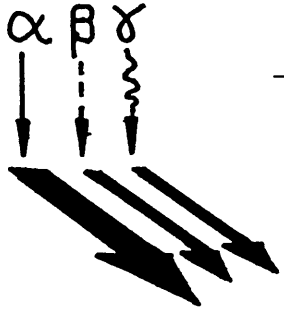


Curve A - cost of protection

Curve B - cost of health detriment

Curve A+B - cost of radiation protection + radiation health detriment

Figure 1.4. Optimization of radiation protection



Absorbed Dose: Energy imparted by radiation per gram of tissue.

Dose equivalent: Absorbed dose weighted for the potential of different radiations to do damage.

Effective dose equivalent: Dose equivalent weighted for the susceptibility to harm of different tissues.

Collective effective dose equivalent: Effective dose equivalent to a group of people from a source of radiation.

Collective effective dose equivalent commitment: Collective effective dose equivalent delivered over time to generations of people.

Figure 1.5. Outline of dose terms used in radiation protection (UNEP, 1986).

In recommending dose limits, the ICRP recognises two categories of individuals - adults exposed in the course of their work and individual members of the public. The hazards to which radiation workers may be exposed can be anticipated and the workers are individually monitored and their exposures controlled to ensure that authorized dose limits are not exceeded. The general public, however, being such an extensive population, cannot have such attention directed towards each individual. Since the public usually has no choice in determining its exposure (e.g. fallout, natural radiation) and is exposed for periods greater than the typical duration of employment, the recommended annual dose limit for individual members of the public, (including children and embryos which are more sensitive to radiation) is one fiftieth (1mSv) of the annual dose limit for radiation workers (50mSv) (natural sources and medical exposures excluded) (NRPB, 1986). In rare cases in which a few individuals may be exposed over prolonged periods and the received dose is known rather than based on maximizing assumptions, the average annual effective dose equivalent to an individual member of the public should not exceed 1mSv, although most recent recommendations (NRPB, 1987) suggest that steps should be taken to reduce the total dose to be as low as reasonably achievable below $0.5mSvy^{-1}$ in the near future.

Since the actual dose equivalents received by individual members of the public are extremely variable due to the influential factors of age, size, metabolism, dietary and other habits, the identification of a critical group is used in radiological protection to account for this variability. The group must be small enough to be relatively homogeneous with respect to age, etc. and also be representative of those individuals of the population expected to receive the highest dose equivalents. Frequent use of the critical group concept has been practised in UK by MAFF and BNF in their health physics programmes (Hunt 1981-86; BNF 1982-86); for example when expressing the individual radiation exposure resulting from ingestion of seafood.

1.3.2 Exposure from low-level liquid discharges

In the vicinity of nuclear reactors and reprocessing plants, man is exposed to artificial radioactivity, derived from low-level liquid discharges from these plants, via a number of exposure pathways. These are

i external irradiation, e.g. from walking on contaminated sand and muds in estuarine areas exposed at low tides,

ii internal irradiation, e.g. via ingestion of contaminated foodstuffs, and

iii inhalation of radioactive gases or resuspended particulates of marine origin.

The management of low-level liquid discharges to the marine environment is related to the consequent exposures of individual members of the public and of the total population (Woodhead, 1984). Three different control procedures have been used so that radiation exposures in excess of appropriate limits are avoided.

The simplest of these is the 'point of discharge control' approach practised widely in the USSR and the USA (Pentreath, 1980). This depends merely on ensuring that the concentrations of the various radionuclides in the liquid effluent do not exceed recommended limits. The advantage of this system is that, in using specified effluent concentrations, it can be applied easily by the plant operator, monitoring of the environment becoming a more straightforward task. However, actual site-specific radiation exposures of either individuals or populations, cannot be assessed directly by this method (IAEA, 1978).

The 'specific activity' approach is based on conversion of the recommended maximum permissible body or organ burdens for each radionuclide into specific activities (activity of radionuclide per gram of element) relative to the normal

quantities of the corresponding stable elements in the body or organ. Thus, if discharges to an aquatic environment are regulated such that the specific activities of the radionuclides in the receiving water are held below those permitted for man, then they cannot be exceeded at any point in the food chain or in man. Despite the apparent elimination of marine food chain contributions towards man's radionuclide intake inherent in this approach, several shortcomings are evident. It is only applicable to elements that are metabolized, ignoring those that are taken orally and are not absorbed. External dose rates are not considered and application to freshwater systems is not as straightforward as for the marine situation, because of high variability of some major elements (Ca, K) in freshwaters (Pentreath, 1980). There still remain some nuclides which are very difficult to measure precisely and which have no naturally occurring isotopes or analogues (particularly the transuranics). It is assumed in this approach that the radionuclide under consideration will be in precisely the same chemical form as the stable element. Not all chemical forms of an element, however, readily exchange with each other, especially when elements are complexed to organic molecules.

Balancing these deficiencies is the conservative assumption that all of the individual's food supply is obtained from the receiving waters. However, it is evident that, in view of the large number of unknowns involved, this approach is not sufficiently thorough.

The third control procedure is the 'critical pathway approach' practised in UK (Figure 1.6). This method of discharge limitation requires a considerable amount of investigative effort. The ICRP (ICRP, 1966) recognised that, despite there being several exposure pathways available to man from discharged radionuclides, only one or two would in practice be found to be limiting at any one site, a similar selective approach being applied to the 'cocktail' of radionuclides discharged

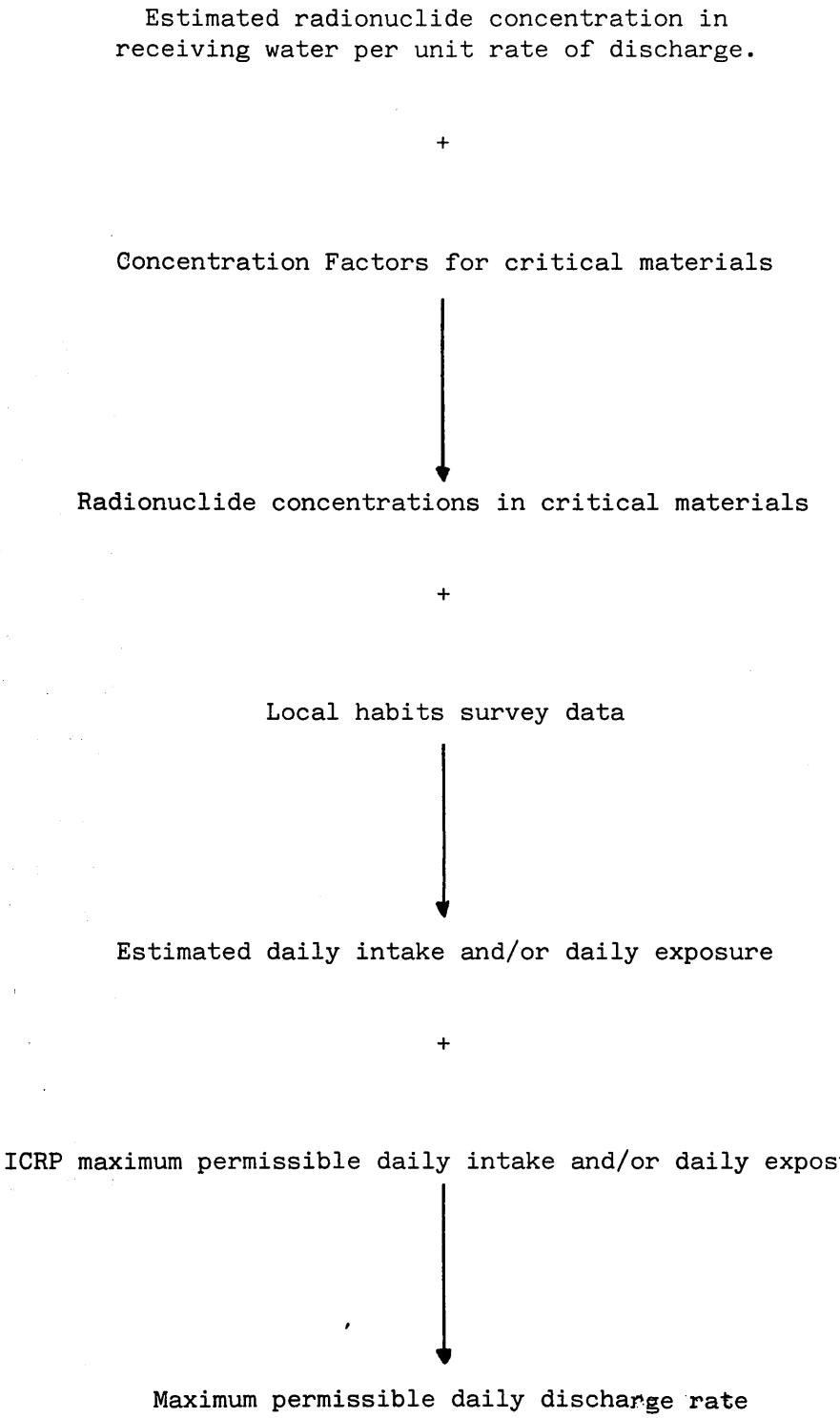


Figure 1.6. The critical pathway approach to the discharge of aqueous radioactive wastes (Pentreath, 1980).

relative to those actually predominating in the edible portions of marine organisms. Usually one combination of critical radionuclides with critical pathways predominates over the others (Pentreath, 1980).

The assessment of potential exposure pathways requires good estimates of the turnover and movement of water at the discharge site and of the concentration factors of the radionuclides in the marine organisms likely to provide a pathway back to man. To make quantitative estimates of aquatic food intake, the working, dietary and recreational habits of the local population are established from habit surveys. The exposure to each radionuclide (internally and externally) is then estimated with respect to unit rate of discharge. Having set the maximum permissible discharge rates, the theoretical values are checked using the measured concentrations of radionuclides in the critical materials (fish, shellfish or sediment).

Since the early 1970's, the critical pathways studied in assessing the radiation doses received by critical groups from Sellafield discharges to sea have included:

i ingestion of laverbread, made from edible seaweed (Porphyra umbilicalis), especially relevant to consumers in south-west Wales,

ii ingestion of seafood (fish, crustaceans, molluscs) harvested in and around the Irish Sea, and

iii external exposure from contaminated muds and sands particularly at low tides.

Habit surveys of these critical groups have revealed that principal consumers in each of the component sub-groups are not necessarily members of other sub-groups. Conversely, members belonging to more than one sub-group do exist and for these the exposures received by each pathway are added to avoid underestimation of total exposure (Hunt, 1985).

Harvesting Porphyra from the Cumbrian coastline was effectively halted in 1972 (Woodhead, 1984). At that time, 130gd^{-1} of laverbread (20% Porphyra) was being consumed within the critical group in south Wales (Mitchell, 1975). Continuous monitoring of this pathway is still carried out, Porphyra being used also as a biological indicator of waste radionuclides.

The principal marine foodstuffs regularly monitored in the seafood critical pathway are cod, plaice, crab, lobster, mussel and winkle. Consumption habits in this pathway have varied frequently since 1972 (Table 1.11), such fluctuations within sub-groups influencing the contribution which seafood ingestion makes towards the overall critical group radiation dose. External exposure of the public requires review of the lengths of time spent on intertidal areas. Such times for Cumbria range from 650hy^{-1} to 3500hy^{-1}, members of this critical group being boat-dwellers in the Ribble estuary (Hunt, 1987). The doses delivered to the skin of fishermen handling their fishing gear (500hy^{-1}) have also been reported recently by MAFF (Hunt, 1985) although this pathway is considered to be of minor importance.

Assessments of critical group doses from seafood ingestion have been subject to calculational changes. For example, in 1980 the National Radiological Protection Board (NRPB) advised that the absorption of plutonium from food to gut was a factor of 5 higher than the previously assumed value (Hunt, 1982). Since then, estimates of critical group doses have increased (Table 1.11) (comparative doses not involving this enhanced Pu absorption factor are also presented). The critical group doses from the ingestion of seafood are presented as percentages of the ICRP-recommended subsidiary dose limit of 5mSvy^{-1}. This limit has been applied to the critical group as long as the committed effective dose equivalent over a lifetime does not exceed 1mSvy^{-1}. If, however, the subsidiary dose limit should be reduced in the future then the fraction of the dose limit received by the critical group would increase accordingly, assuming exposure levels remained constant.

TABLE 1.11

Radiation exposures of critical groups in the vicinity of Sellafield. Based on MAFF reports for 1975-1987 (Mitchell, 1975, 1977; Hetherington, 1976; Hunt, 1977-87). Exposures expressed as % of ICRP subsidiary dose limit of $5mSvy^{-1}$ for members of the public.

Year	Exposure pathway								
	Porphyra/ laverbread	Seafood fish, crustaceans, molluscs	Pu enhancement x5	External Irradiation	Exposure time (hy^{-1}) Unshielded muds	Handling fishing gear	Consumption rates fish	crustacean	molluscs
1972/3	2%	3%	-	7%	-	-	300	-	- $130gd^{-1}$ laverbread
1974	0.2%	14%	-	7%	-	-	224	41 (crab)	-
1976	0.2%	44%	-	8%	-	-	224	41 (crab)	-
1977	0.2%	31% (29%)		4.2%	-	-	224	41 (crab)	
1978	0.1%	26%	29%	3.7%	-	-	170	15	6
1979	0.1%	21%	22%	3.2%	-	-	170	15	6
1980	0.1%	24%	39%	17%	-	-	100	18	18
1981	0.1%	46%	69%	14%	710	-	100	18	45
		*24%	34%				100	18	18
1982	0.1%	34%	54%	12%	650	-	100	18	45
1983	0.1%	29%	45%	11%	650	500	100	18	45
1984	0.002%	11%	17%	9%	650	500	100	18	16
		*24%	40%				100	18	45
1985	0.002%	10%	15%	7%	650	500	100	18	26
		*15%	24%				100	18	45
1986	0.01%	2.4%	6-8%	6-8%	3500	500	100	18	18

Between 1972 and 1976 recommendations from ICRP publication 9 were used. From 1977 to 1986 recommendations from ICRP publication 26 were used. Enhancement factor for Pu in seafood (x5) introduced in 1980 figures (Hunt, 1982) and have been applied to figures back to 1978. The most recent dose limit recommendations from NRPB, (1987) of $1mSvy^{-1}$ would result in above figures being increased by a factor of 5.

Percentage in brackets (1977) refers to dose received if recommendations from ICRP publication 9 were used.

* Figures based on previous years consumption rates.

Prior to 1972-73, the principal exposure pathway to the critical group was via ingestion of laverbread because of the presence in the latter of major activities of ^{106}Ru and ^{137}Cs. Once the collection of Porphyra was stopped,external exposure generated the major dose (7% of ICRP subsidiary limit of $5mSvy^{-1}$) in 1972-73. Since then, however, ingestion of seafood has been the principal dose contributor. During the mid-to-late 1970's ingestion of ^{137}Cs in fish provided the largest fraction to the dose received by the critical group . With introduction of the plutonium gut-transfer enhancement factor, however, along with implementation of the ICRP-26 recommendations (ICRP, 1977) and inclusion of ^{241}Pu data, the ingestion of transuranic nuclides (mainly Pu and Am in mussels and winkles) is now responsible for generation of the major component of critical group dose (Table 1.12). Although α-emitting plutonium discharges from Sellafield have, since 1975, been consistently larger than americuim discharges the latter has generally exerted a greater influence on the critical group dose. This is a direct consequence of the high discharge levels of ^{241}Pu, a β-emitter (Table 1.5) which decays with a half-life of 14 years to produce ^{241}Am. Actual inventories of ^{241}Am in the Irish Sea are therefore greater than the cumulative discharge because of ingrowth from ^{241}Pu. By 1986, ~300 TBq of ^{241}Am had ingrown from ^{241}Pu, whilst 530 TBq had been discharged from Sellafield.

Other transuranics in discharged effluent, curium and neptunium, are present at such low levels (BNF, 1983-87) that they make no significant contribution to critical group doses.

Critical groups more distant from Sellafield, i.e. at Whitehaven, Fleetwood and Morecambe Bay, receive lower doses than the near-site critical groups. Their major pathway of exposure has consistently been from the ingestion of ^{137}Cs in fish rather than from the presence of transuranics.

The maximum dose calculated for seafood ingestion by the Sellafield critical group was 69% of the ICRP-subsidiary limit of $5mSvy^{-1}$ in 1981 (since when the dose has gradually fallen to 6.8% in 1986).

TABLE 1.12

Transuranic contribution to the annual dose received by the Sellafield critical group from the ingestion of seafood (Based on Hunt, 1979-87).

Year	Transuranic dose contribution	Comments
1977	9.6%	Only ^{241}Am reported
1978	28.2%	$^{239+240}Pu$, ^{241}Am reported
1979	18.6%	$^{239+240}Pu$, ^{241}Am reported
1980	61.8%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1981	71.9%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1982	73.7%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1983	72.4%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1984	67.8%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1985	76.7%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported
1986	83.2%	^{238}Pu, $^{239+240}Pu$, ^{241}Pu, ^{241}Am reported

It is only since 1984 that the critical group dose has been below $1mSvy^{-1}$. This trend is expected to continue as the annual discharges from Sellafield are consistently decreasing. Monitoring of critical group exposure pathways will however continue in view of the need to review them continuously in the light of their dynamic nature.

1.3.3 Potential exposure from solid-waste disposal

One of the options for disposal of radioactive wastes, namely dumping at sea, has been carried out in the north-east Atlantic for over thirty years. Sea disposal is subject to national and international controls in order to minimise the radiological effects on man and the environment.

Several locations have been used since 1949 for disposal operations (Figure 1.7) involving several European countries: UK, Belgium, France, Netherlands, Federal Republic of Germany, Italy, Sweden and Switzerland of which only the UK was involved in every dumping exercise (NEA, 1985). The site most recently used (1971-1982) was a rectangular area bounded by latitudes 45°50'N-46°10'N and longitudes 16°00'W-17°30'W with an average water depth of ~ 4400m and an average residual bottom water outflow initially to the north-west of $1-2cms^{-1}$ (NEA, 1985). Dumping of solid radioactive waste in the north-east Atlantic was suspended in 1983 because of industrial action by the National Union of Seamen (Holliday, 1984) and resumption of this practice depends on the outcome of further international reviews (Holliday, 1984).

The sources of the radioactive waste dumped in the north-east Atlantic are principally from nuclear power plant and fuel cycle operations and from radionuclide use in medicine, research and industry (NEA, 1985). The waste includes items with surface contamination, chemically incorporated radioactivity and induced radioactivity. Waste transuranics are predominantly produced by the nuclear fuel reprocessing operations.

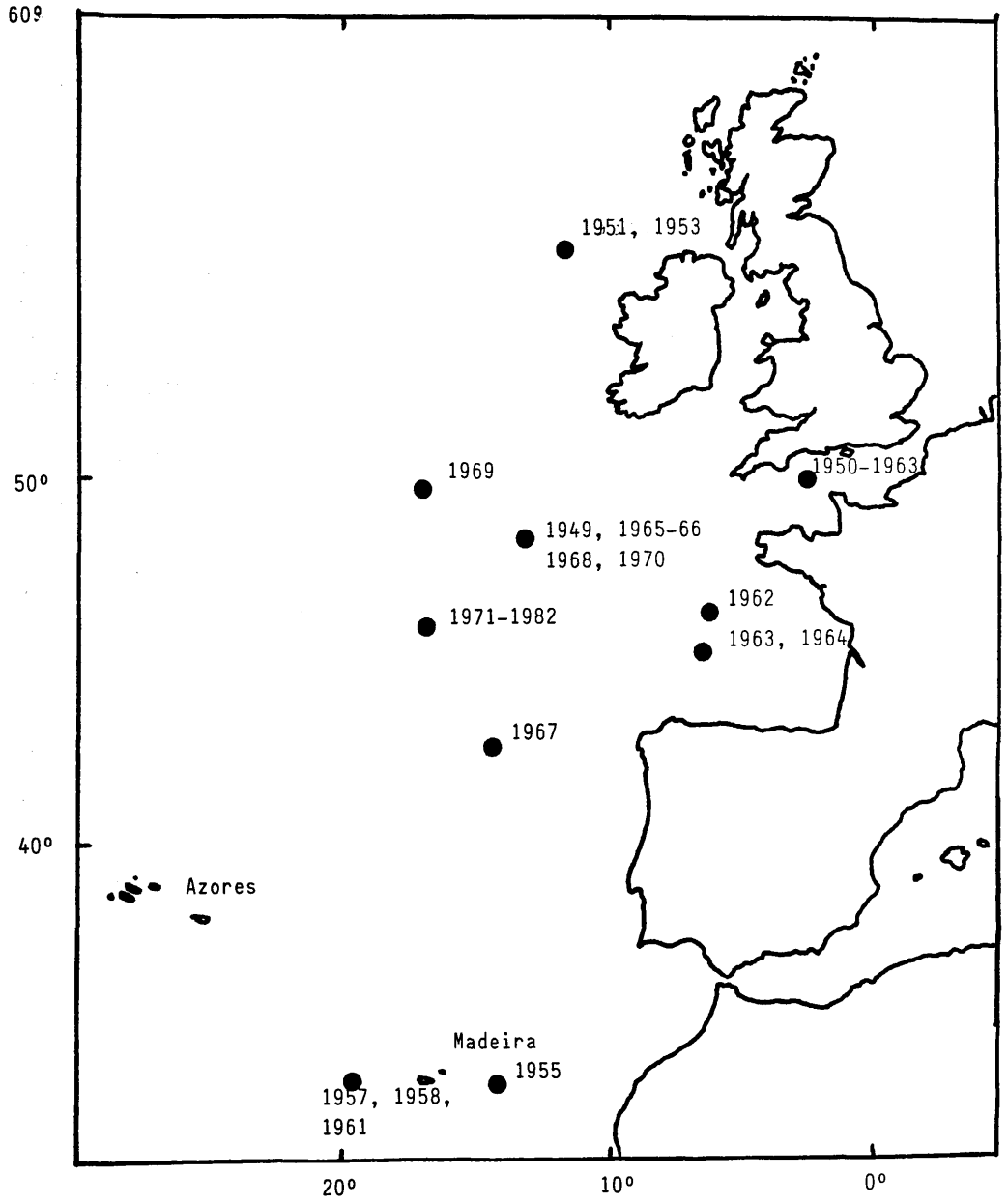


Figure 1.7. North-east Atlantic radioactive waste disposal sites (NEA, 1985).

The radionuclide composition of the waste dumped between 1949 and 1982 (Figures 1.8 and 1.9) reveals that over 96% of the alpha activity disposed of is attributable to plutonium isotopes and ^{241}Am, with ^{241}Pu and tritium contributing 87% of the β/γ activity (Holliday, 1984). By 1982, 666 TBq of total-α activity had been disposed of to the north-east Atlantic (cf. Pu discharged from Sellafield, Cumbria 1960-1985, 708 TBq (Table 1.5)).

The waste packages used are designed to provide both shielding and containment of the waste during handling and transport and also a means of delivering the waste to the seabed ($\sim$4400m depth) without loss during downward travel. Packages are produced to two basic designs, either containing air spaces (voids) or monolithic (waste incorporated in a matrix of cement, bitumen or polymer). The majority of the wastes disposed of in the north-east Atlantic has been contained in void-containing packages (NEA, 1985).

Radiological assessment of the north-east Atlantic dump site requires the use of appropriate predictive mathematical models. The framework of such a model, as used by the NEA in reviewing the suitability of the north-east Atlantic dump site (Figure 1.10), subdivides the 'system' (the waste and the environment) into component parts. The waste package model is used to predict the rates of release of the radionuclides into the ocean (Figure 1.11), these rates then providing the input to the composite ocean dispersion and sediment interaction model which generates predicted radionuclide concentrations which are used to calculate doses to man and marine organisms.

In view of the long time periods of interest in the radiological assessment of sea dumping, it is appropriate to consider not only those exposure pathways which could exist at present but also those which could become important in the future. In modelling the north-east Atlantic dump site, the 'actual' pathway considered is via mollusc consumption and the 'hypothetical' pathway relates to consumption of deep sea fish and plankton (NEA, 1985).

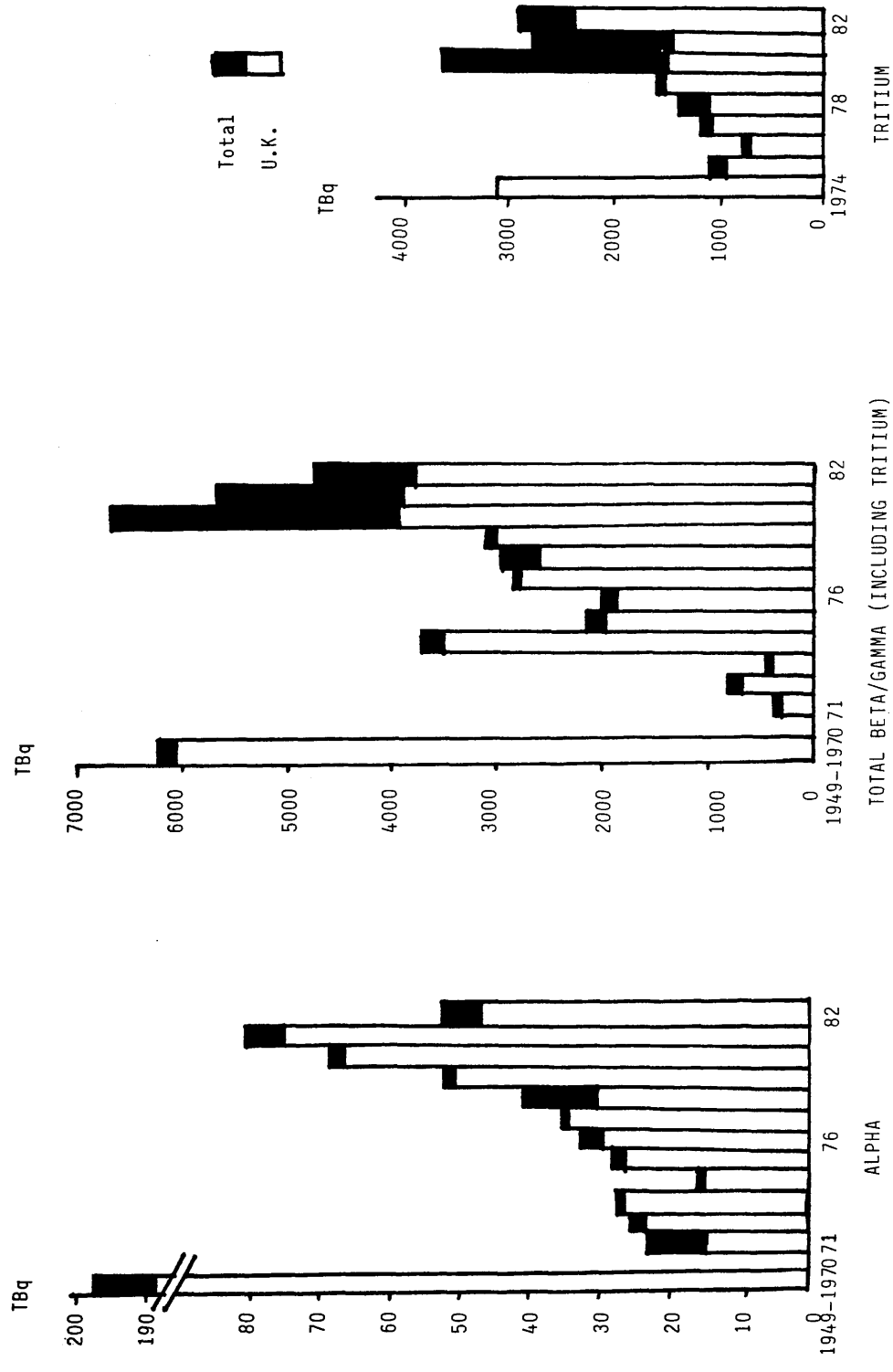


Figure 1.8. Quantities of radioactive waste dumped by year (Holliday, 1984).

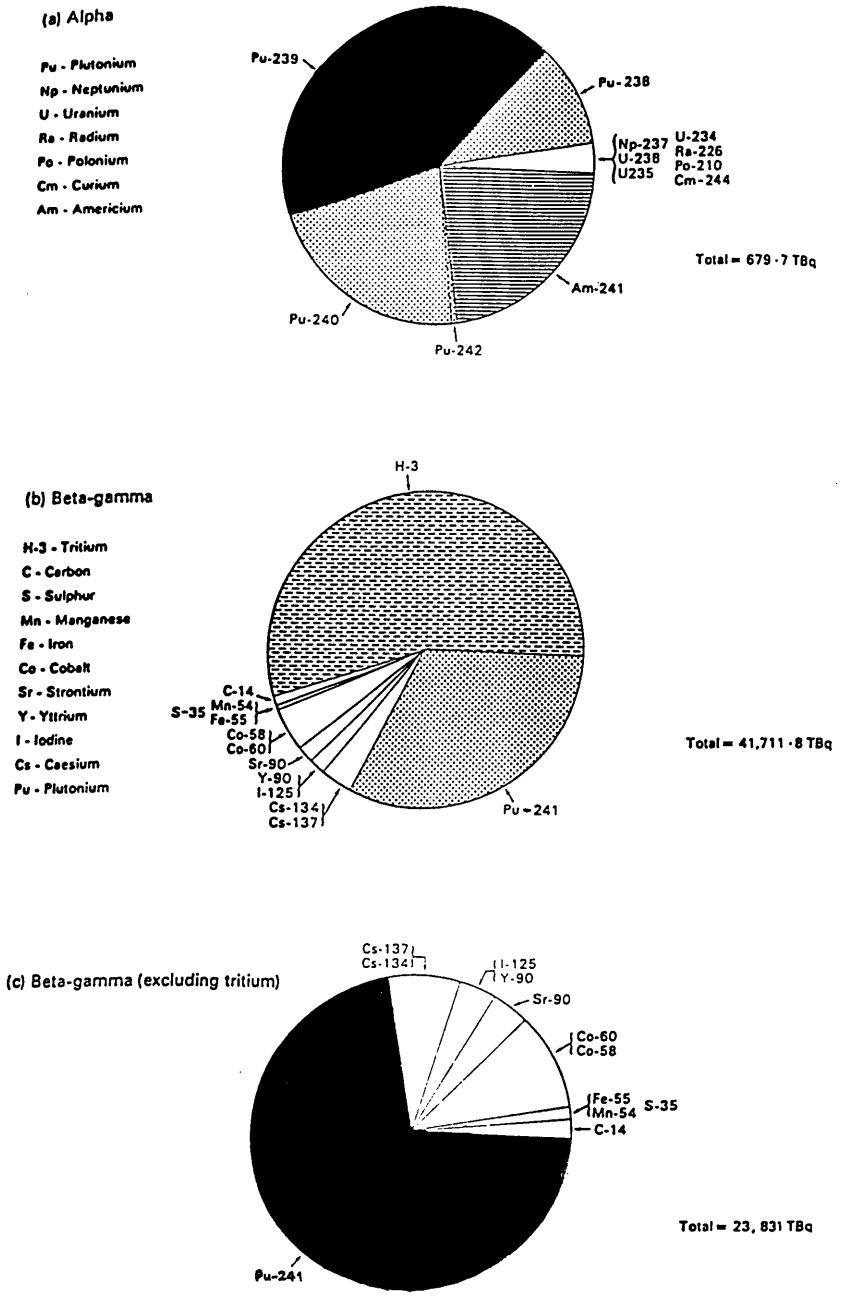


Figure 1.9. Radionuclides dumped 1949 - 1982 (Holliday, 1984).

Parts of system included in model	Model	Major processes included in model
Canister and lining Waste form	Waste Package	Canister corrosion Degradation of package linings and caps Release of radionuclides from waste forms
	rates of release of radionuclides into the ocean, as a function of time	
Bottom sediments Benthic boundary layer (water and particulates) Open ocean (water and suspended particulates)	Ocean Dispersion	Diffusion and advection Interactions between radionuclides and suspended particulates and bottom sediments
	radionuclide concentration in water and sediments, as a function of time.	
Exposure pathways - sea foods, beaches atmosphere, salt, water Marine organisms	Dose to man and Organisms	Reconcentration of radionuclides in marine organisms, beach sediments, aerosols Radionuclide intake and metabolism by man and organisms

Figure 1.10. Modelling Framework used in the radiological assessment (NEA, 1985).

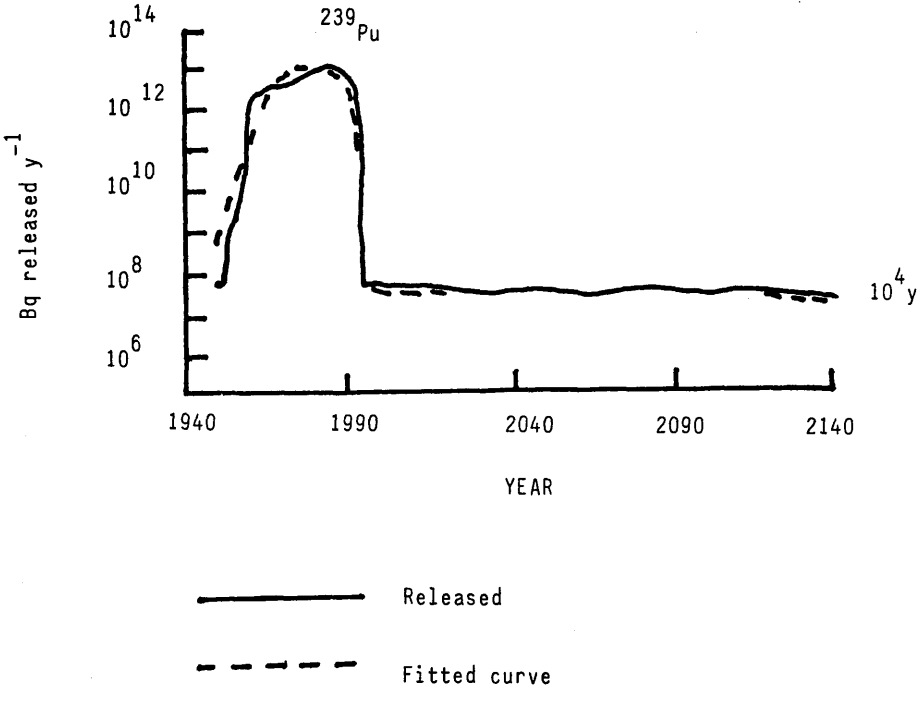


Figure 1.11. Release rates from past dumping practices (NEA, 1985).

Three dumping scenarios have been modelled, i.e.

Scenario A - past dumping

Scenario B - past dumping plus 5 years' dumping at rates typical of recent years

Scenario C - past dumping plus 5 years' dumping at rates 10 times those typical of recent years.

The findings (Tables 1.13 and 1.14, Figures 1.12 and 1.13) are that doses via 'actual' pathways from all three scenarios are less than or equal to $10^{-7}Svy^{-1}$, with the dominant contributors to dose being the transuranics ^{237}Pu and ^{241}Am in molluscs.

The calculated peak doses via 'actual' pathways from all three scenarios arise at times between 100 and 500 years after commencement of dumping. These peak doses are predicted to occur in the Antarctic Ocean following deep water movement from the dump site along isopycnal surfaces to outcrop at the poles. Concentrations in the Arctic are lower than in the Antarctic because the latter area receives water (and hence waste nuclides) which have travelled north then west and south as well as those moving directly south (NEA, 1985).

Doses via the 'hypothetical' deep fish pathway (fish caught in the vicinity of the dump site) are higher and occur earlier than those calculated for the 'actual' pathways. The dose maximum occurs immediately after dumping has ceased and before dispersion, decay and particle scavenging have reduced radionuclide concentrations at the dump site location.

Modelling of the north-east Atlantic dump site has shown that critical group doses from all three scenarios are at all times very small fractions of the committed effective dose equivalent of $1mSvy^{-1}$ (recommended dose limit for members of the public). Preliminary calculations have also indicated that, if dumping

TABLE 1.13

Peak annual doses to individual members of critical groups, 'actual' pathways (NEA, 1985).

Radionuclides	Peak annual individual dose (Sv)	Time of peak dose (years after dumping started)	Exposure pathway
Scenario A - past dumping			
^{239}Pu	$9\ 10^{-9}$	$2\ 10^{2}$	MOLL
^{241}Am	$7\ 10^{-9}$	$2\ 10^{2}$	MOLL
^{240}Pu	$5\ 10^{-9}$	$2\ 10^{2}$	MOLL
^{210}Po	$8\ 10^{-10}$	$5\ 10^{2}$	CRUST
^{238}Pu	$6\ 10^{-10}$	$2\ 10^{2}$	MOLL
^{14}C	$5\ 10^{-10}$	$5\ 10^{2}$	FISH
^{242}Pu	$1\ 10^{-10}$	$2\ 10^{2}$	MOLL
All radionuclides	$2\ 10^{-8}$	$2\ 10^{2}$	MOLL
Scenario B - past dumping plus 5 years' dumping at rates typical of recent years			
^{241}Am	$1\ 10^{-8}$	$2\ 10^{2}$	MOLL
^{239}Pu	$1\ 10^{-8}$	$2\ 10^{2}$	MOLL
^{240}Pu	$6\ 10^{-9}$	$2\ 10^{2}$	MOLL
^{14}C	$2\ 10^{-9}$	$5\ 10^{2}$	FISH
^{210}Po	$1\ 10^{-10}$	$5\ 10^{2}$	CRUST
^{238}Pu	$7\ 10^{-10}$	$2\ 10^{2}$	MOLL
^{242}Pu	$1\ 10^{-10}$	$2\ 10^{2}$	MOLL
All radionuclides	$3\ 10^{-8}$	$2\ 10^{2}$	MOLL
Scenario C - past dumping plus 5 years' dumping at 10 times rates typical of recent years			
^{239}Pu	$6\ 10^{-8}$	$5\ 10^{2}$	MOLL
^{241}Am	$4\ 10^{-8}$	$2\ 10^{2}$	MOLL
^{240}Pu	$3\ 10^{-8}$	$5\ 10^{2}$	MOLL
^{210}Po	$5\ 10^{-9}$	$5\ 10^{2}$	CRUST
^{14}C	$5\ 10^{-9}$	$5\ 10^{2}$	FISH
^{238}Pu	$3\ 10^{-9}$	$2\ 10^{2}$	MOLL
^{242}Pu	$6\ 10^{-10}$	$5\ 10^{2}$	MOLL
^{226}Ra	$5\ 10^{-10}$	$5\ 10^{2}$	FISH
^{210}Pb	$4\ 10^{-10}$	$5\ 10^{2}$	FISH
^{241}Pu	$3\ 10^{-10}$	$1\ 10^{4}$	MOLL
^{227}Ac	$1\ 10^{-10}$	$5\ 10^{2}$	BEACH (skin)
All radionuclides	$1\ 10^{-7}$	$2\ 10^{2}$	MOLL

Notes

1. Doses less than 10^{-10} Sv y^{-1} are not shown.
2. All doses are committed effective dose equivalents from one year's intake of radionuclides, except where otherwise indicated.
3. The 'all radionuclides' dose is the dose via the mollusc pathway, summed over all radionuclides.
4. Dumping in the NE Atlantic started in 1949.

TABLE 1.14

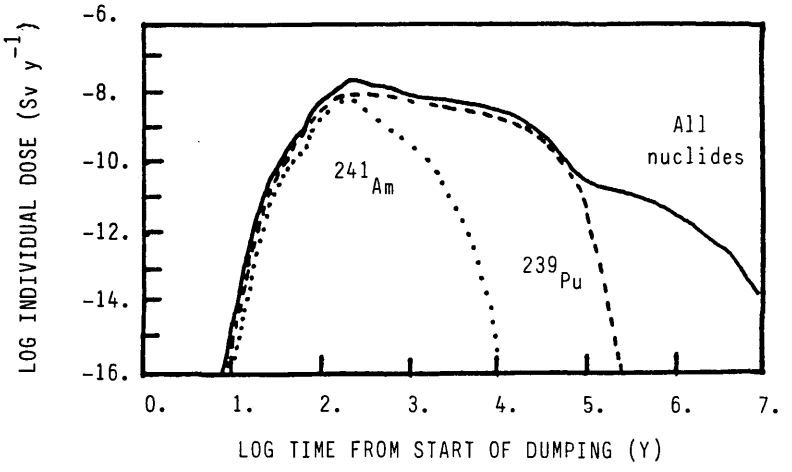
Peak annual doses to individual members of critical groups, 'hypothetical' pathways. (NEA, 1985)

FISH-D			.PLANK		
Radionuclides	Peak annual individual dose (Sv)	Time of peak dose (years after dumping started)	Radionuclides	Peak annual individual dose (Sv)	Time of peak dose (years after dumping started)
Scenario A - past dumping					
^{239}Pu	$1\ 10^{-8}$	$4\ 10^{1}$	^{239}Pu	$9\ 10^{-11}$	$2\ 10^{2}$
^{241}Pu	$7\ 10^{-9}$	$4\ 10^{1}$	^{240}Pu	$5\ 10^{-11}$	$2\ 10^{2}$
^{240}Pu	$6\ 10^{-9}$	$4\ 10^{1}$	^{241}Am	$2\ 10^{-11}$	$2\ 10^{2}$
^{241}Am	$6\ 10^{-9}$	$5\ 10^{1}$	^{210}Po	$1\ 10^{-11}$	$5\ 10^{2}$
^{14}C	$3\ 10^{-9}$	$5\ 10^{1}$	^{238}Pu	$6\ 10^{-12}$	$2\ 10^{2}$
^{238}Pu	$2\ 10^{-9}$	$4\ 10^{1}$	^{14}C	$3\ 10^{-12}$	$5\ 10^{2}$
^{137}Cs	$2\ 10^{-9}$	$4\ 10^{1}$	^{210}Pb	$1\ 10^{-12}$	$5\ 10^{2}$
^{226}Ra	$7\ 10^{-10}$	$5\ 10^{1}$	^{242}Pu	$1\ 10^{-12}$	$2\ 10^{2}$
^{242}Pu	$1\ 10^{-10}$	$5\ 10^{1}$	^{227}Ac	$9\ 10^{-13}$	$5\ 10^{4}$
All radionuclides	$3\ 10^{-8}$	$4\ 10^{1}$	All radionuclides	$2\ 10^{-10}$	$2\ 10^{2}$
Scenario B - past dumping plus 5 years' dumping at typical rates					
^{241}Pu	$1\ 10^{-8}$	$4\ 10^{1}$	^{239}Pu	$1\ 10^{-10}$	$2\ 10^{2}$
^{239}Pu	$1\ 10^{-8}$	$5\ 10^{1}$	^{240}Pu	$6\ 10^{-11}$	$2\ 10^{2}$
^{14}C	$9\ 10^{-9}$	$5\ 10^{1}$	^{241}Am	$3\ 10^{-11}$	$3\ 10^{2}$
^{241}Am	$7\ 10^{-9}$	$5\ 10^{1}$	^{210}Po	$2\ 10^{-11}$	$5\ 10^{2}$
^{240}Pu	$6\ 10^{-9}$	$4\ 10^{1}$	^{14}C	$8\ 10^{-12}$	$5\ 10^{2}$
^{137}Cs	$3\ 10^{-9}$	$5\ 10^{1}$	^{238}Pu	$7\ 10^{-12}$	$2\ 10^{2}$
^{238}Pu	$3\ 10^{-9}$	$4\ 10^{1}$	^{210}Pb	$2\ 10^{-12}$	$5\ 10^{2}$
^{226}Ra	$9\ 10^{-10}$	$5\ 10^{1}$	^{242}Pu	$1\ 10^{-12}$	$2\ 10^{2}$
^{242}Pu	$2\ 10^{-10}$	$5\ 10^{1}$	^{227}Ac	$1\ 10^{-12}$	$5\ 10^{4}$
All radionuclides	$5\ 10^{-8}$	$5\ 10^{1}$	All radionuclides	$2\ 10^{-10}$	$2\ 10^{2}$
Scenario C - past dumping plus 5 years' dumping at 10 times typical rates					
^{239}Pu	$7\ 10^{-8}$	$5\ 10^{1}$	^{239}Pu	$6\ 10^{-10}$	$5\ 10^{2}$
^{241}Pu	$4\ 10^{-8}$	$5\ 10^{1}$	^{240}Pu	$3\ 10^{-10}$	$5\ 10^{2}$
^{240}Pu	$4\ 10^{-8}$	$5\ 10^{1}$	^{241}Am	$1\ 10^{-10}$	$2\ 10^{2}$
^{241}Am	$4\ 10^{-8}$	$6\ 10^{1}$	^{210}Po	$1\ 10^{-10}$	$5\ 10^{2}$
^{14}C	$3\ 10^{-8}$	$6\ 10^{1}$	^{238}Pu	$3\ 10^{-11}$	$3\ 10^{2}$
^{238}Pu	$1\ 10^{-8}$	$5\ 10^{1}$	^{14}C	$2\ 10^{-11}$	$5\ 10^{2}$
^{137}Cs	$7\ 10^{-9}$	$5\ 10^{1}$	^{210}Pb	$9\ 10^{-12}$	$5\ 10^{2}$
^{226}Ra	$5\ 10^{-9}$	$5\ 10^{1}$	^{242}Pu	$6\ 10^{-12}$	$5\ 10^{2}$
^{242}Pu	$8\ 10^{-10}$	$5\ 10^{1}$	^{227}Ac	$4\ 10^{-12}$	$5\ 10^{4}$
^{210}Po	$4\ 10^{-10}$	$8\ 10^{1}$	^{241}Pu	$3\ 10^{-12}$	$1\ 10^{2}$
^{90}Sr	$2\ 10^{-10}$	$5\ 10^{1}$	^{226}Ra	$5\ 10^{-13}$	$5\ 10^{2}$
^{60}Co	$2\ 10^{-10}$	$5\ 10^{1}$	^{229}Th	$5\ 10^{-13}$	$5\ 10^{5}$
All radionuclides	$2\ 10^{-7}$	$5\ 10^{1}$	All radionuclides	$1\ 10^{-9}$	$2\ 10^{2}$

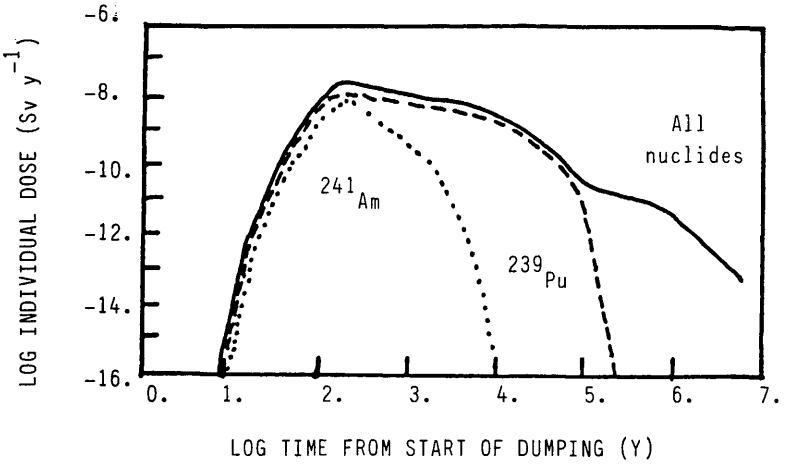
Notes

1. Doses less than 10^{-10} Sv y^{-1} are not shown.
2. All doses are committed effective dose equivalents from one year's intake of radionuclides, except where otherwise indicated.
3. The "all radionuclides' dose is the dose via the mollusc pathway, summed over all radionuclides.
4. Dumping in the NE Atlantic started in 1949.

SCENARIO A - PAST DUMPING



SCENARIO B - PAST DUMPING PLUS FIVE YEARS DUMPING AT RATES TYPICAL OF RECENT YEARS



SCENARIO C - PAST DUMPING PLUS FIVE YEARS DUMPING AT RATES TEN TIMES THOSE TYPICAL OF RECENT YEARS

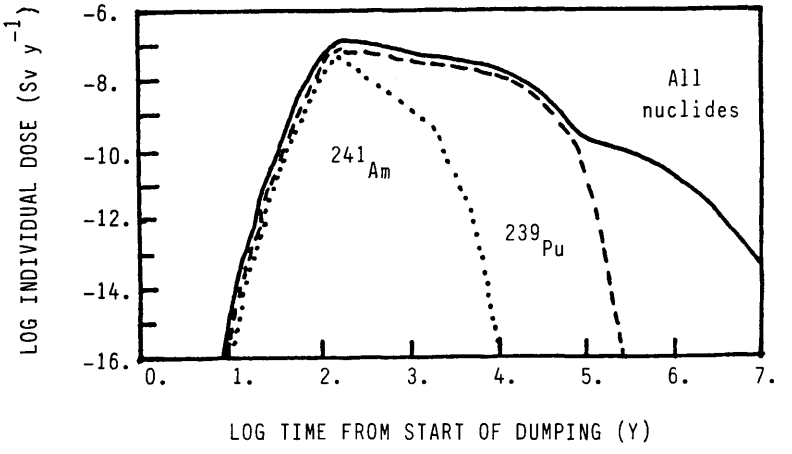
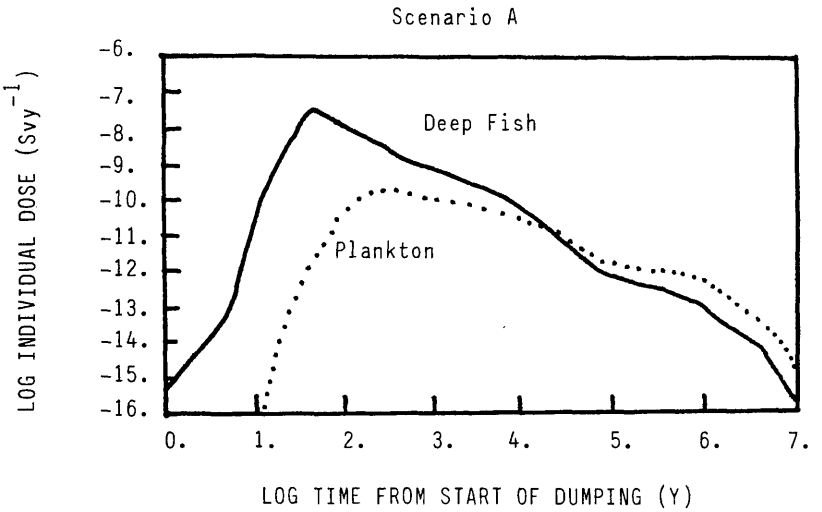
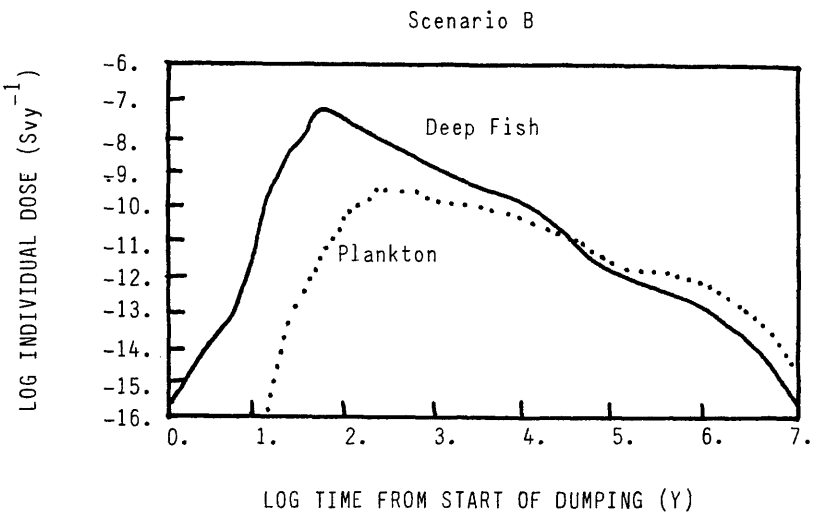


Figure 1.12. Doses to individuals in critical groups via the mollusc pathway (NEA, 1985).





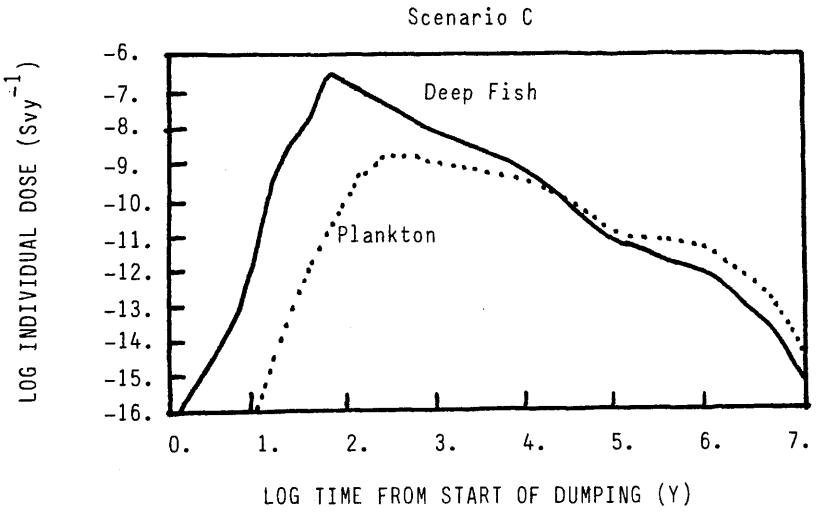


Figure 1.13. Doses to individual members of critical groups via "hypothetical" pathways (NEA, 1985).

were to be continued for 500 years at present rates, the doses to individuals would still be more than three orders of magnitude below the appropriate limits (NEA, 1985).

Although there are large differences between the doses received by the critical groups exposed to low level liquid discharges from Sellafield and those received from deep sea radioactive waste disposal, the principal contributing radionuclides in both cases are the isotopes of the transuranic elements plutonium and americium. Thus, in many ways, the marine behaviour of transuranic nuclides is fundamental to radiological assessment of future waste disposal practices.

1.4 TRANSURANIC BIOKINETICS IN MARINE ORGANISMS

1.4.1 Introduction

In describing the kinetics of transuranic nuclides in marine organisms, it is appropriate to begin with an explanation of some of the terminology employed in this field.

Biological half-times are used to quantify the turn-over times and rates of depuration exhibited by an organism in cycling specific nuclides. The biological half-time is analogous to the radioactive half-life of a nuclide, e.g. a biological half-time of 30 days indicates the loss after 30 days of 50% of the quantity of 'labelled' atoms present at time zero. This term, $T_{b½}$, when combined with the half-life of a particular radionuclide (Tp), produces the effective half-life (Te) the various parameters being related via the following equation:

$$Te = \frac{T_{b½} \times Tp}{T_{b½} + Tp}$$

Comparison of laboratory-derived biological half-times with those obtained from field experiments for plutonium in mussels has been performed by Fowler et al. (1975). The laboratory studies

revealed two loss compartments, 35% of the plutonium being lost with a biological half-time of 7 days and 65% with $T_{b½}$ 776 days. The field experiments produced much shorter half-times, 70% of $T_{b½}$ ~ 14 days and 30% of $T_{b½}$ 192 days. Clifton et al. (1983) carried out further field experiments involving the loss of plutonium from mussels and found different biological half-time values of ~50% $T_{b½}$ ~700 days once the data had been corrected for weight changes during the experiment. Clearly, further studies are required with emphasis on the physiological and biochemical systems present in such organisms, to help further an understanding of depuration processes. With respect to biological half-times, Phillips (1980) emphasised that laboratory derived values could only be considered as order-of-magnitude approximations. Field measurements of $T_{b½}$ are of greatest value producing figures which are fully representative of natural conditions and values which can be quite distinct from those obtained via laboratory-based experiments.

The concentration factor (CF) of a radionuclide in biological materials is defined as

$$CF = \frac{\text{Activity per unit weight of fresh weight of the organism}}{\text{Activity per unit weight of water}}$$

It should be noted that the CF does not imply that all of the radionuclide within the organism is concentrated from the water alone. Rather it simply relates the concentration in the organism - whether derived by accumulation from sea water, particulate matter or from food (or any combination thereof) - to that in the medium in which it lives. Concentration factors are used widely to assess the uptake (or accumulation) of radionuclides by aquatic organisms, particularly with regard to their role in providing an exposure pathway to man via seafood ingestion. The use of CFs in mathematical models used in critical pathway analysis (Coughtrey and Thorne, 1983) is very convenient because of its arithmetical simplicity. It does, however, have certain limitations since it assumes some form of steady state condition

in the environment and that the rate of input of a radionuclide is more or less constant.

Although CFs are regularly reported in biokinetic studies (See Tables 1.15 to 1.19), there is still a lack of standardisation and understanding of their use (Freke, 1967; Beasley and Cross, 1980; Pentreath, 1984). Beasley and Cross (1980) identified four different conditions on which CFs have been based, i.e. on: 1) dissolved concentrations in the water, 2) total concentrations in the water, 3) concentrations in food organisms, and 4) concentrations in sediment. Thus the interpretation of CFs often depends on the author's subjective view of the source of element supply. The major cause of variance in CF data is related to whether filtered or unfiltered seawater values are used in deriving the denominator of the parameter (IAEA, 1985).

Differences commonly occur between CFs obtained under field and laboratory-controlled conditions. There are many reasons for these discrepancies and the use of CFs should be approached critically and with caution (Freke, 1967; Beasley and Cross, 1980; IAEA, 1985).

Hence, the use of the parameter CF depends on an understanding of the physical and chemical factors involved in the uptake of nutrients and other materials by aquatic organisms and on an understanding of how the radionuclide concentrations in water or sediments are derived.

The transfer factor (TF) can be expressed in terms of radionuclide concentration in the food (prey) and in the predator such that

$$TF = \frac{f\ r'}{(k + \lambda)}$$

where r' - fractional feeding rate
f - fraction of radionuclide absorbed
k - biological excretion constant
λ - physical decay constant.

and can be used as an alternative approach to CF (Pentreath, 1984).

The interpretation of TF again poses some major difficulty because accumulation from ingested sediment must be differentiated from that resulting from desorption from interstitial waters (Pentreath, 1984). In estimating TFs, as with CFs, steady state conditions must be assumed.

Further biokinetic parameters mentioned in the following sections include the speciation of the nuclide, which influences the extent of its bioavailability to the organism. Speciation studies are concerned with the chemical form of the nuclide and with the nuclide source (food, sea water, sediment).

1.4.2 Neptunium

Only a relatively small published data set exists on neptunium uptake by marine organisms. The study of neptunium in environmental samples has been reported from the immediate environs of Sellafield (1.81TBq of ^{237}Np discharged into the Irish Sea between 1981 and 1985 (BNF, 1982-86)). Pentreath and Harvey, (1981) found that ^{237}Np was markedly accumulated by biological materials. As ^{237}Np was detected in the internal tissues of the starfish, Asterias rubens, and the sea urchin, Echinus esculentus, accumulation of ^{237}Np involves further mechanisms other than adsorption on to external surfaces. Neptunium appeared to be biologically less available than $^{239+240}Pu$, a conclusion which at the time was considered presumptious (Pentreath and Harvey, 1981) but since has been validated.

Laboratory radiotracer experiments amongst various marine trophic levels have provided much needed information on bioconcentration of neptunium by marine organisms (Table 1.15). Studying transuranic biokinetics in marine phytoplankton, Fisher et al. (1983a) found a striking contrast between ^{235}Np and the other three radionuclides tested (^{237}Pu, ^{241}Am and ^{252}Cf) in that the CF for neptunium ($\sim$ 150) was around 10^3 - 10^4 times lower than those for the other nuclides. They suggested that this difference could reflect neptunium's existence in their sea water system as an anionic

TABLE 1.15

Concentration factors of neptunium from labelled sea water to marine organisms

Organism/Species	Exposure Time (days)	CF	Reference
Phytoplankton	4	150	Fisher et al., 1983a
Zooplankton	2-6	14-20	Fowler and Aston, 1982
Polychaete:			
Arenicola marina	13	2	Germain et al., 1987
Molluscs:			
Mytilus galloprovincialis	50	15-20	Guary and Fowler, 1977
Cerastoderma edule	13	40	Germain et al., 1987
Crustaceans:			
Lysmata seticaudata	50	15-20	Guary and Fowler, 1977
Cancer pagarus	50	30	Guary and Fowler, 1978

complex similar to those for uranium and technetium (Holm, 1981), i.e. largely as $UO_2(CO_3)_3^{4-}$ (Stumm and Brauner, 1975) and pertechnetate (TcO_4^-) (Till et al., 1979) respectively. Both uranium and technetium have correspondingly low concentration factors in phytoplankton (3-23(Szefer and Ostrowski, 1980) and ~ 20 (Fisher, 1982) respectively).

Fowler and Aston (1982) found that ^{235}Np concentration factors for macrozooplankton (viz.euphausiids) were in the range 14-20 at the termination of the uptake exposure period (2-6 days), values which are much lower than those for plutonium (~ 50) and americium (~ 125) measured at comparable times in the same species (Fowler and Heyraud, 1974; Fowler et al., 1975). Zooplankton was also noted to lose all its accumulated ^{235}Np with its moulted exoskeleton material which did not appear to bind the neptunium to itself firmly. Furthermore, assimilation of ingested neptunium was found to be poor since 95% of the radioisotope initially ingested was excreted with the faeces after only 30 hours. (Fowler and Aston, 1982).

The biokinetic behaviour of ^{237}Np has been studied in mussels, shrimps and crabs by Guary and Fowler (1977, 1978). Direct uptake from water by both the mussel and shrimp appeared to be much less than that for plutonium, concentration factors of 15 to 20 being observed for both species after exposure for 50 days. The distribution of ^{237}Np in the mussel was similar to that of plutonium in that high concentrations were found in the shell and lesser amounts in the flesh. The exoskeleton of the shrimp accumulated the major portion of neptunium and loss rates were strongly influenced by moulting. The crab accumulated the nuclide largely by adsorption (CF exoskeleton = 70; CF whole animal = 30, after 50 day uptake period) and Guary and Fowler (1978) concluded that the results indicated a behaviour very similar to that for plutonium. Germain et al. (1987) exposed the polychaete, Arenicola marina, and the cockle, Cerastoderma edule, to sea water labelled with ^{239}Np. After 13 days exposure, the cockles exhibited a CF of ~ 40, 88% of which was found on the shell, and the polychaete worms a CF of ~ 2.

From the information presented here it appears that neptunium is largely associated with the external surfaces, such as the shell and exoskeleton of marine organisms, but to a lesser extent than the other transuranic nuclide (Pu, Am, Cm, Cf). A small fraction of neptunium, however, can be transferred across biological membranes and incorporated into internal tissues.

1.4.3 Plutonium

As discussed earlier, plutonium is the most widely studied of the environmental transuranic elements because of its presence in fallout from nuclear weapons tests and in wastes produced by the nuclear power industry. There is a resulting wealth of data on environmental samples; however, some results are of limited value in assessing biological availability or in understanding the mechanisms of accumulation and loss, because of the probability of contamination of some samples with sedimentary materials which tend to obscure the effects of biological assimilation.

Fallout levels of plutonium ($^{239+240}Pu$) in surface waters (~ 1-2 m) in the Pacific Ocean (0.08-0.80 $\mu Bqkg^{-1}$ water) have been reported by Fowler et al. (1983) and Livingston et al. (1987). Previous particulate-associated plutonium studies in the Pacific by Krishwaswami et al. (1976) and Koide et al. (1981) provided plutonium concentrations 3-15 times lower than above. Livingston et al. (1987) assigned this difference to be either an artefact related to the type of filter used at the time of sample collection or a seasonal effect operating to differing extents during the individual cruises.

A range of 0.01-3.1 $Bqkg^{-1}$ (wet weight) for the concentration of fallout ^{239}Pu in phytoplankton (Woodhead, 1984) is supported by the findings of Fowler et al. (1983) who obtained a concentration of 0.103 $Bqkg^{-1}$ (wet) for $^{239+240}Pu$ in phytoplankton (< 60μm) in the N.E. Pacific Ocean. (Fowler et al. (1983) plutonium concentration figures have been converted from $pCikg^{-1}$ (dry) to $Bqkg^{-1}$ (wet) using the wet:dry ratio for phytoplankton of 10 quoted by Fisher et al. (1983a). A review of published

concentration factors for plutonium in phytoplankton from a variety of the world's seas and oceans shows a consensus of values between 10^5 - 10^6 (Gromov, 1976; Krishnaswami et al., 1976; Santschi et al., 1980). This range is in accordance with the findings of Fisher et al. (1983a) from experimental studies on the interactions of marine plankton with transuranic elements. Fisher et al. (1983b) also calculated CFs for Mediterranean phytoplankton from previous Work performed by Holm et al. (1980), producing a value of 2.7×10^5. Based on laboratory tracer experiments, Fisher et al. (1983b) noted that both forms of plutonium, Pu (III - IV) and Pu (V - VI), were rapidly accumulated by the algal cells in roughly equal amounts.

Zooplankton concentrate fallout plutonium to a lesser extent than do phytoplankton, giving a range of 0.003-0.102 $Bqkg^{-1}$ (wet) (Pillai et al., 1964; Wong, 1971; Noshkin, 1972; Higgo et al., 1977; Fowler et al., 1983). Whole euphausiid versus sea water $^{239+240}Pu$ concentrations result in a CF value of 100 (Higgo et al., 1977). In a study of zooplankton (mainly copepods) in the Pacific Ocean, a CF value of 10^4 was estimated (Fowler et al., 1983). This value is higher than those quoted by Fisher and Fowler (1985) indicating CF values of $< 1x10^4$ for copepods.

Experimental studies on the euphausiid Meganyctiphanes norvegica have shown that they accumulate both ^{237}Pu (IV) and (VI) directly from sea water; approximately equal concentration factors were attained with each form. It was also observed that both forms were poorly retained from labelled food (Fowler and Heyraud, 1974). The accumulation process from water is by passive adsorption onto exoskeleta, the same process being exhibited when using americium (Fisher et al., 1983a).

Seaweed accumulates plutonium to a similar extent as does zooplankton, having a range of CF's from $5x10^2$ to $5x10^3$ (IAEA, 1985), based on measurements from many sites throughout the world (Pillai et al., 1964; Wong et al., 1972; Noshkin, 1972; Nilsson et al., 1981 Pentreath et al., 1982; Aarkrog et al., 1982) and covering concentration values from 0.010 $Bqkg^{-1}$ (wet) in Pacific Ocean sargassum seaweed

(Noshkin, 1972) to 80.4 $Bqkg^{-1}$ (wet) in the vicinity of Sellafield (Hamilton and Clifton, 1980) (Wet:dry ratio of 7.5 (Cherry and Shannon, 1974) was used in calculating Sellafield seaweed figure).

Early studies on the accumulation of plutonium by benthic algae (Zlobin, 1971) concluded that the element was absorbed rather than adsorbed. More recent data, with different species, suggest that adsorption is the primary mechanism of accumulation, the plutonium being concentrated in extremely thin outer surface layers of the laminae, passing through the surface boundary films by attachment to large macromolecules or micelles (Wong et al., 1972; Hodge et al., 1974; Folsom et al., 1975; Folsom and Hodge, 1975).

The use of mussels as sentinels of marine pollution has been explored for a variety of environmental contaminants including the transuranic radionuclides, mainly plutonium and americium (Goldberg et al., 1978, 1983). Findings to date indicate that plutonium derived from atmospheric fallout and released from nuclear reprocessing plants are detectable in various species of Mytilus from many geographic regions (Goldberg et al., 1978, 1983; Hamilton and Clifton, 1980; Ballestra et al., 1982; Clifton et al., 1983; BNF, 1977-87; Hunt, 1979-1987). Mussels collected in 1977 and 1978 from the west coast of the United States generally had higher levels of plutonium in their soft parts than east coast mussels (Goldberg et al., 1983). Hamilton and Clifton (1980) measured the distribution of plutonium in Mytilus edulis sampled from the Esk estuary at Ravenglass, 10km south of Sellafield. (Using their '% water' figures for the tissues sampled, the plutonium concentrations were converted from $pCig^{-1}$ (dry) to $Bqkg^{-1}$(wet)). The total soft part plutonium concentration was $34Bqkg^{-1}$ $^{239+240}Pu$ in 1977 and increased markedly from $62Bqkg^{-1}$ in 1978 to $238Bqkg^{-1}$ in 1979. Figures from Clifton et al. (1983) show a similarly major fall to $24Bqkg^{-1}$ in 1980. These fluctuations reflect the decreasing Sellafield discharge trend. Of the soft tissues, the digestive gland is consistently one of the most active tissues, 160 ± 9 $Bqkg^{-1}$ in 1977 and 1504 ± 1060 $Bqkg^{-1}$ in 1979. Other parts of the mussel of comparable plutonium activity

are the periostracum (a thin protein layer on the surface of the shell) and the byssal threads (used to anchor the mussel to the substratum on which it rests); both of these are generally removed before the mussel is prepared for consumption.

Experimental studies by Fowler et al. (1975) on the biokinetics of plutonium uptake by mussels produced concentration factors of 27-70 after 25 days exposure to Pu (VI) labelled seawater, Byssal threads were found to contain 30-63% of the mussel's total ^{237}Pu content (CF 1860-4100). Fowler et al. (1975) observed that most of the ^{237}Pu accumulated by mussels directly from the sea water could be accounted for by the shell and byssal threads, whereas Noshkin et al. (1971) found similar concentrations of plutonium in both the soft parts and the shells of mussels labelled in the environment.

Loss of plutonium from mussels labelled with Pu (IV) and Pu (VI) via sea water revealed no difference between the oxidation states, each producing two short-lived compartments of $T_{b½}$ 1-2 days and $T_{b½}$ 10-13 days, containing ~ 70% of the ^{237}Pu taken up, and a third longer-lived compartment of $T_{b½}$ ~ 190 days (Guary and Fowler, 1981).

Bjerregaard et al. (1985) studied the biokinetics of plutonium in mussels labelled from sea water and food. Plutonium kinetics in mussels fed Pu(III-IV) and Pu(V-VI) labelled diatoms were identical. Concentration factors of 20-25 were obtained after 5 days exposure to labelled sea water and a CF of ~ 7 was obtained from labelled diatoms. Plutonium was concentrated from sea water more by shell than by soft parts but was lost faster after uptake from labelled diatoms. Following ingestion of labelled diatoms, Pu was lost from soft parts faster than from shell, while Pu accumulated from sea water was lost from soft parts and shells at similar rates.

Other than mussels, various benthic species have been used in laboratory studies (Table 1.16). These cited in Table 1.16, however, are not the complete range but serve as an indication

TABLE 1.16
Some biokinetic properties of plutonium in marine organisms

Species/Organism	Labelling medium	Whole body CF/TF	Biological half times ($T_{b\frac{1}{2}}$) (days) Compartment			Comments/Sources
			1	2	3	
Phytoplankton	Natural environment	10^5-10^6	-	-	-	Gromov, 1976; Krishnaswami et al., 1976; Santschi et al., 1980; Fowler et al., 1983
Zooplankton	Natural environment	10^2-10^4	-	-	-	Higgo et al., 1977; Fowler et al., 1983
Macroalgae	Natural environment	$5x10^2$-5.10^3	-	-	-	Pillai et al., 1964; Wong, 1970; Noshkin, 1972; Nilsson et al., 1981; Pentreath et al., 1982; Aarkrog et al., 1982
Annelids:						
Nereis diversicolor	Sea water	200	79	-	-	15 day exposure, Fowler et al., 1975
Hermione hystrix	Sea water	275-375	-	-	-	Aston and Fowler, 1985
	Sediment	$5x10^{-2}$	-	-	-	Aston and Fowler, 1985
Molluscs:						
Mytilus edulis (Mussel)	Sea water	27-70	-	-	-	25 day exposure, Fowler et al., 1975
	Sea water	-	1-2	10-13	190	Guary and Fowler, 1981
	Sea water	20-25	-	-	-	5 day exposure, Bjerregaard et al., 1985
	Diatoms (food)	~ 7	-	-	-	5 day exposure, Bjerregaard et al., 1985
Littorina littorea (Winkle)	Sea water	34	10	193		50 days exposure, Swift and Pentreath, 1988
	Seaweed (food)	-	1	69		9 days feeding, Swift and Pentreath, 1988
	Silt	0.004	1	69		2 days exposure, Swift and Pentreath, 1988

TABLE 1.16 (Continued)

Species/Organism	Labelling medium	Whole body CF/TF	Biological half times ($T_{b\frac{1}{2}}$) (days) Compartment			Comments/Sources
			1	2	3	
Venerupis decussata (Clam)	Sea water	61-74	-	-	-	Aston and Fowler, 1984
	Sediment	6×10^{-3}	-	-	-	Aston and Fowler, 1984
Cerastoderma edule (Cockle)	Sea water	140	-	-	-	Miramand and Germain, 1985
	Sediment	1.4×10^{-2}	-	-	-	Miramand and Germain, 1985
Octopus vulgaris (Octopus)	Sea water	65	2	680	-	Guary et al., 1981 Miramand and Guary, 1981
Crustaceans:						CF strongly influenced by moulting
Lysmata seticaudeta (Shrimp)	Sea water	19	42			Fowler et al., 1975
Echinoderm:						
Coscinasterias tenuispina (Starfish)	Sea water	10^2-10^3	-	-	-	10 day exposure, Guary et al., 1982
Fish	Natural	5×10^{-1}-2×10^2				IAEA, 1985

to the type of studies performed to date. Swift and Pentreath (1988) exposed the winkle Littorina littorea to ^{237}Pu from sea water, food (seaweed) and silt. A whole body CF of 34 was obtained after a 50d exposure period to sea water, with 83% of activity being contained on the shell. An assimilation efficiency of ~7% was calculated from labelled seaweed with an estimated transfer factor from silt of 0.004. The authors concluded that the food pathway is the major source of accumulated Pu in the winkle, the ingestion of silt contributing significantly to the total Pu concentration. The small benthic shrimp Lysmata seticaudata, has been shown by Fowler et al. (1975) to accumulate ^{237}Pu(IV) slowly from sea water, the degree of accumulation being highly dependent on the rate of moulting. In excretion experiments, first moults accounted for a large fraction of the body burden. Retention from labelled food indicated an absorption efficiency of ~15%.

Larger crustacea (Carcinus maenas) have been shown to retain 20-60% of ^{237}Pu ingested from labelled Nereis. No appreciable difference in retention was observed between crabs fed Nereis which had been exposed either to Pu(IV) or Pu(VI) labelled sea water (Fowler and Guary, 1977). The metabolism of plutonium by Cancer pagarus has been studied in some detail (Guary and Negrel, 1980). It appears that plutonium and iron within the digestive gland are bound to different proteins but that both elements are carried in the haemolymph by a common carrier-protein which could be a sub-unit of haemocyamin.

Noshkin et al. (1971) noted that $^{239+240}$Pu concentration in starfish were four times higher than those in the mussels upon which they feed. Guary et al. (1982) compared distributions of plutonium in environmentally-labelled starfish with those from laboratory-labelled starfish (from both sea water and food tracers). Their observations led to the conclusion that, in the environment, the water-derived pathway dominates the uptake of plutonium by asteroids. Although some additional transfer does take place when asteroids feed on mussels, the high $^{239+240}$Pu levels which have been noted in starfish result rather from the strong affinity of colloidal/particulate or soluble Pu for the animal's mucous-covered epidermal layer which is in continual contact with sea water.

The common octopus Octopus vulgaris, a benthic cephalopod, has the ability to concentrate radionuclides to relatively high levels compared to other invertebrates (Guary et al., 1981; Miramand and Guary, 1981). Guary and Fowler, (1982) performed biokinetic studies on the octopus using Pu and Am tracers. After 2 weeks' exposure to labelled sea water, a CF of 65 for Pu had been reached, 41% of the total body burden being present in the branchial hearts (CF 9300). Whole-body loss of ^{237}Pu produced 2 pools of $T_{b½}$ ~2d and $T_{b½}$ ~680d.

The ability of the branchial hearts to concentrate many elements including plutonium and americium, may be linked to the presence of intracellular granules composed of a brownish-purple pigment called adenochromes and in which the metallic elements are localised. Miramand and Guary (1981) used autoradiographic techniques to demonstrate the close association of ^{241}Am with adenochromes but could not identify the exact nature of the radionuclide binding mechanism. It is most probable that the adenochromes are implicated in a process of detoxification of heavy metals.

The polychaete worm Nereis diversicolor has been used in several laboratory experiments to determine its potential role in redistribution of transuranic nuclides in both near-shore and deep-ocean sediments. Fowler et al. (1975) found that Nereis readily accumulated Pu from sea water, reaching a CF of ~200 after 15 days' exposure. Retention studies produced a $T_{b½}$ of 79 days. Plutonium quotient analysis on Nereis showed no differences in the bioavailability of ^{238}Pu and ^{239}Pu from sea water. Beasley and Fowler (1976a) similarly found no difference in the bioavailability of ^{238}Pu and $^{239+240}$Pu from sediment labelled with known chemical forms of plutonium or as a function of whether the sediments contained plutonium from aged nuclear test debris or fresh plutonium from fuel reprocessing wastes. The plutonium transfer factor from Sellafield sediment to Nereis was found to be ~0.0016 (Beasley and Fowler, 1976b). After reviewing the measured plutonium transfer factors

from sediment and concentration factors from water (Fowler et al., 1975; Noshkin, 1972), Beasley and Fowler (1976b) suggested that water may be the dominant source of plutonium in its bioaccumulation by deposit-feeding worms like Nereis diversicolor.

Aston and Fowler (1984) performed laboratory experiments using the polychaete worm Hermione hystrix and the clam Venerupis decussata to study Pu accumulation from sea water and from a deep-sea sediment. Significant differences in the behaviour of Pu introduced into the uptake and loss experiments in different oxidation states (III + IV) and (V + VI) were not generally observed. Both benthic species exhibited extremely low transfer factors for Pu accumulation from sediment (TF clam, $6x10^{-3}$; TF worm, $5x10^{-2}$) compared to Pu accumulation from sea water (CF clam 61-74, CF worm 275-375). These findings support those of Beasley and Fowler (1976b) in confirming that water is clearly an important source of Pu to the marine biosphere. Similar "sediment v sea water" labelling media experiments were performed by Miramand and Germain (1985) using the edible cockle Cerastoderma edule. A low TF ($1.4x10^{-2}$) from sediment to organism was found, with a CF of 140 attained after a 56 day exposure period (CF shell ~200, CF soft parts ~160) to sea water.

Grillo et al. (1981) used various benthic invertebrates to perform several uptake and loss experiments of ^{237}Pu and ^{241}Am in labelled sea water: molluscs, the bivalve clam Tapes decussatus and the detritivorous gastropod Aporrhais pespelicani; echinoderms, the ophiuroid starfish Ophiura texturata and the holothurian Stichopus regalis and annelids, the polychaete worm Hermione hystrix. In general, the order of transuranic accumulation was polychaetes > molluscs > echinoderms and, for radionuclide retention, echinoderms ($T_{b½}$ 68-410 days) > molluscs ($T_{b½}$ 53-80 days) > polychaetes ($T_{b½}$ 66 days).

The concentrations of plutonium in marine fish differ markedly from organ to organ. The highest concentrations in bottom feeding fish such as the plaice (Pleuronectes platessa) are observed in the gut contents, due mainly to contaminated sediment ingested with the food (Pentreath and Lovett, 1978; Guary et al., 1976). The highest organ concentrations are those in kidney, spleen and liver, with the lowest in muscle. Plutonium concentrations of 0.55 $Bqkg^{-1}$ (wet) in the liver of the mackerel (Scomber scombrus) and 1.48 $Bqkg^{-1}$ (wet) in the liver of the cod (Gadus morhua), caught within 5km of the Sellafield pipeline, were determined by Pentreath et al. (1979). Plutonium concentrations were also measured in cod caught at varying distances from Sellafield, reflecting lower concentrations with greater distance. Pentreath et al. (1979) also recorded higher concentrations of plutonium in the organs of pelagic fish, such as mackerel, than in the demersal plaice.

1.4.4 Americium

Americium is present in the marine environment through fallout from nuclear weapons tests and marine discharges by the nuclear industry. In fallout, the only source of ^{241}Am is ingrowth from ^{241}Pu, so that the ^{241}Am detected within an organism arises either from in situ production or from sources external to it or from both. In contrast, the Irish Sea does receive ^{241}Am directly from Sellafield discharges. Considerable quantities of ^{241}Pu, however, are also discharged and thus again there are two potential sources of ^{241}Am available to the marine organisms.

Americium has been measured in oceanic particulate material from the Pacific Ocean (Koide et al., 1981; Fowler et al., 1983; Livingston et al., 1987), the Mediterranean Sea (Holm et al., 1980; Ballestra et al., 1981) and the Irish Sea (Pentreath, 1980). Fowler et al. (1983) presented Am concentrations of 0.0218 $Bqkg^{-1}$ (wet) (CF $\sim 10^4$) and 0.0197$Bqkg^{-1}$ (wet) (CF 6×10^3) in phytoplankton and zooplankton collected in the north-east

Pacific Ocean. (Wet to dry conversion calculation for phytoplankton used a ratio of 10 (Fisher et al., 1983a) and for zooplankton a ratio of 6 (Cherry and Shannon, 1974)). Comparative studies by Fisher et al. (1983a) gave a CF estimate of 700 for zooplankton in the Mediterranean and a CF of ~10^5 for phytoplankton from laboratory experiments. The adsorptive properties of phytoplankton and zooplankton towards Am and other transuranic elements are governed by organic coatings involving ion-exchange, sorption and chelation processes. Environmental levels of Am measured in the coastal regions of the Irish Sea (Hamilton and Clifton, 1980; Pentreath, 1980; BNF, 1977-87) and in Scandinavian waters (Holm and Persson, 1980; Nilsson et al., 1981; Aarkrog et al., 1982), produced a CF range of $5x10^3$ - $1x10^4$ for brown algae. Experimental evidence provided by Carvalho and Fowler (1985) indicates that Am accumulation is a passive non-metabolic process and adsorption takes place mainly on the thin outer organic coating of the seaweed.

As with plutonium, the mussel has been popular as a test organism for study of Am biokinetics (Guary and Fowler, 1981; Clifton et al., 1983; Bjerregaard et al., 1985) (Table 1.17). Fisher and Teyssie (1986) performed a series of tracer experiments to investigate the influence of food type on the biokinetics of Am in mussels using a diatom, green alga, glass beads (pure mineral source) and albumin particles (pure protein source). Over a 5 day labelling period, CFs from labelled diatoms and algae were 25-33 and from albumin and glass beads ~12. They concluded that the quality of food itself appeared to have little impact on the accumulation, assimilation, tissue distribution and retention of radionuclides in mussels.

In studying the bioavailability of Am from sediments, Beasley and Fowler (1976b) exposed the polychaete worm Nereis diversicolor to sediments from the Irish Sea and Bikini Atoll (nuclear weapon test site). They found that sediments were not the major source of americium to the worm. Vanganechten et al. (1983), in exposing the bivalve mollusc Venerupis decussata, the polychaete

TABLE 1.17

Biokinetics of americium in marine organisms

Species/Organism	Labelling medium	CF/TF	Biological half time Compartments (days) 1	2	3	Comments/Sources
Phytoplankton	Sea water	10^4				In Pacific Ocean, Fowler et al., 1983
		10^5				Laboratory labelled, Fisher et al., 1983a
Zooplankton	Sea water	$6x10^3$				In Pacific Ocean, Fowler et al., 1983
		700				In Mediterranean Sea, Fisher et al., 1983a
Macroalgae	Sea water	$5x10^3$-$1x10^4$				Hamilton and Clifton, 1980; Holm and Persson, 1980; Pentreath, 1980; Nilsson et al., 1981; Aarkrog et al., 1982
Annelids:						
Nereis diversicolor	Sediment	0.0003				Sediment from Bravo crater, Beasley and Fowler, 1976 a
		0.0006				Sediment from Irish Sea, Beasley and Fowler, 1976a
	Sea water	4×10^3	24	368		97% accumulated ^{241}Am on mucous layer, Carvalho and Fowler, 1984
Hermione hystrix	Sea water	10^3				Grillo et al., 1981
	Sediment	0.12				Pacific sediment, Vangenechten et al., 1983
		0.05				Atlantic sediment, Vangenechten et al., 1983
Arenicola marina	Sediment	0.003				French coastal sediment, Miramand et al., 1982
Isopods:						
Cirolana borealis	Sediment	0.032				Pacific sediment, Vangenechten et al., 1983
		0.006				Atlantic sediment, Vangenechten et al., 1983

Table 1.17 (Continued)

Species/Organism	Labelling medium	CF/TF	Biological half time Compartments (days) 1	2	3	Comments/Sources
Molluscs:						
Tapes decussatus (Clam)	Sea water	320	6	80		82% of ^{241}Am total body burden in shell, Grillo et al., 1981
Scrobicularia plana	Sediment	0.009				French coastal sediment, Miramand et al., 1982
Venerupis decussata (Clam)	Sediment	0.02				Pacific sediment, Vangenechten et al., 1983
		0.004				Atlantic sediment, Vangenechten et al., 1983
Cerastoderma edule (Cockle)	Sea water	340				Miramand and Germain, 1985
	Sediment	0.008				French coastal sediment, Miramand and Germain, 1985
Mytilus galloprovincialis (Mussel)	Sea water	-	11	22	480	Guary and Fowler, 1981
Octopus vulgaris (Octopus)	Sea water	35	2	680		Guary and Fowler, 1982
	Crabs (Food)	-	17	160		33% assimilation of ^{241}Am, Guary and Fowler, 1982
Aporrhais pespelicani (Gastropod)	Sea water	550				89% ^{241}Am total body burden in shell $T_{b\frac{1}{2}}$ similar to Tapes decussatus, Grillo et al., 1981

TABLE 1.17 (Continued)

Species/Organism	Labelling medium	CF/TF	Biological half time Compartments (days)			Comments/Sources
			1	2	3	
Echinoderms:						
Ophiura texturata (Brittle star)	Sea water	60	313			97% ^{241}Am total body burden in body wall, Grillo et al., 1981
Stichopus regalis (Sea cucumber)	Sea water	20	6	68		Up to 84% ^{241}Am total body burden in body wall, Grillo et al., 1981
Crustaceans:						
Corophium volutator	Sediment	0.12				French coastal sediment, Miramand et al., 1982
Galathea strigosa (Squat lobster)	Sea water	770	0.6	7	139	88% ^{241}Am total body burden after uptake in exoskeleton 95% ^{241}Am total body burden after depuration in exoskeleton, Carvalho and Fowler, 1984
Fish	Sea water	50				IAEA, 1985

Hermione hystrix and the isopod Cirolana borealis to ^{241}Am contaminated sediments, found all measured factors to be less than unity. They concluded that ^{241}Am uptake depends on the geochemical fractionation of the americium in the sediment since the reported uptake figures could not be related to the measured K_d values of the sediments used. Other sediment transfer experiments using a variety of benthic species (Miramand et al. (1982); Germain et al. (1983); Miramand and Germain (1985)) have all produced low transfer factors indicating that the direct uptake of americium (and plutonium) by benthic fauna from deep-sea sediments is likely to be a quantitatively unimportant route for the transfer of waste radionuclides to the marine food chain and hence to man. Grillo et al. (1981), studying transuranic biokinetics from labelled sea water, used several taxonomic groups: molluscs, echinoderms and annelids. Most of the Am was associated with the organisms body wall or shell (80-90%), particularly high concentration factors (10^3-10^4) being noted in the chitinous setae of the polychaete and the digestive tissues and gonads of the ophiuroid. Benthic species inhabiting the sediment-water interface could therefore readily accumulate Am from the surrounding waters and retain the contaminant in their tissues for relatively long periods of time (ophiuroid $T_{b½}$, 313d; polychaete $T_{b½}$, 66d).

The cephalopod Octopus vulgaris, when exposed to ^{241}Am labelled sea water, obtained a whole body CF of 35 (Guary and Fowler, 1982), with 73% being located in the branchial hearts. Miramand and Guary (1981) demonstrated that Am (like Pu) is closely associated with the granular pigment concretions, adenochromes, located within the cells of the branchial hearts.

The distribution of ^{241}Am in fish studies by Pentreath et al. (1979) revealed that, although plaice exhibited higher Am concentrations in the gut, similar concentrations to the plaice were observed in the muscle and liver of the cod. The mackerel, however, showed higher Am concentrations in the liver and bone than those found in the respective tissues of the cod or plaice.

1.4.5 Curium

Compared with plutonium and americium, there is very little information available on the behaviour of curium in the marine environment. Detectable concentrations of curium have been reported in soils and water near fuel reprocessing plants and waste storage facilities (Means et al., 1978; Eicke, 1981) and in marine organisms from the Irish Sea (Pentreath and Lovett, 1978; Pentreath, 1980; Pentreath et al., 1980). A total of 1.42TBq of curium (0.97TBq ^{242}Cm, 0.45TBq $^{243+244}$Cm) has been discharged from Sellafield between 1981 and 1984 (BNF, 1982-85), resulting in curium levels being 50-100 times lower than the plutonium concentrations detected in the same samples. It should be noted that, as little is known of the rates of accumulation and loss of curium, there is no indication as to whether or not the samples for which data have been reported are even in approximate equilibrium with the surrounding concentrations.

The use of a curium tracer in biokinetic experiments has not thus far been widely practised. Grillo et al. (1981) exposed the clam Tapes decussatus to curium-labelled sea water for 20 days, resulting in a whole body CF of 330 (cf. ^{241}Am CF of 320). Miramand et al. (1987) carried out a similar set of experiments using five benthic marine species. Concentration factors of 700 for the amphipod crustaceans, 80-140 for two bivalve molluscs and ~30 for two annelids were reported. Mucous samples from the polychaete annelids showed a very strong affinity for curium (CF 500-6400) and Miramand et al. (1987) attributed this to curium's high affinity for mucopolysaccharides. The latter has been observed for other transuranics in other tissues containing mucopolysaccharides - byssus threads, periostracum in mussels; chitin in crustaceans (Guary, 1980; Hamilton and Clifton, 1980).

Dahlgaard (1984) obtained CF estimates of 1550-3730 for the seaweed Fucus vesiculosus from labelled sea water (calculated using dry weight concentrations). In this and related work on marine organisms (Grillo et al., 1981; Miramand et al, 1987) and sediments (Sibley et al., 1986), a close similarity between the behaviours of americium and curium under identical laboratory conditions has been consistently observed. This similarity has been used in an extrapolative manner to estimate CFs of curium in various marine trophic levels for which americium values are known but curium values are not (IAEA, 1985) (Table 1.18).

1.4.6 Californium

The total lack of environmental data on the marine radioecology of californium precludes direct comparison of laboratory experimental results with those from natural ecosystems. Several biokinetic experiments have been performed using ^{252}Cf on various marine organisms at the IAEA, International Laboratory of Marine Radioactivity, Monaco. Californium -252 is used for radioecological and other in vivo experiments due to the detectability of the prompt photons which accompany the spontaneous fission decay of ^{252}Cf. Detection of > 2.6 MeV photons by a NaI(Tl) detector eliminates most natural background radiation and successful experiments can be carried out with 10-100 Bq levels of ^{252}Cf (Aston, 1984).

Fisher et al. (1983a), in studying the interactions of marine plankton with transuranic elements, determined the affinity of ^{252}Cf for seven species of marine phytoplankton. The concentration factors obtained were in the region of 10^5 - 10^6, a range found to be common for plutonium and americium, making these three elements amongst the most reactive metals known. Phytoplankton particles with associated transuranics may sink slowly, transporting these elements to deeper water or to sediments, or they may be ingested by herbivores in surface waters, providing an early and vital step in the distribution of transuranic nuclides throughout the marine environment.

TABLE 1.18

Concentration Factors of curium in biological material (After IAEA, 1985).

	FISH	CRUSTACEANS	MOLLUSCS	MACRO-ALGAE	ZOOPLANKTON	PHYTOPLANKTON
Recommended Value	5×10^{1}	[a] 5×10^{2}	3×10^{4}	8×10^{3}	(2×10^{3})	3×10^{5}
Range	5×10^{-1} - 2×10^{2}	1×10^{2} - 1×10^{3}	5×10^{3} - 5×10^{4}	5×10^{3} - 1×10^{4}	5×10^{2} - 5×10^{3}	1×10^{5} - 6×10^{5}

( ) = best estimates

a - This value assumes similar behaviour to Am

Aston and Fowler (1983), found that the planktonic euphausiid (Meganyctiphanes norvegica), after being exposed to ^{252}Cf in sea water for 1 week, had a CF of ~300. With reference to the estimated figures given by the NEA (1980), this concentration factor value is similar to those suggested for marine crustacea but is an order of magnitude less than those estimated for 'plankton'. Surface adsorption is the most likely mechanism responsible for the uptake process. When ingested with food, ^{252}Cf is poorly assimilated and is rapidly excreted with faecal pellets in a mode similar to that previously demonstrated for other transuranic nuclides (Fowler and Heyraud, 1974; Fowler et al., 1975; Higgo et al., 1980; Fowler and Aston, 1982). From their work with euphausiids, Aston and Fowler suggested that zooplankton moults and faecal pellets, as well as dead zooplankton, are expected to be important vectors for effecting the downward vertical transport of ^{252}Cf from contaminated waters.

Fowler et al. (1986) performed a series of experiments exposing several benthic species to ^{252}Cf. Systems studied were accumulation and depuration from sea water, assimilation from food and uptake from sediment (Table 1.19). The primary feature of ^{252}Cf whole-body uptake from water by molluscs, polychaetes and crustacea is that bioaccumulation is mainly a result of surface adsorptive phenomena and therefore is largely dependent on the composition and texture of exposed surfaces. Californium is also transferred readily to invertebrates via the food chain (Fowler et al., 1986). The high assimilation efficiency (~23%) of ^{252}Cf in Carcinus is approximately the same as that found for Pu in the species of crab (Fowler and Guary, 1977) but is considerably higher than the 4-5% measured for ^{252}Cf in small crustaceans such as planktonic euphausiids (Aston and Fowler, 1983) and benthic isopods (Carvalho and Fowler, 1985).

Galey et al. (1983) found similar distributions of ^{252}Cf in the pyloric caeca (a glandular complex involved with digestive and food storage processes) of the seastar Marthasterias glacialis,

TABLE 1.19

Biokinetics of ^{252}Cf in benthic invertebrates (Fowler et al., 1986)

Species/Organism	Labelling medium	CF/TF	Biological half-times (days) Compartments		Comments
			1	2	
Hermione hystrix	Sea water	763	2	50	96% of total radionuclide body burden contained in chitinous setae and body walls
	Sediment	0.05	-	-	
Venerupis decussata	Sea water	78	5	126	Greatest fraction incorporated in shell: 67% after uptake, 73% after 73 day depuration
	Sediment	0.006	-	-	
Lysmata seticaudata	Sea water	220	61	-	65-75% ^{252}Cf lost with cast moults. $T_{b\frac{1}{2}}$ calculated from cast moults.
Pilumnus hirtellus	Sea water	665	3	50	80% of total body burden associated with exoskeleton
	Nereis diversicolor	-	2	18	23% assimilation of ^{252}Cf into tissue of which 81-92% located in the hepatopancreas
Ophuira texturata	Mussel tissue (Food)	-	36		97% assimilation of ^{252}Cf into tissue of which 93% located in gut and pyloric caeca

91-98%, to those obtained by Fowler et al. (1986), 93%. Galey et al. (1983), in studying the tissue and subcellular distribution of ^{252}Cf in the seastar, found that ^{252}Cf was associated primarily with the mitochondria of the pyloric caeca cells.

1.5 AIMS OF THE PROJECT

The aims of this project were to investigate the uptake of selected transuranic elements via laboratory tank tracer studies along with parallel analyses of environmental samples collected from the vicinity of the BNF plc reprocessing plant at Sellafield. The analytical methods were to involve a combination of both conventional radiochemical methods and α-autoradiography. Alpha-track detection techniques had previously been established at the Department of Chemistry, University of Glasgow, but had been applied primarily to sedimentary samples (Crawford, 1982; Toole, 1984) and not to biological materials. Thus the incorporation here of α-autoradiographic techniques on marine organisms would require the development of appropriate histological practices such as organism dissection, freezing-microtome sectioning and tissue staining so that high quality microscopy could be performed on radiographs of tissue slices. The fundamental aim of the work, as implied above, was to define the within-organism distributions of the transuranic nuclides following their uptake from water, foods etc., i.e. to establish the internal organs and tissues which bioconcentrate transuranics and to examine whether these distributions are homogeneous or heterogeneous. Such information is not only of academic interest in indicating metabolic mechanisms but is also clearly important in helping an understanding of nuclide transfer potential within the marine food web.

In essence, the study, funded by the Natural Environment Research Council, sought to combine the radiochemical/autoradiographic experience at the University of Glasgow (now at SURRC) with the expertise in marine radioecology, particularly in radiotracer laboratory studies, at the International Atomic Energy Agency's

Marine Radioactivity Laboratory in Monaco. In the latter context and as implied by previous frequent referencing, a major data base has already been generated on the quantitative uptake of key radiotracers by a range of marine organisms. Prior to this project, however, very little experience had been gained in performing laboratory tank experiments specifically designed towards α-autoradiography. In particular, the levels of tracer radioactivity used in these experiments had to be carefully controlled so that exposure of the α-track detector to the labelled biological tissue section would produce a distinctive track distribution of useful density over convenient time periods.

The extrapolation of laboratory-derived tracer information to nuclide uptake under natural conditions has long been a topic of considerable controversy amongst marine radioecologists (Beasley and Cross, 1980).

It was hoped here that, by studying samples from both categories, i.e. by comparing and contrasting the α-track distributions of transuranic nuclides within the organs and tissues of both field and laboratory exposed organisms, further light would be shed on the validity of this extrapolative step. Similarly, the research would hopefully also distinguish between the relative importance of food and water as the dominant source medium for nuclide uptake by marine organisms. Any differences in within-organism nuclide distributions following uptake from different media would perhaps be highlighted. Such information is important to waste disposal assessment programmes in defining the major exposure pathways, if any.

It was hoped also that the observed internal distributions of the transuranic nuclides in the various tissues and organs of the organisms studied could ultimately be interpreted in relation to the biological functions of these organs/tissues. This information could consolidate knowledge of the internal mechanisms involved in the bioaccumulation of transuranic nuclides. The nuclides judged to be most suitable for the

radiotracer experiments were ^{237}Np, ^{239}Pu and ^{241}Am. The use of a curium tracer was also contemplated but, as its behaviour in biological systems corresponds so closely with that of americium (Grillo et al., 1981; Dahlgaard, 1984; Miramand et al., 1987), this was not considered justifiable. An additional and important advantage of the chosen nuclides is that all three are present and detectable in low-level wastes discharged from Sellafield into the Irish Sea. Information derived from the labelling experiments would then have a direct relevance in comparing laboratory findings against those obtained from environmental samples. As the ^{241}Am isotope also emits rays (59.57 keV, 35.4 % abundance), this tracer can be relatively easily monitored throughout labelling experiments by counting the samples in a well-type NaI(Tl) gamma detector.

The marine organism selected for study under laboratory conditions were the mussel (Mytilus edulis), the winkle (Littorina littorea) and the Dublin Bay prawn (Nephrops norvegicus). Disposal of low-level transuranic nuclides either in coastal waters or at deep-sea sites results in ~95% of these nuclides being adsorbed onto particulate material and subsequently being deposited into sediments. The study of marine organisms living in contact with the sediment (benthic organisms), especially at the dumping areas, will obviously contribute to an understanding of the natural processes governing the availability and redistribution of the waste nuclides between sediment, sea water and these species. Furthermore, of great interest is the exposure of benthic species commonly consumed by the public as this route results in an increase of the public's radiation exposure. The mussel, winkle and Dublin Bay prawn are all benthic species having a widespread popularity as seafood items.

The mussel is readily available and rapidly adapts to laboratory conditions for which it has become a common test organism for trace metals and organochlorines (Phillips, 1980), as well as for transuranic biokinetic experiments (see Section 1.4). As a result of previous radiolabelling experiments involving mussels, a useful database is available to this study.

At the commencement of this project, no published radiotracer studies on winkles or Dublin Bay prawns had been reported. The winkle was known to accumulate transuranics to a similar degree as mussels, under environmental conditions (Hunt 1979-87), and this factor was strongly relied upon when performing initial radiotracer experiments on winkles. The winkle is known to be a major contributor to the radiation dose received by the critical group in the vicinity of Sellafield. As with the mussel, the winkle readily adapts to laboratory conditions and is easily handled during experiments.

The Dublic Bay prawn is now commercially the most important shellfish species in the UK (Howard, 1982). It is extremely fished in the Irish Sea, in particular in an area of very fine silt close to the Sellafield waste pipeline, which has greatly enhanced sedimentary activities of the transuranic nuclides. As the Dublin Bay prawn burrows in such muddy sediments, this potential pathway of discharged radionuclides to man must be investigated. The study of Dublin Bay prawns also provides information on transuranic behaviour at a higher marine trophic level.

The radiochemical analysis of nuclides in environmental samples will provide quantitative activity concentrations which could be used in the process of radiological assessment of the seafood exposure pathways. These values will be of particular relevance since the compatibility of such concentration data will allow comparisons to be readily made with similar studies presently described in the scientific literature. A realistic account of radionuclide inter-tissue distribution in the mussel, winkle and prawn will also be provided, to be used in conjunction with the tissue activity trends obtained from the α-autoradiographic studies.

To maintain a perspective between potential exposures to transuranics and to the naturally occurring α-emitting nuclides and to provide information on the natural contribution to observed

α-track densities in field organisms, polonium was also analysed radiochemically in the Sellafield samples. In the latter context, a sound knowledge of the background radiation field is vital to the α-autoradiographic study on Sellafield samples since they contain a 'cocktail' of α-emitters of both natural (Po, U, Ra) and anthropogenic (Np, Pu, Am, Cm) origins.

CHAPTER 2 : EXPERIMENTAL METHODS

2.1 INTRODUCTION : OUTLINE OF METHODOLOGY

In this chapter, detailed descriptions are presented for the sampling and analytical techniques used to determine the concentrations and distributions of some transuranic and natural radionuclides in selected marine organisms under environmental and laboratory conditions. Alpha-autoradiography was used to detect the distributions of α -emitting nuclides within the tissues and organs of marine organisms. Difference in or similarities between the track distributions were assessed. Environmental samples, namely mussels and winkles from the Esk estuary, Ravenglass, Cumbria, contain a cocktail of both artificial α -emitting nuclides (Np, Pu, Am, Cm, from the effluent of the BNF plc reprocessing plant at Sellafield) and the natural α -emitting nuclides. In addition experimental organisms were exposed to transuranic α -emitters, ^{237}Np, ^{239}Pu and ^{241}Am, using specific labelling media (either food or water), this work being performed at the IAEA International Laboratory of Marine Radioactivity, Monaco. For autoradiographic study each organism, once labelled or collected was dissected into its component tissues and organs and these were processed according to the method outlined in Figure 2.1.

Complementing the environmental α-autoradiographic study, the marine organisms and their component parts were analysed for plutonium using the 'conventional' radioanalytical technique outlined in Figure 2.2. Besides the intrinsic interest of determining concentrations of plutonium in the various tissues and organs of the organisms, the data were also used to estimate the exposure time required in the α-autoradiographic study. The routine procedure for plutonium analysis employed in the Department of Chemistry, University of Glasgow involves the digestion of dried tissue samples

in mineral acids, the radiochemical separation of plutonium from the major and minor components of the sample using ion exchange resins, the electrodeposition of plutonium on a stainless steel disc and the counting of the deposited plutonium using surface barrier α-spectrometry. An example of a typical plutonium α-spectrum is shown in Figure 2.3.

Gamma-emitting nuclides (fission and activation products from Sellafield) were measured in samples to provide further information on the radionuclide content of the marine organisms. Each dried tissue sample was placed in a plastic counting dish of predetermined geometry and counted on a Canberra coaxial Ge(Li) crystal (Section 2.5). A typical γ-spectrum is shown in Figure 2.4.

In conjunction with the α-autoradiographic study of environmental samples, the ^{210}Po contents of samples were measured to indicate the level of natural α-activity in them. It was determined by digesting the sample in acids and plating the polonium (spontaneously deposited) on a silver disc from a dilute solution of HCl, thus providing a thin source suitable for high resolution α-spectrometry (see Figure 2.5). Two polonium analysis techniques as used in Monaco and Glasgow, were employed in this study. Both are briefly outlined in Figure 2.6.

All reagents used in the radioanalytical procedures are, wherever possible, of Analar grade. Between analyses, all glassware was decontaminated in 5% Decon 90 solution (for at least 12 hours) and then acid-washed.

Figure 2.1. Outline of autoradiographic technique

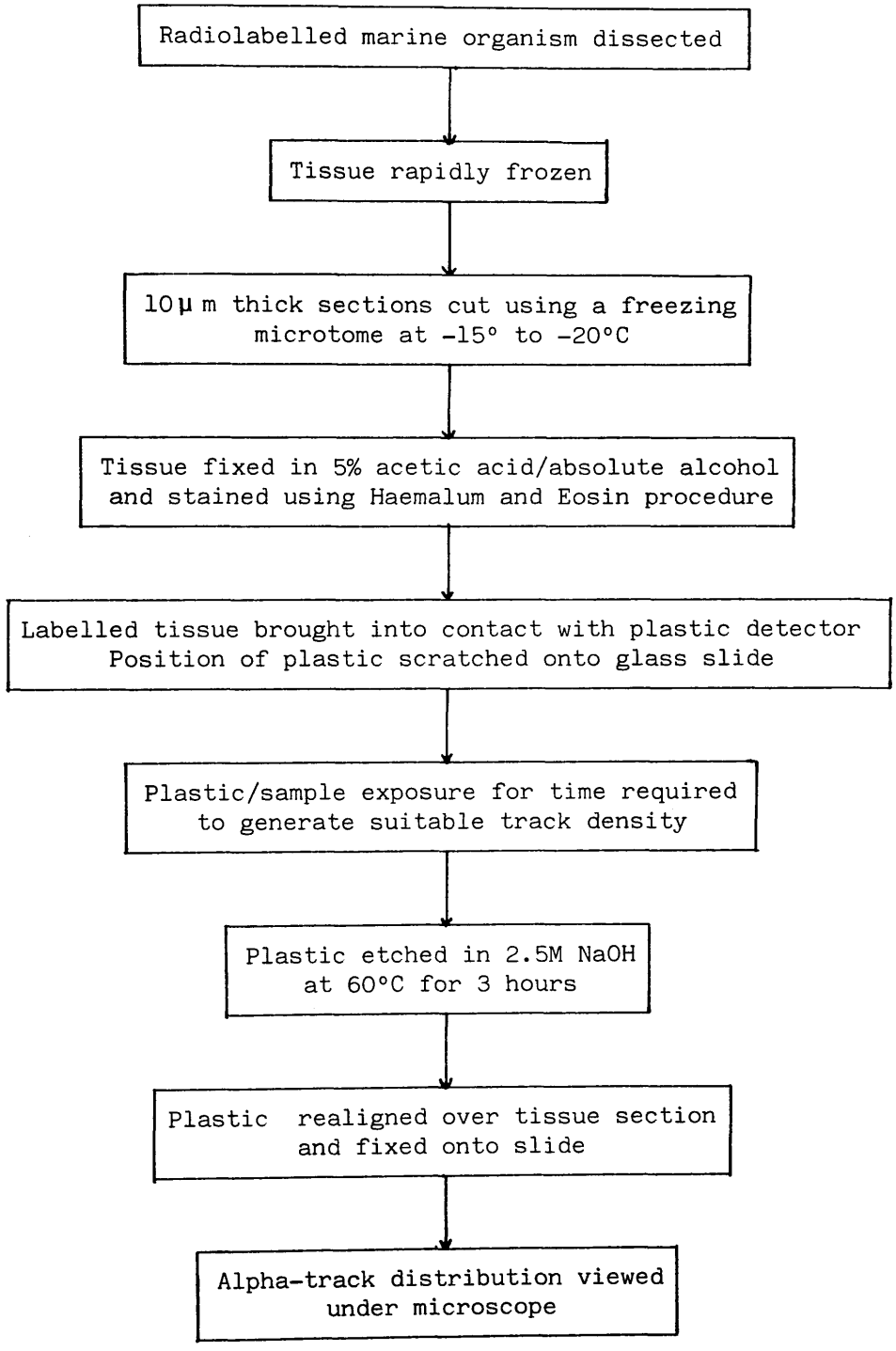
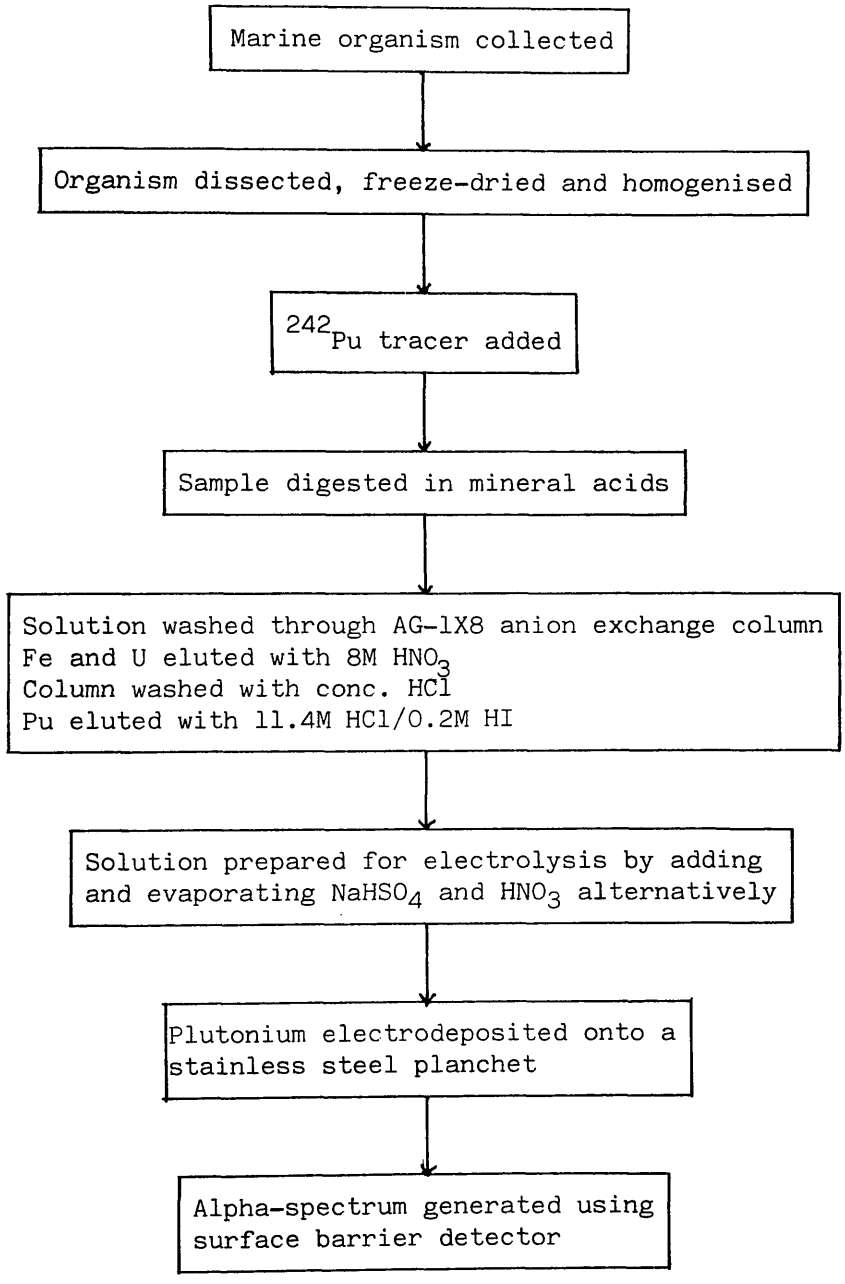


Figure 2.2. Outline of plutonium analysis



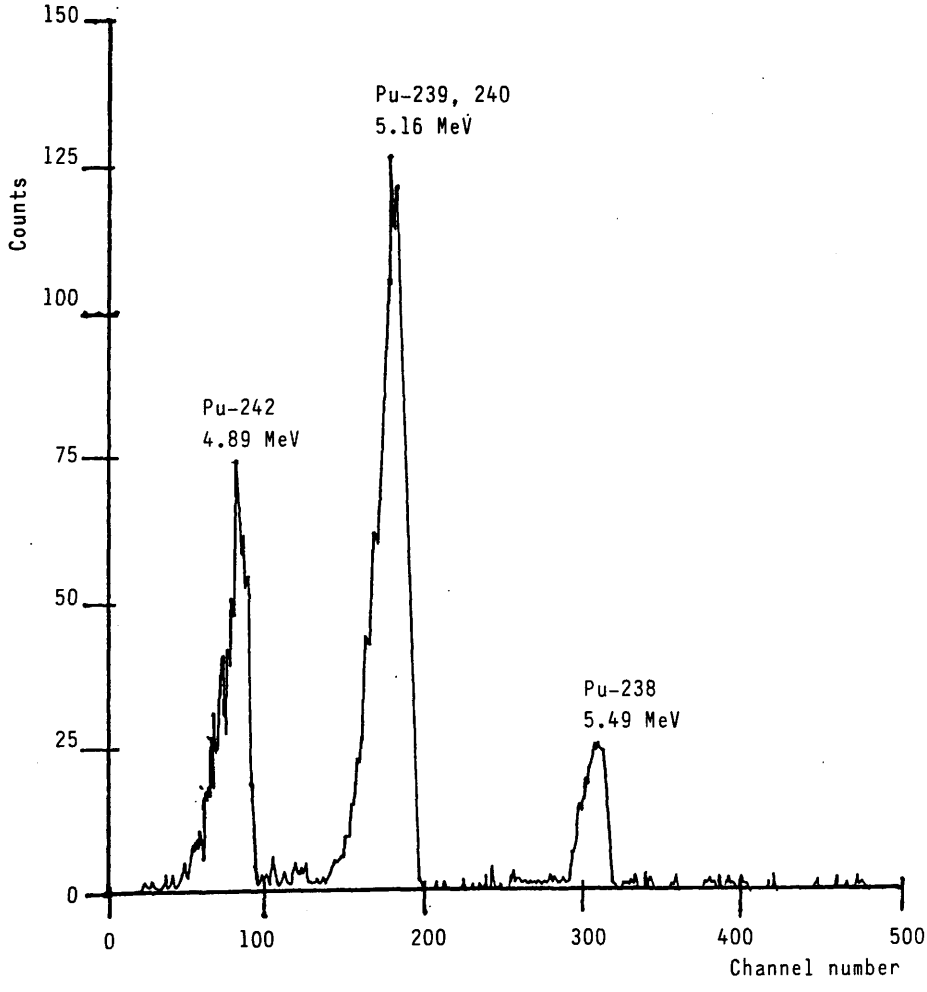
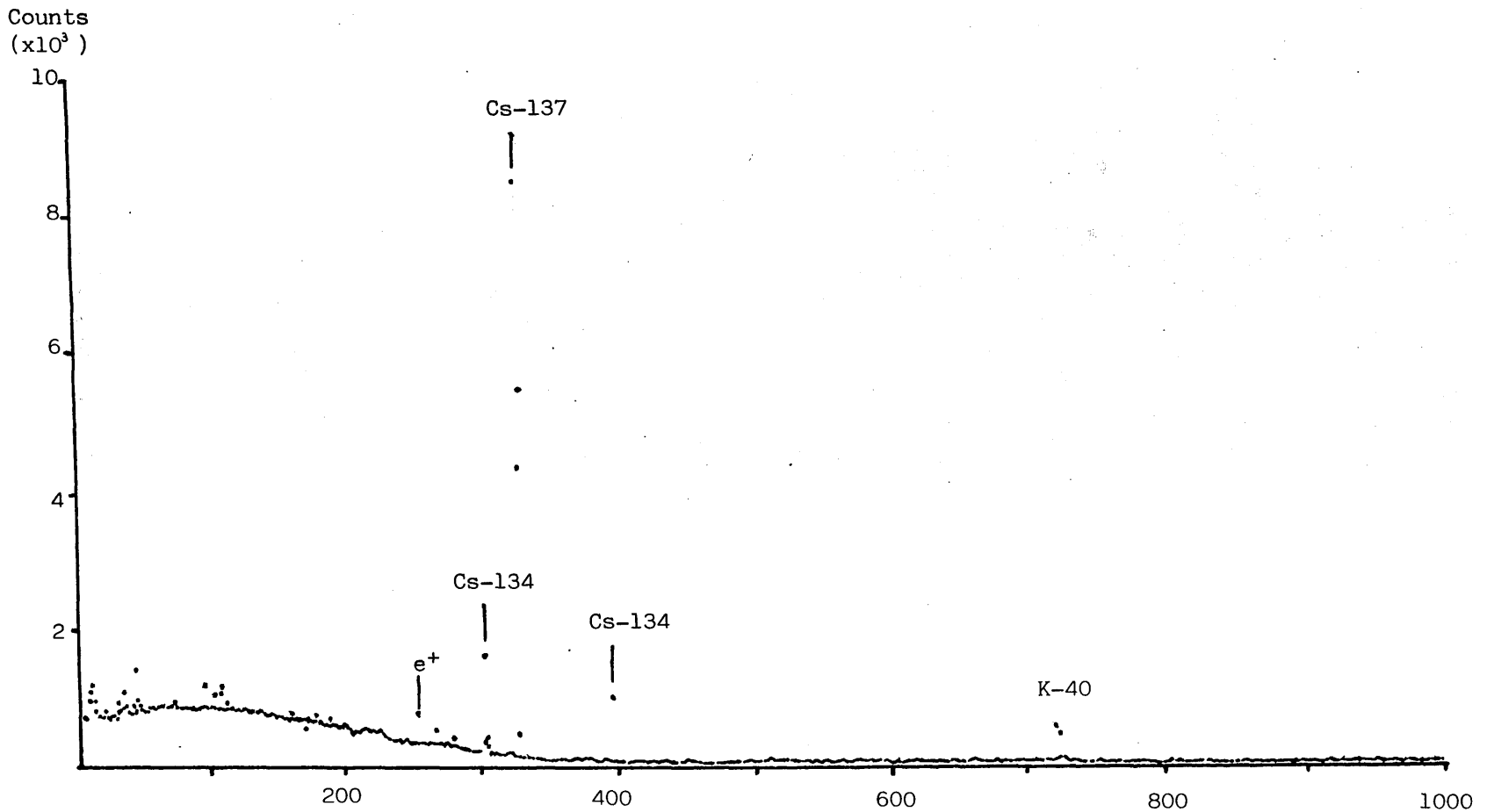


Figure 2.3. Pu alpha-spectrum.

Figure 2.4. Typical γ-spectrum



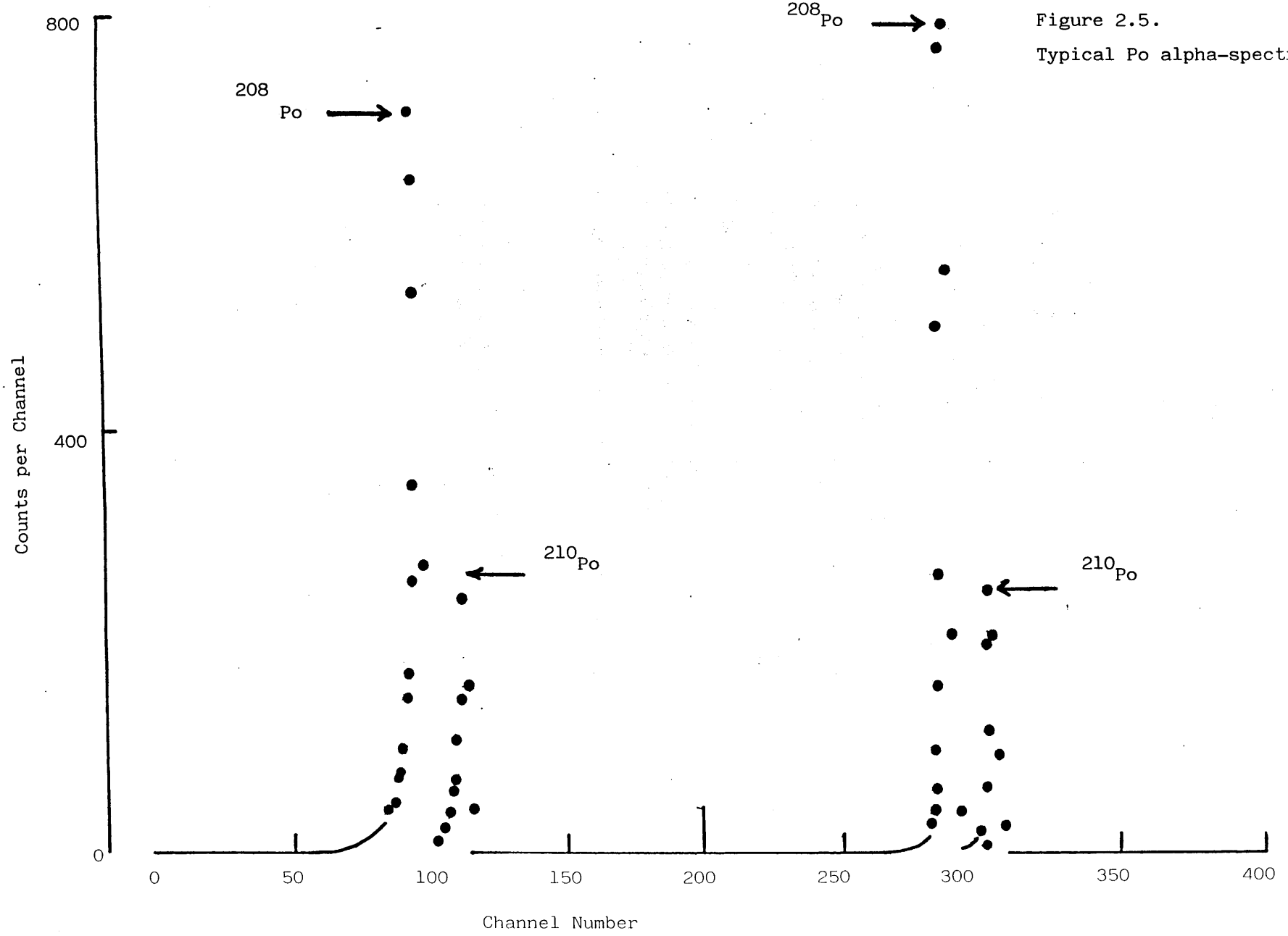
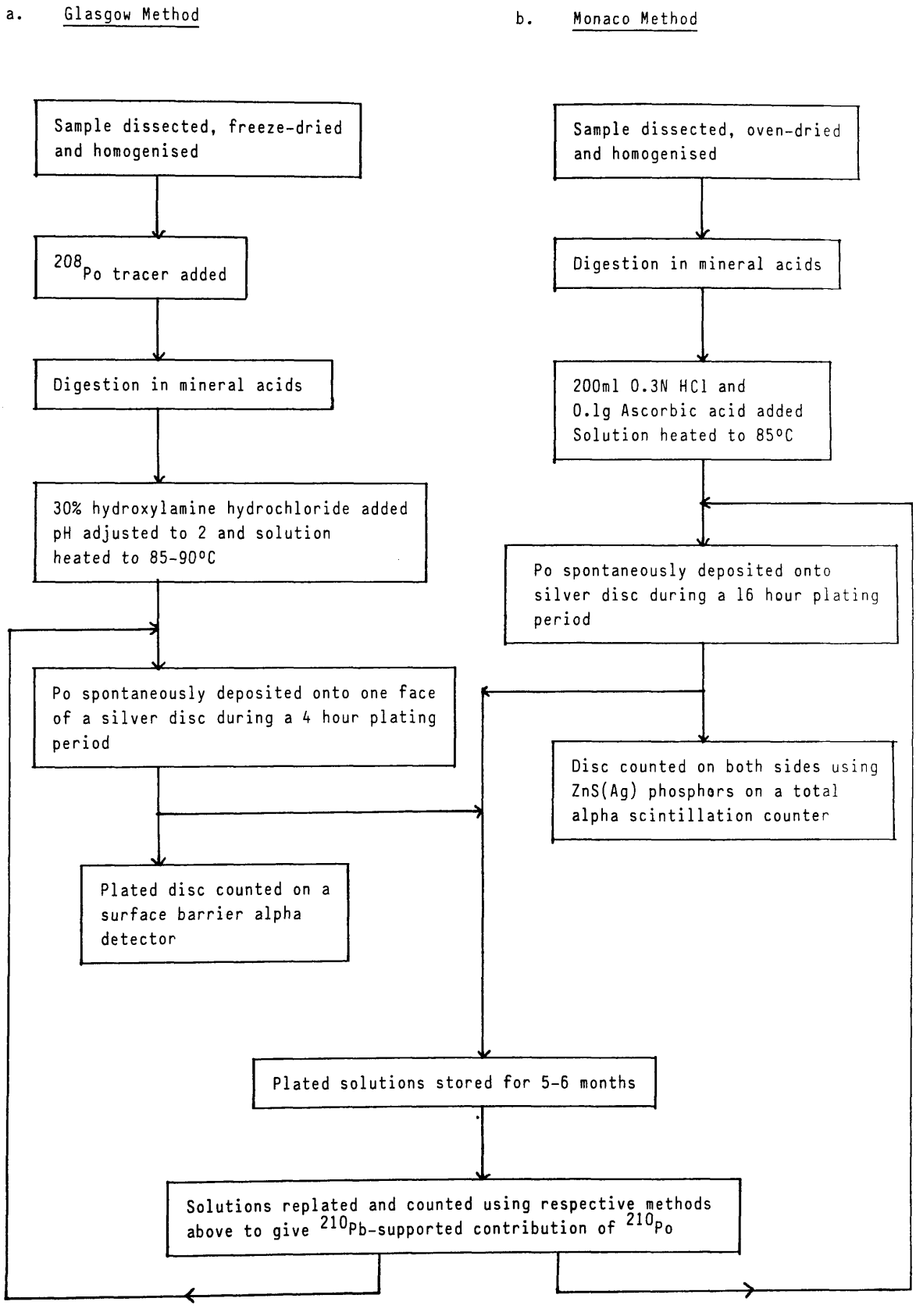


Figure 2.5.

Typical Po alpha-spectrum

Figure 2.6. Outline of polonium analyses

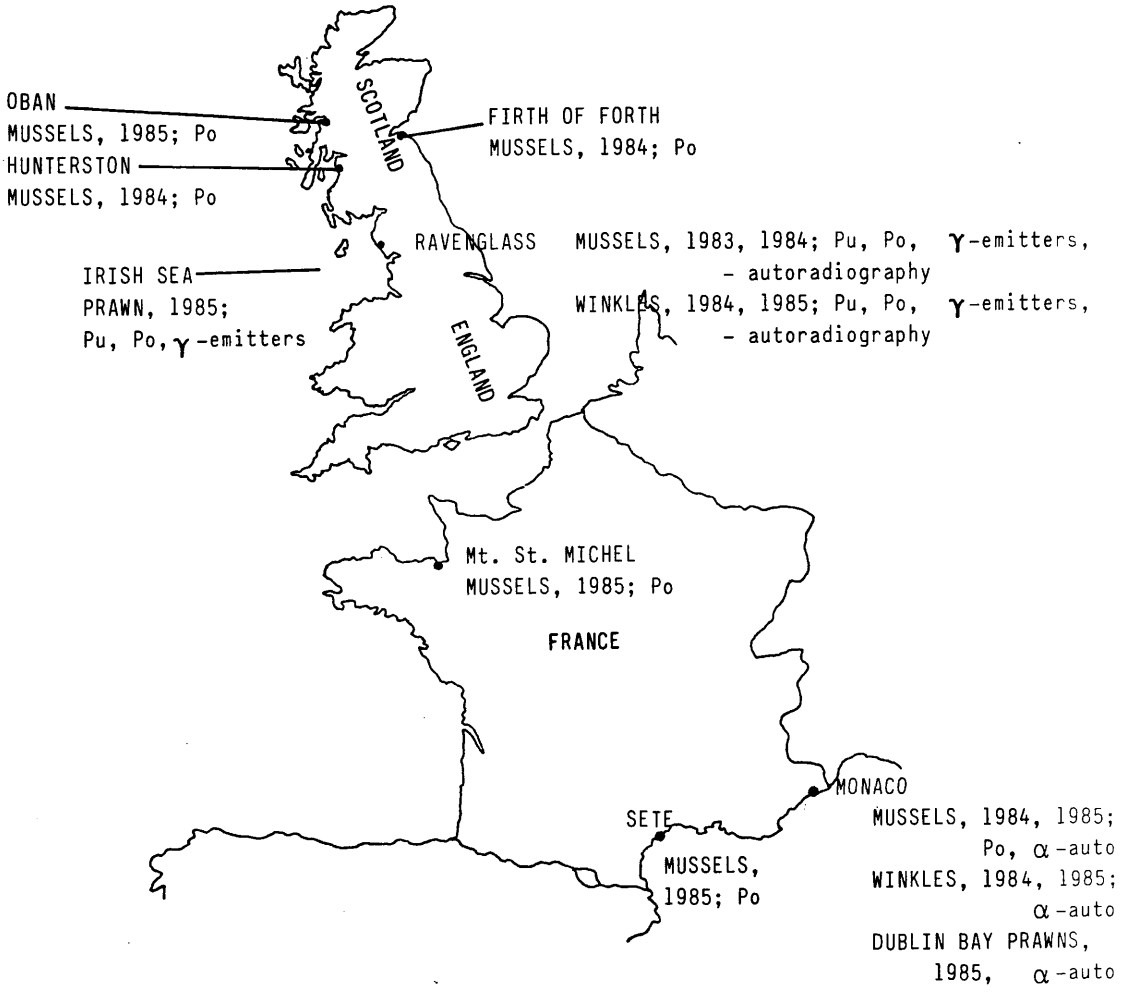


2.2 SAMPLE HANDLING AND PRETREATMENT

Most of the marine organisms collected from the environment and analysed directly for radionuclide content were sampled from the vicinity of the British Nuclear Fuels plc reprocessing plant at Sellafield, Cumbria, England. Mussels (collected in November 1983 and October 1984) and winkles (October 1984 and 1985) were analysed for plutonium, polonium and artificial γ -emitting nuclides in their respective tissues and organs. In addition, the mussels and winkles collected in 1984 were processed for α-autoradiography. In October 1985, prawns (Palaemon serratus) from the Irish Sea, landed locally at Whitehaven, were obtained and assayed for plutonium, polonium and artificial γ -emitting nuclides. For the polonium study mussels were also collected from a variety of sites in Western Europe (Figure 2.7) of which the French mussels were processed at the IAEA International Laboratory of Marine Radioactivity in Monaco. A summary of the sampling sites, organisms taken and investigative procedures performed on them is shown in Figure 2.7.

The samples subjected to radiochemical analysis at Glasgow were pretreated identically; once collected, cleaned and returned to the laboratory, they were dissected into their component tissues and organs as quickly as possible. Ten mussels and 20 winkles were used in the total soft part and shell analysis, whereas 50-60 mussels and 80-100 winkles were dissected to give manageable cumulative sample sizes for the individual organ and tissue types; only 10 prawns were required for the latter purpose. After dissection, the tissues were freeze-dried and the water content of the tissues calculated. Freeze-drying was carried out using an Edward Freeze-Dryer, Model EF03, refrigerated version (code F023-03-000). After freeze-drying the tissues were homogenised in a Moulinex coffee grinder. Small samples, however, were homogenised manually using a mortar and pestle. Aliquots of homogenised material were then taken for subsequent radiochemical analyses.

Figure 2.7. Sampling site details and analyses performed.



Sample pretreatment for polonium analysis in the Monaco laboratory differed in one respect from that in Glasgow in that tissues were oven-dried at 80°C rather than being freeze-dried. The mussels and winkles used for α -autoradiography at Monaco originated from Sete and Mont St. Michel but were purchased at the local market. Because of the laboratory acclimatisation process and the relatively high radiotracer activities to which they were subsequently exposed (compared to environmental levels) for α -autoradiography, they have been assigned to Monaco in Figure 2.7 rather than to their respective areas of origin.

2.3 PLUTONIUM ANALYSIS

2.3.1 Introduction

The amount of plutonium generally found in environmental samples is of the order of picogrammes (10^{-12}g) to femto grammes (10^{-15}g) (1 Bq ^{239}Pu weighs 440pg; 1Bq ^{238}Pu weighs 1.55pg). The samples collected at the Esk estuary have plutonium levels which are enhanced above plutonium fallout concentrations from nuclear weapons testing because of their proximity to the Sellafield waste outfall. In investigating such small elemental quantities it is evident that conventional methods of chemical analysis cannot be used.

Because of its radioactive nature, however, minute quantities of plutonium can be measured by detection of its emitted α-particles. To obtain reliable measurements decontamination of the plutonium is essential to produce a counting source which gives little spectral degradation.

Of the many analytical procedures available for measurement of plutonium the more popular methods employ co-precipitation (de Bortoli; 1967; Wong, 1971; Reynolds and Scott, 1975), solvent extraction (Butler, 1965; Reynolds and Scott, 1975; Singh et al., 1979) or ion-exchange resins (Talvitie, 1971; Holm and Fukai, 1976; Lally and Eakins, 1978). In this present work ion-exchange resins are employed.

The resins used are commercial anion exchangers composed of polystyrene, cross-linked with varying amounts of divinylbenzene with quaternary ammonium functional groups, usually $-N(CH_3)_3^+$ (Cleveland, 1970). Choppin (1959) suggests that plutonium separations are best achieved by anion exchange since changes in complexing ability with oxidation state allow control of adsorption and desorption.

The acid medium used in the ion exchange process is hydrochloric acid although nitric acid medium can be used to give similar results (Ryan, 1960; Cleveland, 1970; Bagawde et al., 1976; Saito, 1984). In hydrochloric acid Pu(IV) is complexed even in very dilute solutions (0.3-0.4M). Stepwise complexing occurs (Grenthe and Norren, 1960) with increasing Cl^- concentration and, above about 7M, essentially all the plutonium is in the anionic forms $(PuCl_5)^-$ and $(PuCl_6)^{2-}$ (Cleveland, 1970). Pu(III) cannot form anionic species in HCl, giving $(PuCl)^{2+}$ in 2-8M HCl and $(PuCl_2)^+$ above 8M (Marcus, 1966). Pu(VI) exists as three charged species; $(PuO_2Cl)^+$ in 2M HCl and $(PuO_2Cl_3)^-$ and $(PuO_2Cl_4)^{2-}$ above 6M. However all these complexes have relatively low stability constants (Cleveland, 1970).

From the above it can be seen that plutonium can be isolated by anion exchange if the sample is applied to the resin in strong (about 8M) hydrochloric acid with the plutonium tetravalent. Relatively few other elements are adsorbed under these conditions (Saito, 1984) and those which are can be selectively eluted. Plutonium itself can be desorbed through complexation by changing chemical conditions to selectively reduce plutonium to Pu(III) using a mixture of hydrochloric acid and hydriodic acid. Many other mixtures can be used to remove the adsorbed plutonium from the ion-exchange resin (de Bortoli, 1967; Talvitie, 1971; Wong, 1971; Reynolds and Scott, 1975).

In the final stage of plutonium analysis, electrodeposition is preferred over evaporation as the former produces a better thin source. The plutonium is held in a carrier, commonly a sulphate forming the basis of an electrolyte. Both ammonium sulphate

(Lally and Eakins, 1978) and sodium sulphate (Kressin, 1977) have been used in this study.

The electrolysis cell consists of a watertight container with a platinum anode and a disc of stainless steel as cathode. A basic region exists just above the cathode and the plutonium migrates into this zone, hydrolyses and deposits on the cathode as a hydrous oxide. After electrodeposition, the plating solution must be made alkaline to prevent redissolution of the plutonium. The prepared source is then used for α-spectrometry.

Alpha-spectrometry is carried out using semiconductor detectors. These consist of a wafer of n-type semiconducting material, which has been exposed to air and then coated with a thin gold film. This forms a surface layer in which p-type conduction occurs.

An incident charged particle dissipates its energy in the sensitive surface region of the detector and generates electron-hole pairs in the conduction and valence bands, the number of promotions being proportional to the particle energy. In silicon, the energy required to form an electron-hole pair is 3.5eV, since some energy is lost by crystal excitation. The charge carriers generated migrate under the applied bias (10-100V), forming a charge at the electrodes. This minute current pulse is amplified and transmitted to the ancillary counting equipment. The purpose of this latter system is to amplify and shape the pulses, discriminate against spurious noise signals and sort the pulses. The important properties of a signal are its time of generation and its height. Its duration is of much less significance. The amplifier, therefore, both boosts the signal (10^2 to 10^4 times) and shortens its duration to reduce pile-up. A discriminator circuit is used to remove small noise pulses and the signal is then transmitted to an analogue-to-digital convertor (ADC). The latter generates a digital signal, proportional to the incident pulse height, which is counted in a binary channel in the memory of a multi-channel analyser (MCA). Channel number in the MCA is proportional to the digital signal size and hence to the energy of the incident charged particle.

2.3.2 Practical plutonium separation

The routine method for plutonium analysis used at Glasgow University although based on the method of Lally and Eakins (1978), is most suitable for soil and sediment samples of 50g. Modifications were therefore made initially to allow analysis of biological materials. Sample size was reduced to 1-3g, the dissolution process slightly changed and only one ion exchange step employed in the analysis of samples. Further modifications were subsequently made to the dissolution process, a double-spiking method was introduced and a different electroplating technique used.

In summary an aliquot of freeze-dried homogenised tissue, weighed accurately, is added to a 250 ml beaker. The tissue is moistened with a few drops of distilled water and an appropriate amount of tracer added. In the early samples only plutonium was analysed and in later samples both plutonium and polonium. Normally 0.075 or 0.15 Bq of pure ^{242}Pu tracer (α ; 4.90 MeV; $t_{1/2}$ = 3.8 x 10^5y) is added depending on the expected activity of the sample and an appropriate amount of ^{208}Po tracer (α ; 5.11 MeV; $t_{1/2}$ = 2.9y), an activity equivalent to at least twice that of the natural ^{210}Po expected in the sample (Fleer and Bacon, 1984). 5ml of conc. nitric acid (s.g. 1.42) is added slowly and the solution warmed gently on a hotplate to help prevent any loss of material through effervescence. The early samples were digested using a method loosely based on that reported by Talvitie(1971) in that conc. HNO_3, 30% H_2O_2, conc. HCl and 8M HCl were used. Once the initial effervescence has ceased, any remaining organic matter is destroyed by adding and evaporating 5ml of 30% H_2O_2 and conc. HNO_3 alternately. This step is repeated several times to ensure complete degradation of any organic matter present. After the nitric acid solution has been evaporated, 5ml of conc. HCl is added and evaporated to ~2ml followed by 50ml conc. HNO_3 which is evaporated to ~2ml again before adding 50ml 8M HCl. The sample is now ready to be passed through the ion exchange column.

Later samples were dissolved using the technique described by Cherry and Heyraud (1981). The initial 5ml conc. HNO_3, after

effervescence has ceased, is evaporated to dryness. 5ml of a 1:1 mixture of conc. HNO_3 and $HClO_4$ (wt per ml 1.70g) is added and evaporated producing dense white fumes. If at this stage the residue is not pale orange, yellow or white, the process is repeated. 5ml of conc. HCl is added and evaporated leaving a white residue, which is dissolved in 20ml 6M HCl.

At this stage the sample is prepared for straightforward plating of polonium onto a silver disc as described in section 2.4.2. After the first plating of polonium from the sample, the solution is acidified by adding 1-2ml of 6M HCl and evaporated to 10ml as a thick pale yellow precipitate is produced which prevents evaporation to dryness. 50ml of conc. HNO_3 is added and evaporated to ~ 2ml, during the course of which the precipatate dissolves. After 50ml of 8M HCl is added, the solution is applied to the ion exchange column.

This column is a 12cm glass tube, 1cm in diameter, with a tap at the base and a glass frit above. There is a B14 socket at the top and the reservoir is a 50ml separating funnel with a B14 cone. The resin bed is 4cm deep, Bio-Rad AG1-X8 (100-200 mesh) with a glass wool plug on top. The column is conditioned with 20ml of 8M HCl. Once the sample (in 8M HCl) has passed through the column, the resin is washed with 40ml 8M HCl. Both washings are retained for further polonium plating. The column is washed with 40ml 8M HNO_3, then 20ml conc. HCl and plutonium eluted with 25ml 0.2M HI/11.1M HCl. 1ml of $NaHSO_4$ solution (10% w/v) is added and the sample dried under an infra-red lamp. 1ml conc. HNO_3 is added and the sample dried again prior to electrolysis.

2.3.3 Electrodeposition of plutonium

The early samples used ammonium sulphate as the electrolytic medium from which plutonium is deposited on to a stainless steel disc used as the counting source. The sample is dissolved with warming in 2ml of 1.8M H_2SO_4 and then 3ml water, 0.2ml saturated Na_2EDTA and a drop of methyl red indicator are added. Ammonia is added dropwise until the solution is alkaline, at which 0.5M H_2SO_4 is added, again

dropwise, until the sample is just acidic. The solution is transferred to an electroplating cell and made up to 45ml with water. The pH is adjusted to 2.4 with 0.5M H_2SO_4 using a pH meter. The sample is electrolysed at 0.5A for the first 30 minutes of plating after which the current is increased to 1A for 3 hours. The electrolyte is then made alkaline by adding ammonia solution (s.g. 0.880) and plating continued for one minute. The plated disc is removed, rinsed with water and ethanol and dried for α-spectrometry.

The electrolysis cell used in plating plutonium from the ammonium sulphate medium is shown in Figure 2.8. It consists of a perspex (or teflon) body, 6 cm in diameter and 10 cm deep, together with a brass base. A perspex support holds the platinum wire anode, housed in a glass sheath except at the extremities, centrally in the cell body, the spiral of wire resting ~0.5cm above the stainless steel disc lying on the raised platform of the brass base. A watertight seal is ensured by fitting a rubber O-ring between the planchet and the cell body. The cell body and brass base fit snugly together using lugs in the brass base and sockets in the cell body to secure them together. The base is also fitted with a locating pin for an electrical contact from the electrolysis power supply.

The later samples used an Na_2SO_4 - $NaHSO_4$ mixture as the electrolytic medium for depositing plutonium. This technique is based on the method used by Kressin (1977). Here the sample is dissolved in 2-3ml of water and allowed to stand for 10 minutes to ensure complete dissolution of the $NaHSO_4$ prior to transferring the sample to the electrodeposition cell. The cell is assembled and rinsed several times with a 1:1 HNO_3 - H_2O mixture followed by 3-4 rinses with distilled water. 4ml of 15% Na_2SO_4 (anhydrous) solution is added to the cell followed by the sample solution. The cell is filled to within 1-2cm of the top and the anode-cathode distance adjusted to 0.5cm. Electrodeposition is performed at 0.5A for 3 hours. Before the power is switched off, 1-2ml of conc. NH_3 (s.g.0.880) is added and electroplating continued for another minute. The plated disc is then removed, rinsed in water and methanol and dried for α-spectrometry.

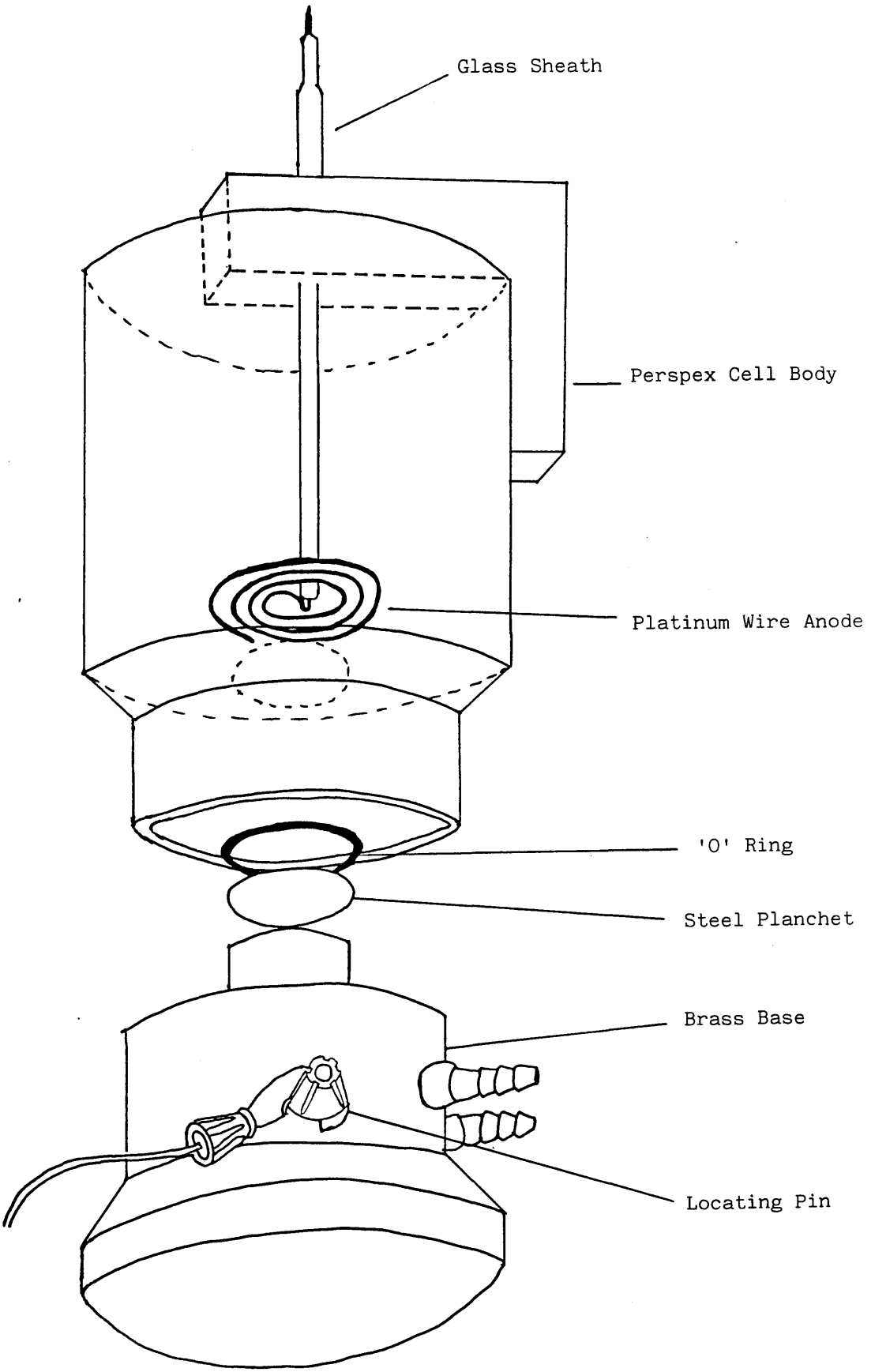


Figure 2.8. Exploded diagram of Perspex cell.

The cell design is given in Figure 2.9. It consists of a modified Universal Container (Alpha Laboratories Cat. No. CW3880) made of polystyrene, 9cm long (with cap off), of 2.5cm diameter at the screw top and it has a volume of 30ml. The conical base is removed by machining. The cathode is formed by inserting a metal pin through the centre of the container cap. The steel disc is placed in the cap, contacting the metal pin. An O-ring is used to provide a water tight seal. The anode is identical to that in the previous cell except that it is slightly shorter. It is supported by another plastic cap which positions it centrally in the tube. Prior to each plating, the assembled cell is checked for leaks.

The advantage of this latter plating procedure are that preparation of the sample is much easier and more convenient, having removed the need for pH adjustments; the polystyrene cells are disposable, therefore exclude any risk of contamination at this late stage of the plutonium analysis; and the plating volume is reduced thus lowering the current supply needed for electrodeposition of plutonium.

2.3.4 Alpha-spectrometry

Alpha-spectrometry is performed by surface barrier detectors linked to a multi-channel pulse height analysis system. The electroplated source is mounted on a platform beneath a silicon surface barrier detector in an evacuated chamber. The vacuum is necessary both to prevent energy loss from α -particles due to collision with gas molecules and to avoid detector breakdown which can occur if a bias is applied to the detector without a vacuum. Sources are raised as close as possible to the detector for maximum efficiency, although this does result in slightly poorer than optimum resolution.

The counting system used at Glasgow University is based on a central Canberra multi-channel analysis facility. The detectors used were supplied by EG and G Ortec and have active areas of 300mm^2. The minimum depletion depth is 100μm, operating voltages range from 50-150V and resolution is typically 30 KeV full width at half

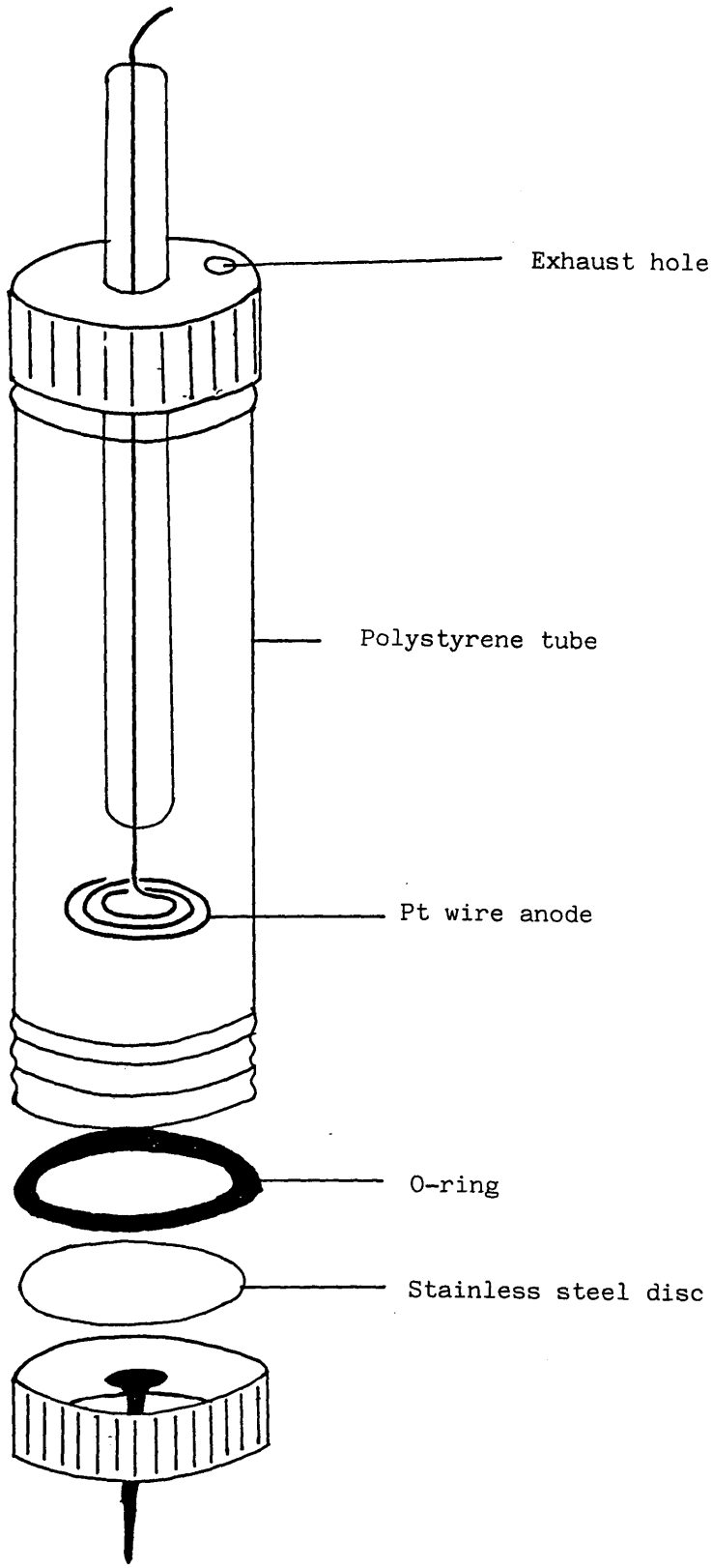


Figure 2.9. Electrolysis cell (Based on Kressin, 1977).

maximum (FWHM). High voltage supplies, pre-amplifiers and spectroscopy amplifiers were all commercially available (Canberra models 3102, 2004 and 2012 respectively).

The pulse height analysis system employs a Canberra Series 80 MCA with 16K memory. The memory is subdivided into 256 byte blocks, two of which are dedicated to each α-counter. The resulting α-spectrum is displayed over 512 channels.

Calculation of the results is straightforward. Assuming that the sample and tracer plutonium were in isotopic equilibrium, then the sample activity can be calculated by simple ratio:

$$A\ (\text{sample}) = \frac{I\ (\text{sample})}{I\ (\text{tracer})} \times A\ (\text{Tracer}) \qquad \begin{matrix} A = \text{activity} \\ I = \text{peak integral} \end{matrix}$$

In practice a number of corrections must be made. First, the background, if any, is subtracted from each integral and then the sample peaks may need to be corrected for cross-contamination. The ^{242}Pu as a tracer, however, is not usually contaminated and has a sufficiently long half-life (3.9×10^5 years) for decay-correction to be unnecessary.

A major source of error in the α-spectrometric analysis - and indeed in any radiometric measurement - is the uncertainty arising from the counting process itself. This error contribution arises from the random nature of radioactive decay. Provided the peak integrals are large (at least a few hundred counts), the distribution of counts is described by the Poisson distribution, which enables modelling of the number of discrete events which occur in a defined interval of space or time. For a peak integral of I counts the counting uncertainty is given by $\sqrt{I}$, so that the relative error is $\sqrt{I}$ / I. The counting error on a final calculated result will be a function of the errors on the tracer and sample peaks and is given by:

$$\sigma_{1,2} = \sqrt{\sigma_1^2 + \sigma_2^2}$$

where $\sigma_{1,2}$ = error in ratio
σ_1 = error in integral 1
σ_2 = error in integral 2

$$= \sqrt{\frac{1}{I_1} + \frac{1}{I_2}}$$

where I_1 = Integral of peak 1
I_2 = Integral of peak 2

2.4 POLONIUM ANALYSIS

2.4.1 Introduction

It is well known that the atmosphere contains appreciable quantities of ^{222}Rn as a result of its emanation from the radioactive precursor materials of the earths crust. ^{210}Pb, the long-lived radionuclide produced in the atmosphere by radon decay, has a half-life of 22 years, much longer than the 20-30 day mean residence time of aerosols in the troposphere and it is therefore returned to the earths surface as a natural component of wet and dry fallout. During residence in the atmosphere sufficient time elapses for ingrowth of most of the equilibrium activity of ^{210}Bi (β; $t_{1/2}$ = 5.01d) and some of ^{210}Po (α; 5.4 MeV; $t_{1/2}$ = 138.4d) and these therefore also participate in the fallout process. ^{222}Rn, ^{210}Pb, ^{210}Bi and ^{210}Po are all members of the natural ^{238}U decay series (Figure 2.10).

In addition to this natural process of production, ^{210}Po may be released into the atmosphere artificially from the nuclear power industry, space satellites (using ^{210}Po as a source of thermal power) and nuclear weapons testing (Hill, 1965).

The marine geochemistry of ^{210}Po exhibits unusual and interesting features, especially when it is compared with its grandparent ^{210}Pb. The $^{210}Po/^{210}Pb$ activity ratio is about 0.1 in the atmospheric particles which fall into the ocean, 0.5 in sea water, 2 in zooplankton faecal pellets, 20 in whole zooplankton and 100 in the hepatopancreas of many marine invertebrates (Cherry and Shannon, 1974; Cherry and Heyraud, 1982). Cherry and Shannon (1974) found typical ^{210}Po concentrations in marine organisms to be generally much higher than for other natural radionuclides such as uranium, thorium, radium and lead.

The high $^{210}Po/^{210}Pb$ quotients in the biological materials reflect high ^{210}Po rather than low ^{210}Pb concentrations. Radiobiologically ^{210}Po provides the major contribution to the natural radiation dose received by most marine organisms (Cherry and Shannon, 1974). In

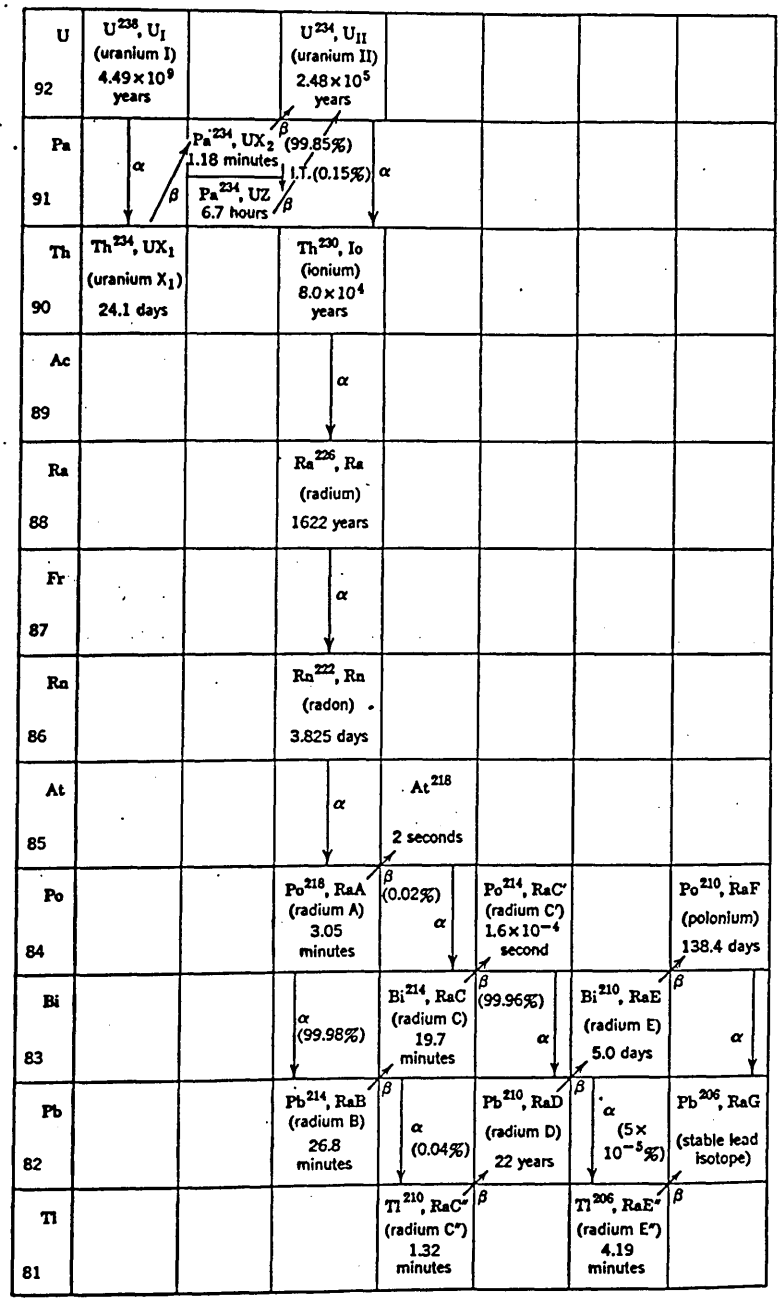


Figure 2.10. Uranium decay series (from Friedlander et al., 1964).

the hepatopancreas of marine invertebrates the radiation dose from ^{210}Po ranges from 0.013 to 2.8Sv yr^{-1} (Heyraud and Cherry, 1979; Cherry and Heyraud, 1981, 1982); in comparison, the human organ which receives the highest natural radiation dose is the lung with a typical dose from all sources of about 4mSv yr^{-1} (UNSCEAR, 1977). Why ^{210}Po is enriched in marine biological materials to such a comparatively high level is not clearly understood at present although Cherry et al. (1983) suggest that an association of ^{210}Po with sulphur-containing amino acids could play a vital role affecting the behaviour of ^{210}Po in the hepatopancreas.

Because of the prominence of ^{210}Po throughout marine biological tissues it was considered essential for the α-autoradiography study to measure the polonium concentration of the samples. Analysis of ^{210}Po in biological samples is similar in principle to that for plutonium in that polonium is first isolated from the sample and a good counting source produced as the quantity of polonium in the sample is calculated from the emission (and detection) of its monoenergetic α-particles.

In recent polonium studies (Mackenzie et al., 1979; Cherry and Heyraud, 1981; Fleer and Bacon, 1984) the determination of ^{210}Po in environmental materials has been strongly based on the procedure described by Flynn (1968). Flynn reviewed existing methods at that time and noted that the most straightforward and popular technique involved spontaneous deposition of polonium on to silver from weakly acidic solutions. This method, however, was subject to interferences from oxidants, organic materials and other elements which also deposit on silver. To overcome these interferences precipitation methods had been employed, involving calcium tannate (Smales et al., 1957) sodium hypophosphite with tellurium carrier (Rundo, 1959) and tin II chloride with tellurium (Rushing, 1966). Flynn described a method for the spontaneous deposition of ^{210}Po in the presence of large quantities of foreign ions requiring no preliminary separation and giving essentially quantitative recoveries.

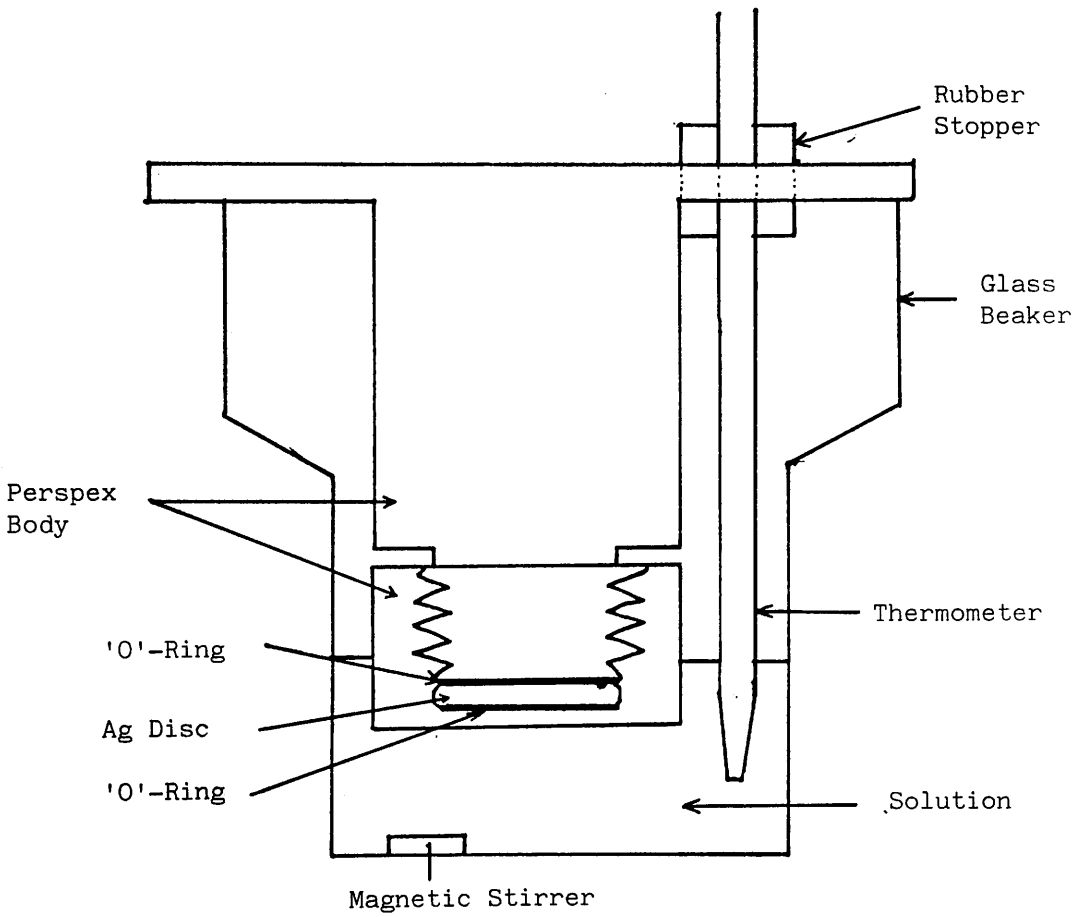
2.4.2 Practical polonium analysis

Since polonium analysis of marine organisms has been performed both at Glasgow University and at the IAEA International Laboratory of Marine Radioactivity, Monaco, two techniques have been used in this study.

The sample digestion method used in Glasgow has already been described in section 2.3.2. After 20ml 6M HCl has been added, the solution is prepared for plating by adding ~0.1g of hydroxylamine hydrochloride (which reduces any Fe^{3+}, Cr^{6+} or other oxidants which would interfere with deposition). Ammonia (s.g. 0.880) is added to increase the pH of the solution to 2 and the solution is heated at 85° to 90°C. The addition of sodium citrate and bismuth hold-back carrier recommeded by Flynn is not performed because previous work at Glasgow (Swan, 1978) showed no yield advantage. The volume of the final solution is maintained below 50ml, elevated temperature and low solution volume favouring efficient deposition.

Plating is performed in the cell shown in Figure 2.11. The perspex holder restricts polonium deposition to one side of the 1" diameter silver discs, maximising counting sensitivity and at the same time minimising evaporative loss during plating. Air bubbles occasionally trapped beneath the silver disc, are periodically removed by manipulation of the plating cell/beaker assembly. Plating is continued for 4 hours at 85° - 90°C with stirring following which the silver disc is removed from the holder, rinsed with distilled water and left to air-dry prior to α-particle counting. Following the first deposition of polonium, the plating solution is stored in the dark for 5-6 months, after plutonium has been removed from it (Section 2.3.2). At the end of this time ^{210}Po which has in the interim grown-in from any ^{210}Pb in the solution is deposited on a new silver disc. Calculation of the ^{210}Pb content enables quantification of the supported and unsupported ^{210}Po components. Plated silver discs are normally left at least overnight before counting to reduce the possibility of detector contamination due to a 'pseudo' recoil

Figure 2.11. Polonium plating cell



effect of polonium, attributed to its own inherent volatility (Sill and Olsen, 1970). This practice is recommended by Fleer and Bacon (1984).

Determination of the α-radioactivity of the deposited silver discs is again by surface barrier detector using the technique and equipment discussed in some detail in section 2.3.4. At Glasgow counting chambers are specifically reserved for particular nuclides and particular activity levels. For polonium α-spectroscopic measurement, bias voltage is applied to the detectors via dual high voltage supplies (Ortec model 428) and detector output signals are fed through duplicate electronic systems consisting of low noise charge sensitive preamplifiers (Ortec model 125), pulse shaping main amplifiers (Ortec model 471) and bias amplifiers (Ortec model 408A). Bias amplifier outputs are transmitted, as are the plutonium α-detectors, to a Canberra Series 80 MCA, resulting in the α-spectrum being displayed over 512 channels. Detector counting efficiencies measured against a calibrated source (Radiochemical Centre, Amersham, code AMR22) containing electrodeposited ^{241}Am (deposit diameter 2mm) with a certified rate of emergence of 1.53×10^4 α-particles/min from the front surface ($\pm$ 2%, 3 σ error) are 27.4% (detector 16/133B) and 25.4% (detector 14/744D) respectively. Efficiencies for silver discs where the deposited activity is spread over a 2cm diameter face are 23.6% and 22.2% respectively.

The system is calibrated and resolution maximised using a 3 nuclide source (Radiochemical Centre, Amersham, Code AMR33) containing ^{239}Pu ($E\alpha$ = 5.15 MeV), ^{241}Am ($E\alpha$ = 5.48 MeV) and ^{244}Cm (E_α = 5.80 MeV) guaranteed capable of resolution to 20 keV at FWHM. The total system resolution for sample sources is 38 to 56 keV (FWHM).

After counting, the overall efficiency of ^{210}Po is corrected via the observed count rate from the known activity of ^{208}Po spike initially added and the concentration of the ^{210}Po in the sample

evaluated. The mean chemical yield using the above analytical procedure is 86.8% (range 73 - 100%).

The product α-spectrum usually shows good separation of the two polonium peaks (Figure 2.5) but small corrections to adjust for tailing of the ^{210}Po peak into the ^{208}Po region are necessary. The corrections rarely exceed 10 per cent of the ^{210}Po counts. Counting times are usually 1 or 2 days, giving typically ~ 4000 counts of the ^{208}Po tracer. Detailed interpretation of the Po α-spectrum requires its subdivision into four regions of interest (Figure 2.12). This is achieved by first locating the ^{208}Po maximum and counting the number of channels between it and the minimum between the ^{208}Po and ^{210}Po peaks. The same number of channels is then taken to the right of the ^{210}Po peak to locate the upper boundary of region 4. The lower boundary is set at the minimum and the other three regions are then each selected to span the same number of channels. It is assumed that some of the counts in regions 2 and 3 but not in 1 are contributed to by the low-energy tail of the ^{210}Po peak. Correction for this effect is based on the assumption that the pure ^{208}Po and ^{210}Po peaks, both mono-energetic have identical shapes, so that the ^{208}Po tail can be used to infer the ^{210}Po tail. The procedure, which is derived from Fleer and Bacon (1984) is illustrated in Figure 2.12. Successive approximations are made iteratively until there is less than 0.1 count change in the estimated ^{210}Po tail.

Once the numbers of counts of ^{208}Po and ^{210}Po have been calculated, simple decay-correction is performed using the primary equation

$$A(t) = A(o)\, e^{-\lambda t}$$

where A(t) = Activity of isotope at time t
A(o) = Activity of isotope at time o
λ = decay constant
t = time of decay

to yield a preliminary value for the ^{210}Po activity in the sample.

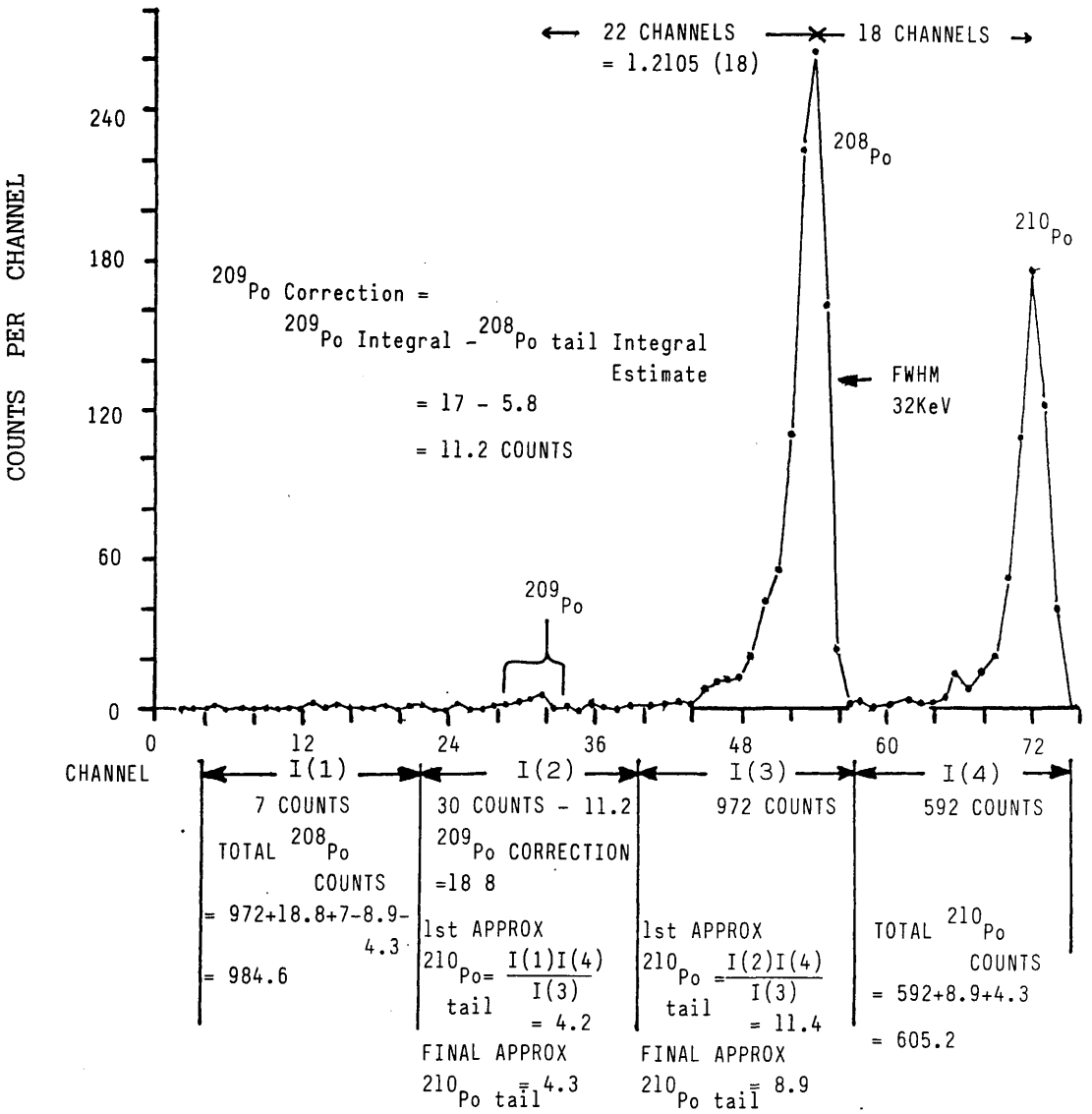


Figure 2.12. Polonium alpha spectrum and illustration of method used to correct for ^{210}Po tailing (based on Fleer and Bacon, 1984).

Decay-correction considerations produce the ^{210}Po activity in the sample at the time of plating (t) which is then used to provide an estimate of the ^{210}Po concentration at the date of sacrifice (t_o).

After 5-6 months, when the solution is replated for ^{210}Pb assay, the subsequent α-spectrum enables calculation of the ^{210}Pb content on the assumption that any ^{210}Po then present in the solution is produced from decay of its grandparent ^{210}Pb. The ^{210}Po sample activity is then calculated on the basis of this known ^{210}Pb contribution to the overall ^{210}Po activity. In this work, this recalculation has produced data modifications of typically $\sim 4\%$ relative to the preliminary values of ^{210}Po. Details of these $^{210}Po/^{210}Pb$ calculations are given in Appendix A.

In Monaco, samples are dissolved using the technique described by Cherry and Heyraud (1981) discussed earlier. No ^{208}Po tracer is used as it has been shown (Heyraud, pers. comm.) that, following radiochemical separation of the sample, the Monaco total α-counting system registers only ^{210}Po counts and does so with reproducible efficiency.

At the end of the dissolution process, after evaporation of the conc. HCl, 220ml of 0.3N HCl is added to dissolve the residue and acts as the plating medium, eliminating any need for pH adjustment. 0.1g of ascorbic acid is added (this has a similar role to the hydroxylamine hydrochloride used at Glasgow), dissolved and the solution heated to 85°C. A silver disc 2.5 cm diameter and 0.0025 inches thick is cut from a roll of silver foil, cleaned in distilled water, acetone, and 0.3N HCl prior to use, and this is then suspended in the plating solution by plastic thread, through a small hole at the edge of the disc. Once the disc has been placed in the plating solution, the temperature is lowered to 60°C and left for 16 hours. After plating, the silver disc is rinsed with water, air-dried and placed between two pieces of ZnS(Ag) phosphor coated paper. These three items are secured in a plastic disc holder using a piece of clear polythene. The holder is carefully placed in contact with a photomultiplier tube to be

α-counted. The photomultiplier tube is sealed in a light-tight unit and connected to a scaler. Alpha particles striking the ZnS(Ag) phosphor produce light pulses which are counted until ~100 counts have been obtained, giving counting errors of ~10%. Without use of tracer, the activity of ^{210}Po in the samples is calculated using calibration data obtained using a ^{239}Pu source of known activity.

After the plating solution has been stored for 5-6 months and replated for ^{210}Po, the calculations of ^{210}Po and ^{210}Pb contents are performed as summarised previously and detailed in Appendix A.

2.4.3 ^{210}Po content in mussel faecal pellets

To assess, as part of this study, the effect of polonium loss from mussels, it was necessary to assay faecal pellets. This aspect of the project was also carried out at Monaco and thus the established Monaco techniques for ^{210}Po analysis were used.

Mussels were collected from Fontvieille pier in Monaco and were immediately cleaned of all epibiotic growth. Five mussels were dissected (total soft parts removed from the shell) and analysed for polonium. Fifteen mussels, 3-5cm long, were placed on a square plastic sieve and submerged in a basin containing 6 litres of 0.22 μm-filtered sea water. Any faecal pellets produced over the 1 day loss period were collected using a plastic pipette and were rinsed in distilled water, weighed and oven-dried. (The mussels were left a second day but very few faecal pellets were produced). At the end of the 1-day loss period, the faecal pellets, mussels and sea water were analysed for polonium. The faecal pellets and mussels were analysed as before but the water required a different preparative procedure to extract the polonium. The Monaco method was as follows:

1.5 litres of water were immediately acidified by addition of 2.5ml conc. HCl at time of sampling. The pH of the water was adjusted

to 2 by addition of conc. NH_3 prior to commencing extraction. The sample was transferred to a 2-litre separating funnel and 15ml of freshly prepared 4% (w/v) APDC (ammonium pyrrolidine dithiocarbamate) solution (0.6g in 15ml) was added. The funnel was shaken vigorously for 1 min, allowed to stand for 5 mins then shaken again for 1 min. 75ml of solvent MIBK (methyl isobutyl ketone) were added, the contents shaken for 5 mins and left to settle for 30 mins. The aqueous portion was discarded and 6ml of conc. HCl added. This acid/organic mixture was evaporated on a hot-plate to remove the bulk of the organic layer (MIBK b.pt. 114-117). The residue was then processed for polonium analysis as described before.

2.5 GAMMA-RAY SPECTROSCOPY

Gamma-ray photons are produced in most radioactive decay processes as excited daughter nuclei return to their ground states (Cunninghame, 1972). A few isotopes decay by pure β^-emission whilst γ-emissions produced after α-decay are generally of relatively low energy comparable to X-rays. In the case of a β^-, γ-emitting nuclide, detection of either radiation is possible. However, in a complex mixture of such nuclides, β^- counting generally becomes impracticable because of extensive interferences caused by overlap of the component β-spectra. Such interferences are much less likely to occur in γ-ray spectroscopy as mono-energetic γ-photons are emitted during transitions between specific nuclear energy levels.

Two types of γ-ray detectors are in common use. These are (a) the thallium - activated sodium iodide detector (NaI(Tl)), which is a solid state scintillation counter and (b) the semiconductor detector of which the lithium-doped germanium detector (Ge(Li)) is the most widely used.

The sodium iodide crystal, used in conjunction with a photo-multiplier and a multi-channel analyser, usually has a high

counting efficiency, detecting almost 100% of incident photons up to 200 keV and about 20% at 1 MeV (Friedlander et al., 1964). The resolution of a NaI(Tl) counter is, however, relatively poor as the dissipation of 100-300 eV is required to generate one electron in the first stage of the photo-multiplier tube. This relatively poor resolution means that NaI(Tl) - based counters are best applied to analysis of simple mixtures of nuclides.

The Ge(Li) detector is ideally suited to γ-ray spectroscopy. It is easily capable of detecting photons in the energy range 40 keV-2 MeV. In comparison with a NaI(Tl) counter the Ge(Li) detector has a greater resolution (1.1 keV FWHM at 122 keV; 2.0 keV FWHM at 1.33 MeV) but has a reduced absolute detection efficiency (5% at 100 keV; 0.5% at 1 MeV).

Extensive calibration is necessary to obtain reliable results from a Ge(Li) spectroscopy system. First, energy calibration is required involving counting a standard source containing several nuclides of known photon energies (Amersham mixed γ-emitter standard; ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y, ^{60}Co) which should ideally bracket the energy range of interest here usually from 59.5 keV (^{241}Am) to 1460 keV (^{40}K).

Efficiency calibration primarily relates to the specific geometry in which the sample is presented for counting and takes into account factors such as the self-absorption of γ rays due to the finite thickness of the source, the inverse-square law of attenuation of all electromagnetic radiation and the solid angle intersected by the detector. Efficiency calibration is generally performed using standards prepared by adding known activities of a number of nuclides to matrix blanks which mimic the sample composition. These standards are counted in the same geometry as the samples. From the standard count rates, the energy/efficiency relationship for a given geometry can be found.

All the quantitative γ-ray spectroscopy carried out at Glasgow used a Canberra coaxial Ge(Li) crystal shielded with 10cm of lead. To provide extra shielding, the base of each crystal was surrounded by bags of lead shot. The crystal has a sensitive area (active area facing window) of $25cm^2$ (nominal efficiency at 1332 keV is 27.5%) and an operating voltage of 4 kV. The crystal is mounted vertically on a cold-finger under vacuum for operation at liquid nitrogen temperatures. Power supplies, pre-amplifiers and spectroscopy amplifiers were all supplied by Canberra (Models 3102, 2001 and 2012 respectively). Homogenised tissue samples were placed in counting dishes (geometry previously determined) which were counted for 90,000 seconds. The spectra were collected in 4096 channels of the multi-channel analyser via combined analogue-to-digital convertors and mixer-router (Canberra Model 8621). At the end of data accumulation, the spectra were stored on a floppy disc for subsequent computer analysis. The software used was Canberra Spectran F1 (Version 2) running on a DEC PDP 11/03-L. A detailed description of the methods used in the programme is presented in the Canberra Spectran - F1 (Version 2) Users Manual, 1981.

Energy calibration generates three relationships:

i) Photon energy as a function of channel number
ii) Peak resolution (FWHM) as a function of energy
iii) Peak tailing (arising from incomplete energy dissipation in the detector) as a function of energy.

The calibration routine takes the raw spectral data, finds the peaks of interest and, using a curve-fitting technique, identifies the 'centroid', and indicator of peak location. After all the peaks have been processed in this way, a quadratic equation is used for energy calibration and polynomial equations used to define the resolution and tailing functions.

All the calibration parameters for the detector, are stored on the Spectran-F system disc for analysis of samples spectra. The mathematical methods used to find peaks are complex, involving the use of 'difference' spectra. Once peaks have been located, their area is determined, using unsmoothed data, by summing the number of counts in each channel of the peak and subtracting the background contribution which is estimated by linear interpolation between several channels beyond each side of the peak. The uncertainty in the peak area measurements is calculated using standard Poisson statistics. Interference from environmental background peaks, principally low energy γ rays from lead in the shielding and 1460 keV γ rays from ^{40}K, is compensated by subtracting a previously stored detector background from the sample peaks.

At this point, the peak energies are determined from the energy calibration parameters and an isotope library searched to identify the nuclide responsible for each peak. In most cases, minor peaks are used to confirm the identification. Quantitative analysis of the sample is then carried out using the efficiency information stored on the system disc and the data are printed out showing nuclide activities at time of counting and decay-corrected to time of sampling.

2.6 ALPHA-AUTORADIOGRAPHY

2.6.1 Introduction

The first confirmed autoradiograph was obtained just over a 100 years ago. In 1867, Niepce de Saint Victor published an account of the blackening produced on emulsions of silver chloride and iodide by uranium nitrate and tartrate. In 1896, Henri Becquerel repeated and extended Niepce's observations, using crystals of uranyl sulphate and showed that, after exposing them to sunlight, they were able to darken a photographic plate through two layers of black paper. After these first, almost accidental, autoradiographs of crystals of uranium salts, the phenomenon remained

a curiosity rather than a scientific technique for the earlier part of the twentieth centry, The revolutionary advances in physics during and after the Second World War, however, brought a new impetus of autoradiography, particularly in the development and production of nuclear emulsions, photographic emulsions with specialised characteristics, which recorded the tracks of charged particles with precision and sensitivity.

The advent of the atomic bomb made it vitally important to know the distribution in plants and animals of the fission products of radioactive fallout. At the same time, new radioisotopes became available, opening up new possibilities in the investigation of biological systems. During the 1950's, a new technique employing a nuclear emulsion made its appearance. At the suggestion of S.R. Pelc, Kodak Ltd. began manufacture of a special autoradiographic stripping film (Berriman et al., 1950; Doniach and Pelc, 1950). Since publication of these two papers, the stripping film technique, which brought great advances in resolution and reproducibility, has probably yielded more autoradiographic information than any other single method.

Both the liquid emulsion and stripping film techniques produce emulsion layers a few microns thick over the surface of the specimen. Charged particles originating in the specimen leave only one or two silver grains to show their passage through this type of preparation.

A few autoradiographers, however, saw possibilities in the more direct application to biology of the physicists techniques of recording particle tracks. This approach is direct and simple in the case of α-particles which leave a very characteristic track which is easy to record and recognise. More recent advances in emulsion autoradiography have included the development of nuclear emulsions to accommodate the use of electron microscopes (Rogers, 1973).

In more recent years, the development and uses of solid state nuclear track detectors (SSNTD) as autoradiographic detection media have mushroomed (Fowler and Clapham, 1982; Durrani and Benton, 1984). The advent of SSNTD in the late 1950's (Young, 1958; Silk and Barnes, 1959) provided a chain of ideas and experiments which soon led to the discovery of particle track etching and helped to create a fascination for particle track research in solids. Particle track techniques have been studied and developed at Glasgow since the late 1970's (Crawford, 1982; Toole, 1984) but are, for the first time, used in the autoradiographic mode in this study.

The passage of heavily ionising nuclear particles through most insulating solids creates narrow paths of intense damage on an atomic scale. These damage tracks may be repeated and made visible in an ordinary optical microscope by treatment with a properly chosen chemical reagent which rapidly and preferentially attacks the damaged material. It less rapidly removes or etches the surrounding bulk undamaged matrix in such a manner as to enlarge the etched holes which make and characterise the sites of original individual damaged regions. This simple technique of observing particles has been used in an extremely wide variety of scientific fields ranging from nuclear science and engineering to botany, from beer stabilisation to cosmic ray astrophysics and from geology, archaeology and sub-oceanic geophysics to lunar science and meteorites (Fleischer et al., 1975).

Particle track analysis of environmental alpha-emitting nuclides, either from the natural decay series or of anthropogenic origin, is a simple and inexpensive technique which offers certain advantages over classical wet radiochemical methods. Very low or high α-activities are detectable since the exposure period of the plastic can be varied from minutes to years. Valuable isotopic data, however, cannot be easily obtained although Qaqish and Besant (1976) have shown that reasonable α-energy estimates may be possible by measuring 90° incident α-track diameters or producing range-energy relations after both carefully controlling etching procedures and ensuring bombardment by α-particles of known energy. Indeed, high resolution α-particle

spectroscopy has been demonstrated by Fews and Henshaw (1981) using the track detector CR-39, an energy spread of $\sim$35 keV (0.6%) being illustrated for 6 MeV α-particles. However, the time and instrumentation needed to measure the many required track parameters are considerable and were not available here; indeed the technical demands are such that these methods have not yet been proven in real environmental applications.

The nuclear track detector used in this study is the Kodak film LR115. This medium consists of a thin film (13 μm) of the α-sensitive cellulose nitrate (CLN), strongly coloured red, which is deposited on a thick (100 μm)) inert polyester base. The cellulose nitrate is specially treated to increase its response to ionising particles having a sufficiently high linear energy transfer (LET). The size and extent of the damage region are characterised by the parameter $(dE/dx)_c$, the critical energy loss rate for track formation (Fleischer et al., 1965). The maximum value of dE/dx for bombarding nuclei increases with atomic number so that, for CLN (or indeed for any other material), there is a lower mass limit for ions which can produce tracks. Consequently, the LR115 films are totally insensitive to X- or γ-ray photons, electrons or to high-energy protons. They can be used to record the tracks of protons of energy $\leqslant$ 100 keV, α-particles of energy $\leqslant$ 4 MeV and heavy ions or fission fragments. In α-track formation, the primary energy-loss mechanism at the high initial α-particle velocities is ionisation and electronic excitation of the CLN molecules. As the energy of the α-particle decreases along its path, the Coulomb interaction time increases, resulting in an increase in the rate of energy loss. When the particle or positive ion reaches velocities comparable to K-shell electron velocities, the ion starts to pick up electrons from the CLN, until velocities comparable to these of valence electrons are reached. The energy loss mechanism then becomes essentially one of elastic collisions between the particle or ion and the atoms of the detector (a process known as nuclear stopping) rather than one of electronic excitation. Thus specific ionisation reaches a maximum at low energies or low residual ranges in the CLN, giving rise to tracks whose etched

diameter shows a corresponding maximum. It is for this reason that, when recording tracks of α-particles whose energies exceed about 4 MeV (for example 10 μm thick tissue sections labelled with Np, Pu or Am isotopes), a deceleration medium such as Al foil or polyester film must be inserted between the sample and the track detector. Aluminium foils of thickness 4.50 mg cm^{-2} were used in this work for autoradiography since the range in Al of α-particles of the isotopes of interest, ^{237}Np (4.78 MeV), ^{239}Pu (5.15 MeV) and ^{241}Am (5.48 MeV) varies between 5 to 8 mg cm^{-2} Al.

In the autoradiographic mode, Kodak LR115 plastic detector, with inserted Al absorber is applied to each radiolabelled histological slide for a period of time sufficiently long to produce a high-density autoradiograph. Laboratory-labelled marine organisms had exposure times ranging from 1 day to 250 days depending on their level of radioactivity, whilst the samples from the Esk estuary were exposed for ~ 1½ years. After the appropriate exposure period, the CLN is etched in 2.5M NaOH at 60°C for 3 hours in a thermostatically controlled water bath, etching being stopped by washing the plastic in a 1:1 mixture of ethanol and distilled water. An initial examination of the plastic under x100 optical magnification is carried out to confirm successful etching. Examination of the track record and qualitative comparisons are easily performed because of the high degree of contrast between the perforations and the red background, an effect which can be further enhanced by use of a green filter or green light source. Non-quantitative α-autoradiography produces a permanent record of the general distribution of α-activity present on the surface of the sample and for the samples under study, can be homogeneous (Figure 2.13) or can include 'hot' regions of activity (Figure 2.14). The α-track distributions using various marine organisms, radiotracers and labelling media (food or water) are compared and contrasted to reveal activity trends within these organisms and between the various experimental conditions.

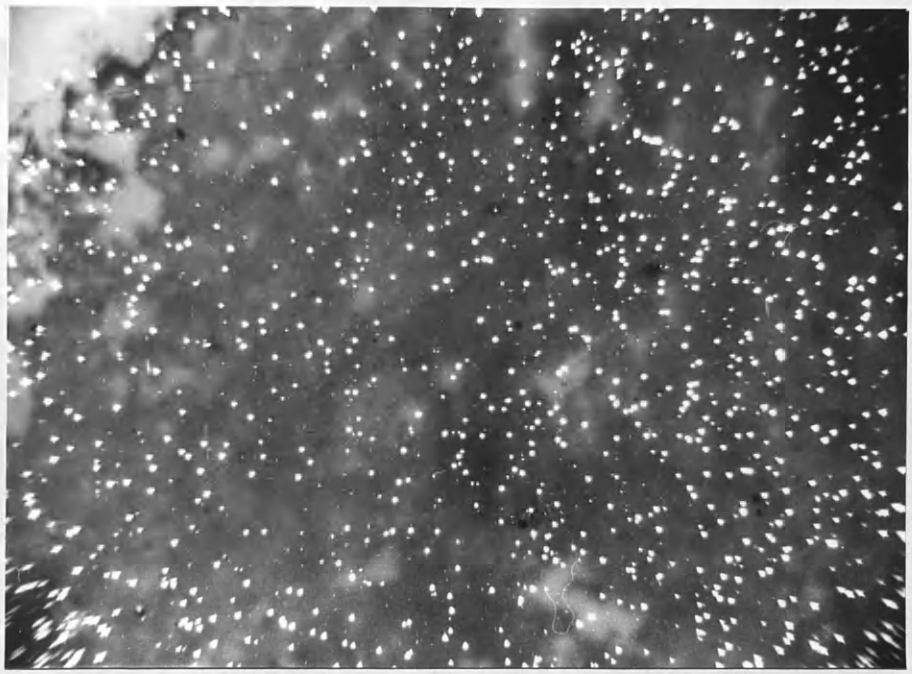


Figure 2.13. Homogeneous alpha-track distribution.

Photographs are taken on an Olympus BHB microscope using a Pentax K1000 camera mounted on a Pentax microscope adaptor K. An exposure period of ⅛ second is used at a magnification of X40, with a green filter which is complementary to the hue of the film.

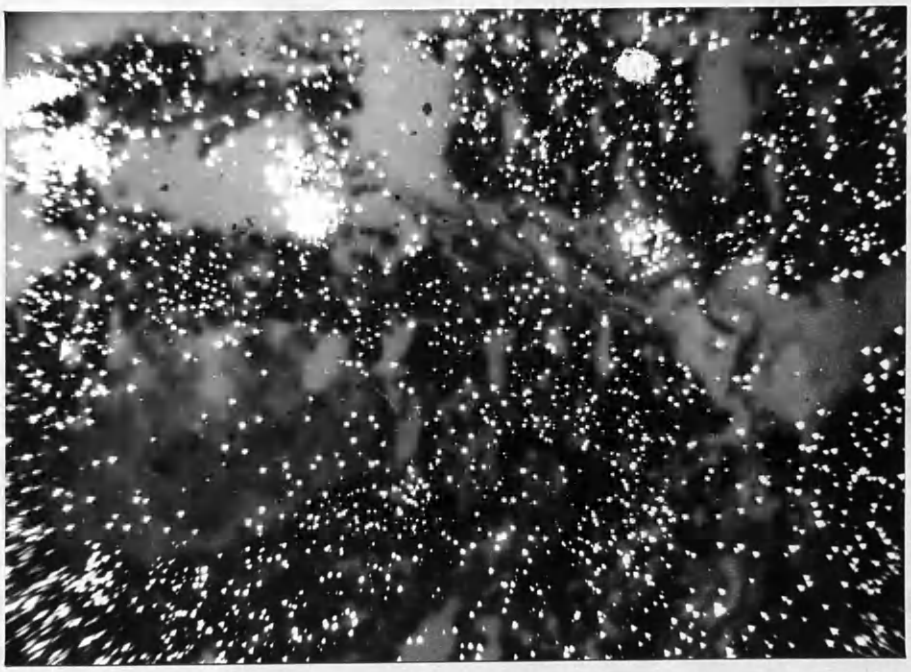


Figure 2.14. Heterogeneous alpha-track distribution.

2.6.2 Preparation of marine organisms for α-autoradiography

2.6.2.1 Radiolabelling experiments

The artificial labelling of mussels, winkles and Dublin Bay prawns with the transuranic nuclides ^{237}Np (α; 4.78 MeV; $t_{½}$ = 2.20 x 10^{6}y), ^{239}Pu (α; 5.15 MeV; $t_{½}$ = 2.44 x 10^{4}y) and ^{241}Am (α ; 5.48 MeV; $t_{½}$ = 432y) was performed at the IAEA International Laboratory of Marine Radioactivity at Monaco. Early biokinetic experiments performed at Monaco involved studies of the uptake and accumulation of ^{51}Cr by the clam (Chipman, 1966), the elimination of ^{55}Zn, ^{137}Cs and ^{144}Ce by euphausiids (Fowler et al., 1971) and the ^{109}Cd flux through mussels and shrimps (Fowler and Benayoun, 1974). The use of transuranic tracers in biokinetic experiments at Monaco was launched in 1975 by experimental studies on plutonium kinetics in mussels, shrimps and worms by Fowler et al. (1975). Since then, ^{237}Pu and ^{241}Am have remained popular tracers (Beasley and Fowler, 1976a; Grillo et al., 1981; Guary and Fowler, 1981, 1983; Bjerregard et al., 1985). Other transuranic tracers used in similarly designed experiments have been ^{235}Np (Fowler and Aston, 1982), ^{242}Cm (Grillo et al., 1983) and ^{252}Cf (Galey et al., 1983; Fowler et al., 1986). These transuranic isotopes were chosen because of their photon-emitting characteristics. ^{252}Cf (96.9% α-decay) can be monitored in environmental and radioecological laboratory experiments by counting the prompt photon energies > 2.6 MeV from spontaneous fission events. The low efficiency (~5%) is compensated by the very low background above 2.5 Mev which allows good counting statistics to be obtained (Aston, 1984).

The experiments at Monaco have been concentrated principally on the study of benthic species which live in close contact with sediments. Figure 2.15 presents the range of species studies thus far, with with their respective Pu concentration factors from contaminated sea water also shown. The most popular species studied have been mussels, shrimps and polychaete worms (Fowler et al., 1976; Beasley and Fowler, 1976a; Guary and Fowler, 1978; Vangenechten et al., 1983).

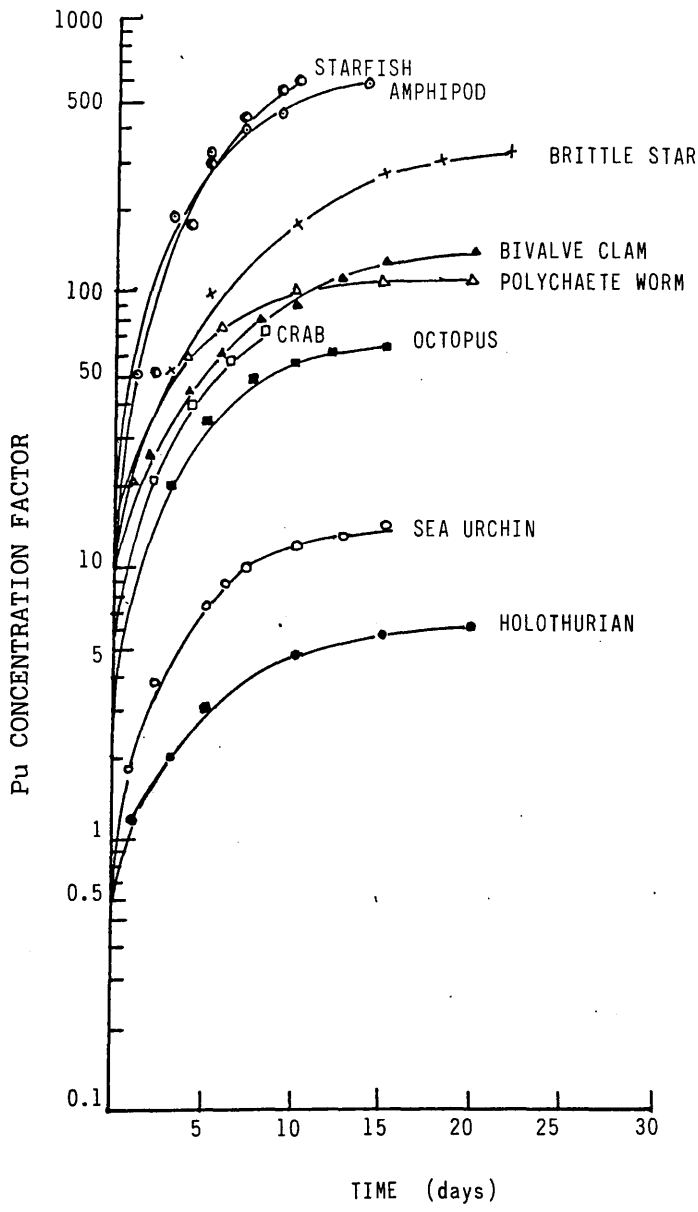


Figure 2.15. Laboratory derived concentration factors for plutonium uptake by marine species (IAEA, 1981).

The subject of the biokinetics of radioactive isotopes of elements and the principle of the extrapolation of laboratory-derived data to the real world has been a consistent point of discussion amongst marine radioecologists. It is extremely difficult to design laboratory experiments which are short-term and simplistic relative to oceanic processes but which will nevertheless provide useful predictive information on the accumulation and redistribution of radionuclides by marine organisms. In addition, field verification of laboratory-derived information is often not possible.

To reflect natural conditions as closely as possible in an experiment, a combination of laboratory and field observations is required along with basic information on the general ecology of the test organism. This is the underlying doctrine developed and followed at Monaco and which is basic to the present project. The laboratory facilities include a fresh-flowing sea water system which operates at sea water temperatures from the seasonal norm ($\sim$ 18°C) to 11-12°C.

Organisms are first acclimatised to the laboratory sea water system for at least several days. During labelling periods, the organisms are fed regularly with one of their natural food sources. Feeding is performed between water changes when water is used as the labelling medium. Monitoring of bioaccumulation and depuration of the radiotracers is performed by counting the samples (test organisms and surrounding labelling medium) on a γ -detector.

At the end of the uptake period, the radiotracer is usually not in full equilibrium with the organism (for the latter condition uptake periods of the order of $\sim$1 year would be required). Generally, however, equilibrium levels of $\sim$75% are attained by the end of the bioaccumulation phase. Some organisms are then chosen for dissection and their tissue activity measurements. The remainder are placed in a flowing water system, again with regular feeding and activity monitoring until the levels of radiotracer in the organisms have appreciably declined.

In this study, the experimental biokinetic techniques used in the traditional biokinetic experiments at Monaco had to be modified to accommodate the α-autoradiography requirements. An initial problem lay in the determination of the quantity of tracer to be added to experimental aquaria to give short α-autoradiographic exposure times in the region of days. The parameters considered were the concentration factors (CF) of an organism for a specific radiotracer, the size of the tissues under study (and hence the number of 10 μm thick tissue sections obtainable) and the number of tracks which would finally be etched onto the plastic detector to give enough information on the distribution of α-emitters in that tissue. The CF's of the mussel and shrimp for plutonium, americium and neptunium were previously quantified by Fowler et al. (1976) and Guary and Fowler (1978, 1981). The CF values for the mussel were also applied to the winkle as the winkle has similar bioaccumulation characteristics (if anything a slightly greater ability to concentrate transuranic nuclides) to the mussel (Hunt, 1984, 1985). The shrimp CF values were applied to the Dublin Bay prawn because of their similarity in habitat and family species. The number of sections obtained from a tissue was easily calculated once the plane of sectioning of the tissue had been decided. The track density required to give useful autoradiographic information was based on the density data given by Toole (pers. comm.) of $\sim$ 1000 tracks in the microscope field of view at X40 magnification.

Since only α-emitters were used in these biokinetic experiments, ^{241}Am (γ, 35.7%) was always used as the 'guinea pig', whenever a new set of experimental conditions was used. It was assumed that ^{239}Pu would behave similarly to ^{241}Am in these experiments. ^{237}Np was added in greater concentrations when bioaccumulation was from the water medium because of its conservative nature in solution. These nuclides were supplied by the C.E.A. (France) in the following oxidation states; ^{237}Np +5; ^{239}Pu +4; ^{241}Am +3. The initial labelling experiment - of mussels with ^{241}Am from sea water - was extremely successful in providing suitable short exposure times.

Once the organisms had been obtained (mussels from Sete; winkles and prawns from the Atlantic coast of Normandy), they were thoroughly cleaned of all epiflora and epifauna (with the exception of the prawns) and were placed in aquaria of flowing sea water. A batch of 10 mussels was originally used in the bioaccumulation of ^{241}Am from sea water. In later experiments on mussels and winkles this number was reduced to 8.

Typically ^{241}Am was added to 5 litres of sea water contained in a plastic basin at a concentration of 1.85 $kBql^{-1}$. A similar concentration was used for plutonium uptake but neptunium was added to give 37 $kBql^{-1}$ because of its conservative nature. The water was gently stirred and the mussels placed into the 2 basins using tweezers (1 mussel per litre). An air stone was inserted to provide an adequate oxygen supply and then a lid placed on the basin. During the uptake periods the aquaria were frequently (every 2 days) replenished with fresh spiked sea water to maintain the radiotracer concentration relatively constant and to eliminate the possibility of complexation between the tracer and excreted metabolites which can reduce nuclide bioavailability. At each medium change, each organism was counted (only when ^{241}Am was the tracer) on a NaI(Tl) γ-ray detector to monitor the degree of tracer accumulation. Occasionally (every 3-4 days) the organisms were fed for $\sim$ 1 hour (mussels with phytoplankton, winkles with seaweed) before being returned to the newly labelled aquaria. After 14 days of labelling, the activities of the organisms were consistently high enough for α-autoradiographic processing (this time period was derived after the first labelling experiment with ^{241}Am). The remaining organisms were transferred to clean basins and held in the laboratory's flowing sea water system. These organisms were monitored (only with ^{241}Am) frequently, samples again being processed for α-autoradiography after 14 days and $\sim$ 48 days depuration periods. An extra modification used in the labelling of winkles via water was that they were held in individual perforated plastic tubes to ensure that they remained submerged during the experiment.

After unsuccessful trials, 19 live prawns were obtained from the coastal waters of northern France and transported to Monaco. These were acclimatised in several 30 litre tanks for a week during which time 5 died. Because of the difficulty in obtaining and maintaining live prawns, only one organism per labelling condition (3 tracers, 2 media: 6 animals in total) was used.

Each individual prawn was placed in 5 litres of 0.22 µm - filtered sea water which was changed and respiked daily for 8 days. Uptake of the radiotracer was monitored daily only with ^{241}Am. No depuration experiment was performed for prawns.

Mussels labelled with ^{241}Am via food (diatoms and green algae) were obtained during the work performed by Fisher and Teyssie (1986). Details of the labelling procedure are described by Bjerregard et al., (1985). The mussels were fed the marine centric diatom, Thalassiorsira pseudonana (clone 3H) and the marine green algae Dunaliella tertiolecta (clone Dun). These phytoplankton cells were derived from unialgal clonal cultures maintained in f/2 medium (Guillard and Ryther, 1962) minus Cu, Zn and EDTA additions prepared from sterile-filtered (Millipore Millistack), Mediterranean surface sea water. The phytoplankton were suspended in unenriched sterile-filtered sea water and exposed to ^{241}Am (359 $kBq l^{-1}$ or 1.25×10^{-8} M) for 96h. The algal cells were then resuspended out of their radiolabelled water using 3 µm Nucleopore filter (~ 93% efficiency for the algal cells) into unlabelled sterile filtered sea water. The stock suspensions of 'hot' cells in 'cold' sea water (~ 10^6 particles ml^{-1}) were maintained in dim light and the particle density and radioactivity per particle monitored daily (Fisher et al., 1983a). Aliquots were removed by pipette and added to polycarbonate beakers, each containing one mussel in 200 ml of sterile-filtered sea water. The particle density was adjusted to 1×10^4 ml^{-1} at the beginning of each feeding day for the algal cells. Fresh feeding suspensions were prepared daily over a 5 day period. The mussels were maintained at 13 $\pm$ 1°C and their radioactivity determined after each 24 hour feeding period. Following the 5 day feeding, mussels were allowed

to depurate in unlabelled filtered sea water, maintained in polycarbonate beakers containing 600ml, and were fed daily on unlabelled 3H or Dunaliella cells. Periodically mussels were removed from their water, counted for their radioactivity and placed into fresh sea water or were dissected and the radioactivity of their various tissues determined.

Labelled mussels were obtained after the 5 day feeding period and after 200 hour, 700 hour and 1000 hour periods of depuration. They were dissected into their various component tissues, counted using a NaI(Tl) γ-ray detector and then processed for α – autoradiography.

Labelling of mussels with ^{239}Pu via food was attempted but serious problems were encountered in producing radioactive food. From the food - labelling experiment using ^{241}Am, a concentration of ^{239}Pu, required to give reasonable exposure times for α -autoradiography was estimated and applied to the culture medium of the diatoms and algae. The concentrations of ^{239}Pu added was 9.8×10^{-7}M (calculated from the specific activity of ^{239}Pu). However, the maximum level of ^{239}Pu toxicity for these diatoms is $\sim 10^{-10}$M. To overcome this problem, either less ^{239}Pu or a larger volume of culture medium would have had to be used, resulting in much longer exposure times, both options being unrealistic solutions to the problem. Thus this feeding option was not implemented.

Winkles were fed with the seaweed Fucus vesiculosus. Initially several pieces of seaweed were washed and placed in 2 litres of 0.22 μm-filtered sea water containing 3.55 $kBql^{-1}$ of ^{241}Am. After an uptake period of 2 days, the labelled seaweed was fed to 8 winkles for a day, after which the seaweed was removed and labelled further in fresh spiked sea water. ^{241}Am activities of the seaweed before and after feeding, of the sea water before and after the insertion of seaweed and of the winkles were regularly monitored throughout. Fresh seaweed was used every

fourth day. This sequence was continued for 22 days, when two winkles were selected for α-autoradiographic processing. After successful autoradiographs had been obtained for the winkles labelled with ^{241}Am via seaweed, some modifications were introduced for labelling experiments with ^{239}Pu and ^{237}Np. Smaller amounts of seaweed were labelled in a smaller volume of sea water, resulting in a greater concentration of tracer in the seaweed. The labelling process was therefore reduced from 22 days to 12-14 days. The quantities of ^{239}Pu and ^{237}Np used during the labelling of the seaweed were 10.66 kBq and 28.67 kBq respectively. Winkles labelled with each tracer were processed in duplicate for α-autoradiography after ~14 day and ~50 day depuration periods.

Prawns were fed 1cm long pieces of the sand smelt (Atherina presbyter) which had been labelled with the appropriate radiotracer using a hypodermic syringe (10 µl). Again ^{241}Am was used to monitor the activity of the various compartments throughout this experiment. The activities of radiotracers used were 17.13 kBq of ^{241}Am, 22.98 kBq of ^{239}Pu and 44.36 kBq of ^{237}Np. After labelling, the prawns were dissected and processed for α-autoradiography.

The environmental samples of mussels and winkles collected in September 1984 from the Esk estuary, were transferred to Glasgow and cleaned and dissected before being sectioned and stained for α-autoradiography within 3 days of collection. The exposure times used ranged between 1 and 1½ years because of the relatively lower levels of radioactivity contained in the tissue sections. A summary of the experimental conditions used in the α-autoradiographic study is given in Table 2.1.

2.6.2.2 Dissection of marine Organisms

The dissection procedure used for the mussel follows the well - described method of Rowett (1953) and Dales (1969).

TABLE 2.1

Summary of experimental conditions used in α-autoradiographic study

Organism	Dissected tissues	Labelling medium	Stage at which organisms were dissected for α-autoradiography								
			Uptake (5-22 days)			21-28 day depuration			43-50 day depuration		
			^{237}Np	^{239}Pu	^{241}Am	^{237}Np	^{239}Pu	^{241}Am	^{237}Np	^{239}Pu	^{241}Am
Mussel	Viscera, Gill, Mantle, Mantle edge, Foot, Muscle	Sea water	✓	✓	✓	✓	✓	✓		✓	✓
		Food (Thalassiorisa pseudonana)			✓			✓			✓
Winkle	Viscera, Head, Foot, Muscle, Pallial complex, Operculum, Mantle	Sea water	✓	✓	✓	✓	✓	✓		✓	✓
		Food (Fucus vesiculosus)	✓	✓	✓	✓	✓	✓	✓	✓	
Dublin Bay Prawn	Hepatopancreas, Gill, Heart, Abdomen muscle, Claw muscle, Cardiac fore-gut	Sea water	✓	✓	✓						
		Food (Atherina presbyter)	✓	✓	✓						

A strong scalpel blade is inserted at the postero-ventral end (the rounded end), between the mantle and the shell lining, cutting through the posterior adductor muscle close to the shell. The fluid contained within the pallial cavity of the mussel drips out and is trapped in containment tray. The blade is carried forward, carefully scraping the mantle edge from one-half of the shell, and the anterior adductor muscle (much smaller than the posterior muscle) is cut at the opposite end of the shell. This releases one half of the shell from the body which can be removed by breaking the ligament at the shell hinge. The mantle edge is removed by trimming it from the mantle lobe using either a scalpel blade or scissors. The exhalent and inhalent siphons are often removed with the mantle edge but the tissue is further cut to use the mantle edge in the sectioning process. The mantle flap (referred to as the mantle in future discussions) is raised from the body and cut off at its line of attachment at the dorsal side of the mussel. This reveals the gill (Figure 2.16) which is a very delicate organ and is easily frayed apart. This is also cut off from its line of attachment. At this stage, the foot is cut at its base after the byssal threads are removed from the base of the foot using a pair of tweezers.

The dissection process described is repeated, once the body has been removed from the remaining shell valve and placed onto a cork board, producing two items of each tissue mentioned (except the foot). This leaves the muscle system and the visceral mass. The posterior adductor muscle is cut from the remaining body to be used for further study. The byssus retractor muscles (6 pairs posterior and one pair anterior) are carefully removed from the visceral mass using a scalpel. The visceral mass (viscera) remaining contains the digestive gland, the stomach, the oesophagus, the intestine and the pericardium.

After many mussels had been processed it was realised that the kidneys were also included in the visceral mass. At this time it was decided to continue processing the mussels as before rather

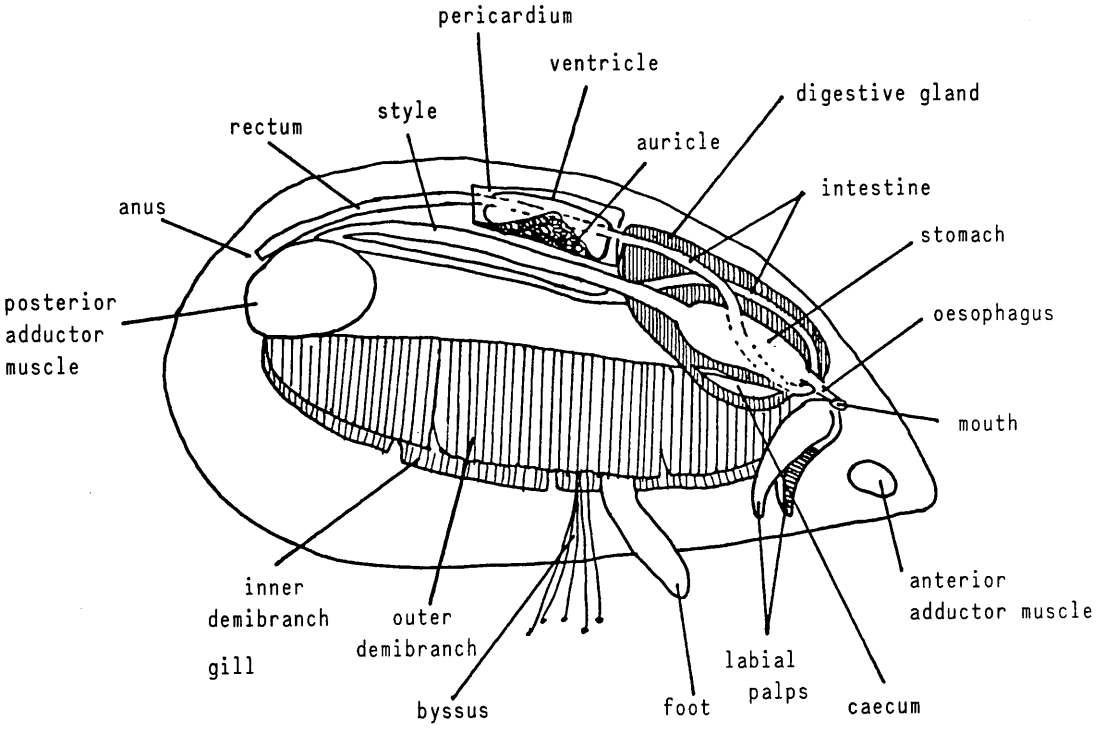


Figure 2.16. Pallial organs of Mytilus edulis viewed from the right side (Based on Dales, 1969).

than producing different tissue distributions which could then not be compared or contrasted. The mussel tissues used for α-autoradiography are therefore foot, mantle edge, mantle, gill, posterior adductor muscle and the visceral mass.

The dissection procedure for the winkle is entirely based on the detailed anatomy described by Fretter and Graham (1976). After preliminary attempts to remove the winkle from its shell, the most effective method was found to be by careful breaking of the shell using a small hammer. Extraction of the winkle using menthol as an anaesthetic was unsuccessful, the organism remaining fixed within the shell even after 1-2 days in this anaesthetic. Pretreatment in boiling water did prove to be effective but the prospect of boiling radioactive winkles for 15 minutes not only suggested a potential loss of radioactive material from the winkle but resulted in denatured tissues for dissection and sectioning. Ideally fresh tissues are required for this study and thus the gentle hammer technique was adopted, with the necessary precautions being taken at every stage to preserve the winkle body and to observe normal safety regulations in working closely with radioactive material.

After gaining experience in winkle dissection, the following tissues were separated and used for α-autoradiography: operculum, foot, head, pallial complex, muscle (columellar) and digestive gland.

In detail, the body of the winkle is removed from the shell using the small hammer, a pair of tweezers and a scalpel (to free the muscle from the shell). Figure 2.17 illustrates the subsequent strategy. The operculum is sliced from the foot using a scalpel. The foot is detached from the base of the head, below the snout. The head is removed from the body by cutting it at the mantle edge. The digestive gland is cut from the posterior end of the columellar muscle to the kidney, resulting in the kidney (and the stomach) being contained in this tissue sample. The remainder of the body, the pallial complex and the columellar muscle is easily dissected

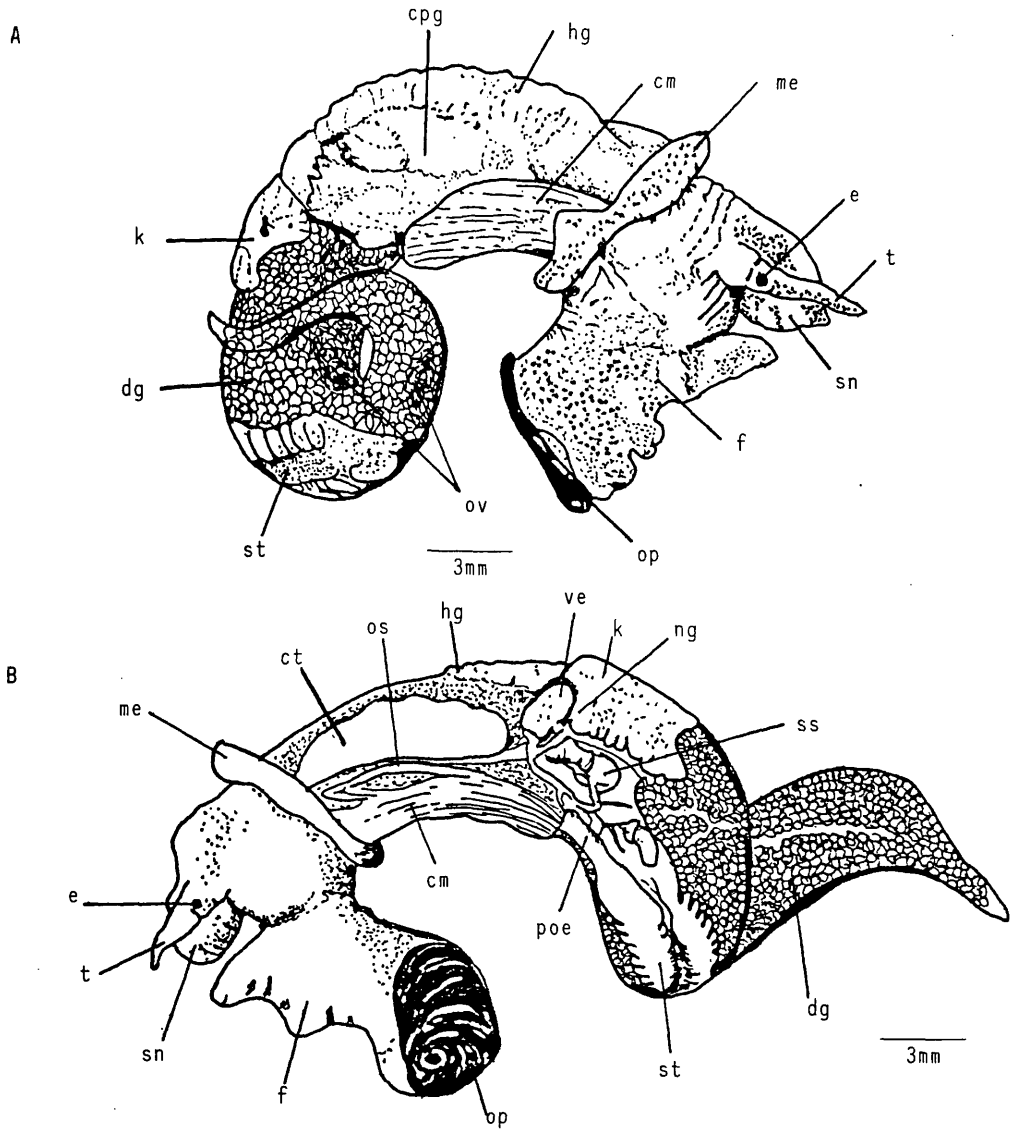


Figure 2.17. Littorina littorea: female removed from the shell and seen A, from the right; B; from the left. Some of the organs are seen by transparency. a, anterior aorta; au, auricle; cm, columellar muscle; cpg, capsule gland; ct, ctenidium; dg, digestive gland; e, eye on eye stalk; f, foot; hg, hypobranchial gland; k, kidney; me, mantle edge; ng, nephridial gland; op, operculum; os, osphradium; ov, ovary; poe, posterior oesophagus; sn, snout; ss, style sac region of stomach leading to intestine; st, stomach; t, tentacle; ve, ventricle

(Based on Fretter and Graham, 1976).

by removing the muscle using a scalpel. The resulting pallial complex contains a variety of organs and glands including the gill (ctenidium), mantle, hypobranchial gland, osphradium and rectum.

The dissection procedure for the prawn incorporates the dissection technique used for the fresh water crayfish Astacus described by Dales (1969) and the anatomy of the Nephrops described by Yonge (1924), de Figueiredo and Thomas (1967) and Howard (1982). To meet the requirements for α-autoradiography, only the soft tissues of the prawn were of concern, namely the heart, hepatopancreas, abdomen (tail muscle), claw muscle, hind gut, cardiac fore-gut and the gills.

The carapace is cut on each side in line with the branchio cardiac groove up to the level of the eyes (Figure 2.18). The flap of shell is lifted carefully, cutting away the tissues as close as possible to the inner surface but taking care not to damage the heart. The cutting of the shell is continued backwards through the abdominal terga to the middle of the terga. From this the hind gut is removed from the abdomen once the abdomen has been cut at the posterior end of the carapace. The remaining shell covering of the abdomen is removed using scissors. The heart is easily identified and removed using a scalpel blade. During the dissection of Nephrops, identification of the various organs and glands contained in the carapace proved extremely difficult, except for the gills. The hepatopancreas is identifiable due to its large size but the other tissues cannot be distinguished easily. The cardiac fore-gut is positioned behind the mouth, is darkly stained and possesses a thick chitinous lining. The gills are removed by first removing the branchiostegite (gill cover) with scissors exposing the gill underneath. The claw muscles are obtained by opening longitudinally the chelipeds with scissors.

2.6.2.3 Histological techniques

Methods for processing tissues histologically and specifically for α-autoradiographic purposes have been included in works by

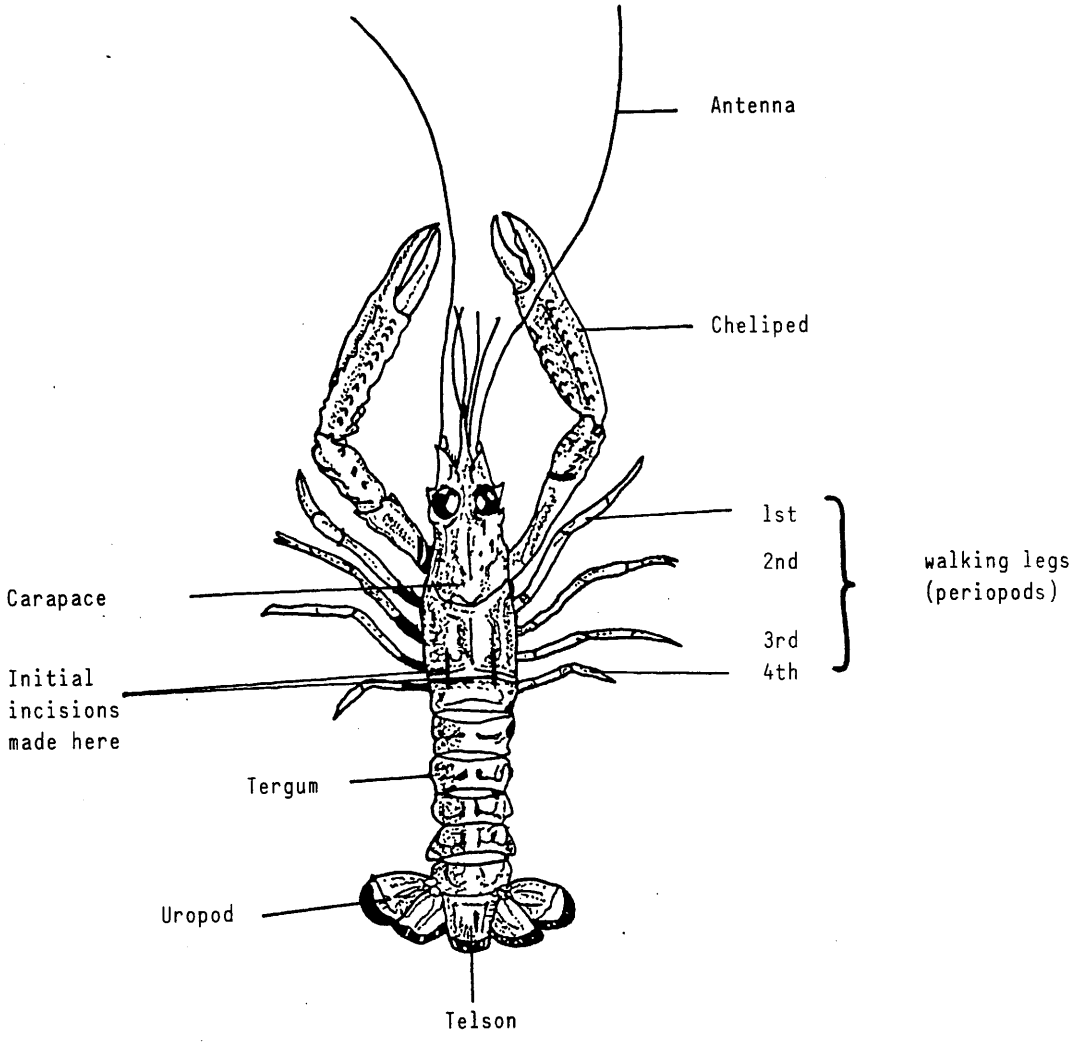


Figure 2.18. Dorsal view of Nephrops norvegicus.

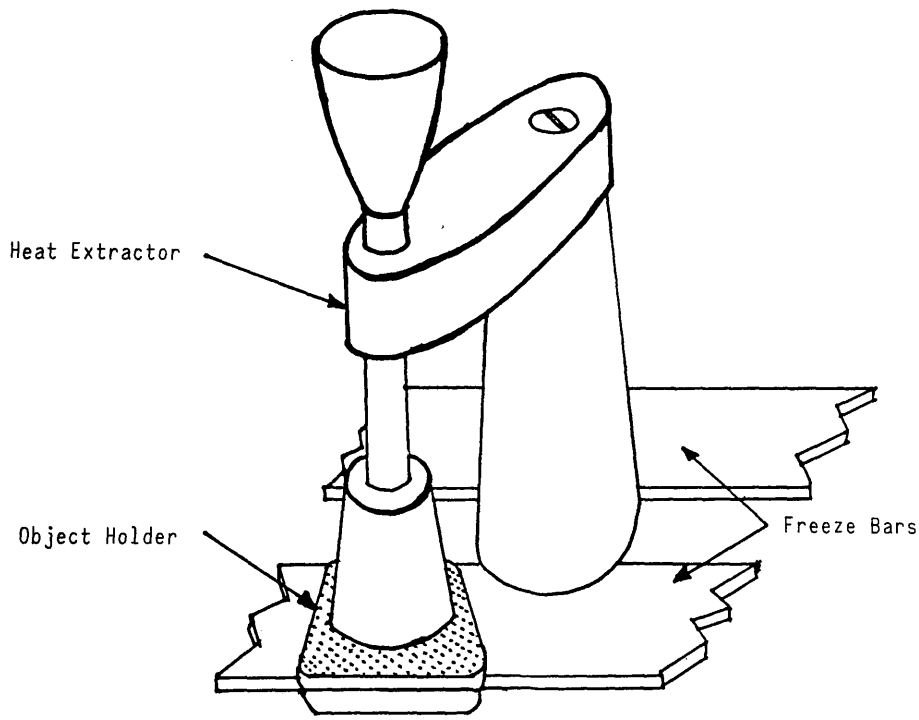
Wyatt et al. (1980), Ellis and Jeffree (1980), Jenner and Thorne (1980), Smith et al. (1980), Hamilton and Clifton (1980), Miramand and Guary (1981) and Miramand and Germain (1985). The majority embed the labelled tissue in paraffin-wax and expose the plastic detector CR-39 to the sections. In this study, however, the sections were prepared using a freezing microtome and exposing Kodak LR115 Type II plastic to the labelled tissue sections.

Although both the paraffin-wax and freezing microtome techniques of preparing tissue sections are used routinely at Glasgow University (Department of Zoology) only the freezing microtome method was available at Monaco.

In using the freezing microtome, tissue sections are prepared rapidly and, when dealing with radiocative specimens, the risks of losing activity from the tissues and hence of contamination of apparatus are reduced.

The operation of the two freezing microtomes used in this study (although not the same models) involve very similar procedures. Discussed in detail here is the system in use at Monaco, using a Tissue-Tek® microtome, model number 4551, cryostat model 4550 115 VAC/60 Hz.

Initially glass microscope slides (3" x 1") are cleaned in ethanol. The microtome blade (always stored in a fridge to reduce cooling time) is fitted into the microtome and allowed to cool to the operating temperature of -20°C. The microtome blade is adjusted to the correct cutting angle. This angle can be optimised only by experience but, once determined, can be recorded using the angular reference marks on the arm of the blade-holder. With the cryostat cooling the operating chamber, the specimen holders, stored on the freeze bars with the heat extractor (Figure 2.19), are cooled also. A few drops of Tissue Tek® OCT compound 4583 (embedding resin) are placed onto the holder and frozen flat, in a few seconds, by placing the heat extractor on top of it. The



. Figure 2.19. Position of heat extractor for freezing tissue.

holder is then removed and a selected piece of tissue, 2-5mm thick, is placed on the holder and covered with more OCT compound and refrozen using the heat extractor. The holder is secured in the chuck and the blade positioned for sectioning by manipulation of the gross adjustment wheel. The thickness of the slices is set at 10 μm on the increment adjusting knob. The anti-roll plate of plastic (with a low coefficient of friction) is positioned to keep the sections flat on the knife blade for subsequent direct mounting onto a slide. The correct positioning of the anti-roll plate relative to the knife is essential and requires careful adjustment. A clearance of 70 μm to accommodate the section can be generated by placing small squares of tape (½ cm x ½ cm) at the two corners of the plate nearest to the specimen.

Sections are cut from the tissue using the hand-wheel which, on turning moves the blade, in this instance, 10 μm towards the specimem. Three or four sections are taken from each tissue for α-autoradiography. In contact with a slide kept at room temperature, the frozen section quickly thaws and adheres to the slide. Throughout operation of the freezing microtome, a soft hair brush, always kept in the freezing chamber, is used to remove any unwanted sections or ice forming on the blade. Aluminium foil is placed within the freezing chamber to collect all the radioactive debris from the sectioning process.

After sectioning, the tissues are fixed in Wolman's fixative (5% acetic in absolute ethanol) for 1-2 minutes. Tissue fixed before sectioning may yield inferior sections to those obtainable on immediately frozen fresh tissue because it can be adversely affected by the fixative, especially its water (ice) content (Drury and Wallington, 1980). Fixation aids optical differentiation of cells and tissue constituents by altering their refractive indices varying degrees. This is of value, since the refractive indices of some elements of the cell are so close to that of their surrounding structures that they are invisible in the living state when examined by conventional microscopy.

Once fixed, the slides are stained using the Haemalum and Eosin staining method (H & E), routinely used at the Department of Zoology, University of Glasgow (Figure 2.20). The haemalum stain used here is Mayers (1903). This uses haematoxylin as its dye and is now commercially available. Haematoxylin is the most widely used and versatile dye for histological techniques and is used in stains for the demonstration of various biological materials (cell nuclei, myelin, elastic fibres etc). For all these purposes, however, haematoxylin must be converted to haematein by oxidation and must be used in conjunction with a mordant such as the salts of aluminium (as is the case with Mayer's haemalum), iron or tungsten. Haematoxylin is most commonly used as a nuclear stain preceding staining of cytoplasm and connective tissue with eosin. Eosin, a red dye, is one of the xanthene group of dyes and derived from fluorescein. It is available in two main shades, yellowish or bluish (a deeper red). Eosin Y (yellowish) is the more commonly used and was employed in this work. With haematoxylin eosin is the routine staining medium for histopathology and much of the present knowledge of morbid histology has been gained using this combination.

Because of the versatility and simplicity of use of the Haemalum and Eosin staining process, it was the only staining technique practised in this work. Although it does not stain all the components of biological tissues, it was more than adequate for the requirements in hand.

After staining, the slides are cleaned then catalogued. Pieces of Kodak LR115 plastic α-detector are placed over the tissues (along with pieces of Al foil), taped down and their position on the glass slide recorded by scratching the outline of the plastic onto the glass using a diamond-tipped pencil. Further score marks can be made to identify the plastic with a particular slide since several pieces of plastic are etched together in the same container. The slides are stored in the dark, at room temperature in perspex presses to ensure intimate and complete sample/detector contact. At this stage exposure timetables are defined.

Figure 2.20. Haemalum and Eosin staining process

Distilled water	Rinse
Haemalum stain	2 min
Scotts tap water	1 min
Distilled water	Rinse
30% Alcohol	3 min
50% Alcohol	3 min
70% Alcohol	3 min
90% Alcohol	3 min
Eosin stain	1 min
Absolute alcohol	1 min

Volumes of all solutions used - 200 ml.

Scotts tap water - dissolve 3.5g sodium hydrogen carbonate and 20g magnesium sulphate in 1 litre of distilled water.

In some places the tap water is not sufficiently alkaline or is even acidic and unsatisfactory for blueing haematoxylin, in which case a tap water substitute modified by Scott (1912) is used for the purpose.

CHAPTER 3 : RESULTS AND DISCUSSION

This chapter presents and discusses the radiochemical and α-autoradiographic data on radionuclide distributions in marine organisms. The more significant observations will be emphasised and interpreted and the conclusions compared to, and assessed in light of, the appropriate information in the scientific literature.

3.1 RADIONUCLIDE DISTRIBUTIONS IN MARINE ORGANISMS LABELLED IN THE ENVIRONMENT

3.1.1 Plutonium

The mussel bed in the Esk estuary at Ravenglass, Cumbria serves usefully as a source of environmentally labelled samples, the mussels having been exposed to enhanced levels of artificial radionuclides throughout their lifetimes. The concentrations of plutonium within the various mussel tissues are presented in Table 3.1. Sampling in 1983 coincided with an accidental release of waste radionuclides from the Sellafield plant which resulted in closure to the public of adjacent beach areas. This discharge, however, had not reached the mussel bed at Ravenglass by time of sampling.

In general, plutonium concentrations in mussels were lower in 1984 than in 1983, the obvious exception relating to the byssal threads. This general decrease reflects the downward trend in plutonium discharges from Sellafield in recent years. The $^{239+240}Pu/^{238}Pu$ activity quotients are consistently in the region of 4, for both years and in all samples, this value being characteristic of the Sellafield discharges. Tissues exhibiting bioaccumulative properties were the viscera, gill, periostracum and byssal threads. Relatively lower plutonium concentrations were observed in the mantle, mantle edge, foot, muscle and scraped shell.

TABLE 3.1

Distribution of plutonium in Ravenglass mussels. Concentrations in Bqkg^{-1} dry weight ($\pm$ 2σ error).

Sample	$^{239+240}Pu$		^{238}Pu		$\frac{^{239+240}Pu}{^{238}Pu}$	
	1983	1984	1983	1984	1983	1984
Total soft tissue	154 $\pm$ 4	71 $\pm$ 2	38 $\pm$ 2	19 $\pm$ 1	4.00 $\pm$ 0.30	3.79 $\pm$ 0.38
Viscera	377 $\pm$ 11	219 $\pm$ 8	93 $\pm$ 4	58 $\pm$ 3	4.06 $\pm$ 0.27	3.73 $\pm$ 0.27
Gill	310 $\pm$ 8	107 $\pm$ 3	77 $\pm$ 3	26 $\pm$ 1	4.01 $\pm$ 0.26	4.07 $\pm$ 0.28
Mantle	63 $\pm$ 2	65 $\pm$ 4	19 $\pm$ 1	17 $\pm$ 2	3.35 $\pm$ 0.29	3.93 $\pm$ 0.10
Muscle	61 $\pm$ 2	43 $\pm$ 4	16 $\pm$ 1	12 $\pm$ 2	3.76 $\pm$ 0.34	3.53 $\pm$ 0.82
Byssal threads	1193 $\pm$ 35	1658 $\pm$ 50	328 $\pm$ 14	428 $\pm$ 17	3.63 $\pm$ 0.26	3.87 $\pm$ 0.28
Periostracum	541 $\pm$ 27	N.M.	126 $\pm$ 9	N.M.	4.30 $\pm$ 0.39	N.M.
Shell	22 $\pm$ 1	N.M.	6.0 $\pm$0.4	N.M.	3.75 $\pm$ 0.30	N.M.
Foot	N.M.	20 $\pm$ 2	N.M.	5.0 $\pm$1.0	N.M.	4.00 $\pm$ 1.00
Mantle edge	N.M.	48 $\pm$ 3	N.M.	31 $\pm$ 3	N.M.	1.56 $\pm$ 0.17

N.M.:- Not measured

The ability of the periostracum and the byssal threads to accumulate plutonium to a higher degree than soft tissues has been previously observed under both laboratory and environmental conditions (Fowler et al., 1975; Goldberg et al., 1978; Hamilton and Clifton, 1980; Koide et al., 1982). The byssal threads and periostracum comprise different forms of tanned proteins; byssal threads are composed of fibrous proteins similar to collagen, substances prominent in trace element binding (Fowler et al., 1975); the periostracum is considered to be a quinone-tanned protein which binds metals via a passive process. Koide et al. (1982), on the basis of uranium behaviour in sea water, proposed that byssal thread accumulation of transuranics occurs from the soluble phase, a suggestion which requires verification.

Despite various reports on plutonium concentrations in mussels in their natural habitat, very little data are in fact available for direct comparison with the results in Table 3.1. Much of the reported data can be used only for comparison of plutonium concentrations in total soft parts of mussels from various sites worldwide. (Results for shell are not so useful as details of whether the periostracum was or was not removed during analysis are commonly not given).

Monitoring programmes including the analysis of plutonium in mussels along the Cumbrian coastline have for many years been carried out by MAFF and BNF plc. Their findings are of limited value in the present context since their quoted results represent average values of measurements made at various intervals throughout the year.

Hamilton and Clifton (1980), however, reported data which are suitable for comparison with the results here. Thus, they measured the distribution of plutonium (and of americium) in the tissues of Ravenglass mussels collected from 1977 to 1979. Byssal threads and periostracum contained the highest plutonium activities. As shown in Table 3.1, in this study,

the soft tissues with higher concentrations of plutonium were the digestive gland and gill (the viscera sample reported in Table 3.1 contained the digestive gland and kidney). Soft tissues of lower plutonium concentrations were the mantle, mantle edge, muscle and foot, although the foot was reported to have the highest plutonium concentration in 1978.

The plutonium concentrations found here in Ravenglass mussels in 1983 and 1984 are lower than those reported for 1977 to 1979 by Hamilton and Clifton (1980). Their data for 1979 are, in fact, unusually high relative to the general concentration trend for the 1977 to 1984 period shown in Table 3.2. Excluding these 1979 values, the 1983 and 1984 results reported here are consistent with the trend of steadily falling plutonium levels in the Ravenglass environment.

It is interesting to attempt to quantify the different bioaccumulation behaviour of the various tissues and organs of the mussel. The concept of the Concentration Factor (CF) provides a suitable approach. The major conditions required for CF consideration of biological materials (as discussed in Chapter 1, Section 1.4.1) are not completely met in Ravenglass samples. This is due to the rate of radionuclide input into this environment not being constant. (Plutonium discharges from Sellafield into the Irish Sea have been consistently decreasing since 1978). CF estimates, therefore, should not be considered as absolute values but more as relative figures for the comparison at order of magnitude level. Each CF has been calculated as

$$\frac{\text{Activity (Bq) per kg of specific wet tissue sample}}{\text{Activity (Bq) per litre of filtered sea water}}$$

Several factors have to be defined to provide compatible data for future comparisons. The wet:dry ratios of all the tissues (determined in this study) have been included in Table 3.3 and subsequently used in determination of the CFs in Table 3.4. The wet:dry ratio for the periostracum

TABLE 3.2

Plutonium concentrations in total soft tissues of Ravenglass mussels as a function of time.		
	$^{239+240}Pu$ $Bqkg^{-1}(wet)^{a}$	Reference
1977	37	Hamilton and Clifton, 1980
1978	68	Hamilton and Clifton, 1980
1979	258	Hamilton and Clifton, 1980
1980	26	Clifton et al., 1983
1981	-	
1982	-	
1983	28	This work
1984	13	This work

[a] - Wet:Dry ratio of 5.4 was used in calculation.

TABLE 3.3

Concentration factors of $^{239+240}Pu$ in Ravenglass mussel tissues.

	Wet:Dry ratio	Year 1984
Total soft tissue	5.4	1400
Viscera	5.1	4800
Gill	11.7	1000
Mantle	5.4	1400
Muscle	5.9	800
Foot	8.7	300
Mantle edge	7.6	700
Byssal threads	6.3	29500
Periostracum	6.3	-
Shell (scraped)	1.0	-

TABLE 3.4

Concentration factors of $^{239+240}Pu$ in mussel tissues from the Cumbrian coastline.

Sample	Year					Comments
	1977	1978	1979	1980	1981	
Total soft tissue	-	6100	3900	6500	8300	Mussels from St. Bees 0.22 μm filtered sea water (Pentreath, 1984)
Total soft tissue	2500	4500	-	-	-	Mussels from Ravenglass 0.45 μm filtered sea water (Hamilton and Clifton, 1980)
Viscera	9000	1100	86900	-	-	
Gill	2800	2700	4900	-	-	
Mantle	500	1400	5300	-	-	Wet:dry ratios of tissues in Table 3.3 used here. Kidney wet:dry ratio assumed to be the same as viscera.
Muscle	500	2500	3100	-	-	
Foot	931	700	1500	-	-	
Mantle edge	800	1800	2800	-	-	
Kidney	3600	2600	37500	-	-	
Byssal threads	41100	31400	58500	-	-	
Shell	800	700	-	-	-	

has been assumed to be the same as for byssal threads and the wet:dry ratio of the kidney (Table 3.4) the same as the viscera. The concentration of $^{239+240}Pu$ in filtered sea water in the region of the Esk estuary at Ravenglass was $8.8mBql^{-1}$ in 1984 (McKay et al., 1987) and $10mBql^{-1}$ in 1985 (Collier, pers. comm.). Presently, there appears to be no account of such $^{239+240}Pu$ data for the Ravenglass area during 1983.

Of particular interest in Table 3.3 is the magnitude of the CF of the byssal threads relative to those of the other tissues. Such a radical difference between these tissues has previously been reported by Fowler et al. (1975) following laboratory studies on mussels.

The CF found here for 'total soft tissue' is consistent with the mollusca 'total soft tissue' CF range, of 500-5000, reported by IAEA (1985). Pentreath (1984) found a $^{239+240}Pu$ CF range of 3900-8300 (Table 3.4) for the total soft tissue of mussels collected from St. Bees between 1978 and 1981. The inclusion of byssal threads during analysis could significantly enhance the mussels $^{239+240}Pu$ load. The reasoning behind the high CF values of St. Bees mussels, however, is presently unclear.

The data for plutonium concentrations in mussel tissues reported by Hamilton and Clifton (1980) can be manipulated to provide CF approximations by assuming the previously used wet:dry ratios and a $^{239+240}Pu$ concentration of $15mBql^{-1}$ in $< 0.45\mu m$ filtered sea water (Clifton et al., 1983), (Table 3.4). As indicated earlier, the 1979 data set from Hamilton and Clifton's (1980) work is anomalously high. Otherwise the distinct differences in CF values between byssal threads and other tissues are maintained as is the general 500-5000 CF range for all the soft tissues.

Plutonium levels observed here in Ravenglass winkles collected in September 1984 and 1985 (Table 3.5) do not show a clear trend between years. Thus, the pallial complex, muscle and head all showed increased plutonium contents in 1985, whilst

TABLE 3.5

Distribution of plutonium in Ravenglass winkles. Concentrations in $Bqkg^{-1}$ dry weight ($\pm 2\sigma$ error).

Sample	$^{239+240}Pu$		^{238}Pu		$\frac{^{239+240}Pu}{^{238}Pu}$	
	1984	1985	1984	1985	1984	1985
Total soft tissue	N.M.	159 ± 7	N.M.	38 ± 3	N.M.	4.21 ± 0.41
Head	B.D.L.	52 ± 4	B.D.L.	10 ± 1	B.D.L.	5.38 ± 0.91
Foot	N.M.	29 ± 3	N.M.	12 ± 2	N.M.	2.47 ± 0.46
Muscle	18.5 ± 2.2	39 ± 4	4.2 ± 1.1	7 ± 2	4.43 ± 1.29	5.30 ± 1.43
Pallial complex	407 ± 11	457 ± 11	96 ± 6	146 ± 7	4.25 ± 0.27	3.13 ± 0.16
Operculum	176 ± 9	96 ± 9	45 ± 5	22 ± 4	3.88 ± 0.46	4.35 ± 0.89
Digestive gland	216 ± 6	178 ± 5	57 ± 3	49 ± 3	3.79 ± 0.25	3.62 ± 0.22
Shell	16.8 ± 0.8	15.1 ± 0.9	4.29 ± 0.41	3.92 ± 0.44	3.92 ± 0.42	3.84 ± 0.49

N.M. - Not Measured

B.D.L. - Below Detection Limit

the operculum, digestive gland and shell each decreased in activity. The pallial complex clearly exhibited the highest plutonium concentrations (407Bqkg^{-1} in 1984, 457Bqkg^{-1} in 1985), the digestive gland and operculum also revealing high accumulative properties. The activity quotients again show that Sellafield discharges are the dominant plutonium source. Because of the various physiological functions of the pallial complex, several pathways are available for radionuclide accumulation. Passage of water through the mantle cavity, ensnaring of detrital particles and excretion of waste material from the digestive system into the mantle cavity provide prime routes for radionuclide accumulation. The high accumulation of radionuclides by mucous-associated tissues has been observed, especially in annelids (Grillo et al., 1981; Carvalho and Fowler, 1984; Miramand, 1984), reinforcing the explanation for the capacity of the pallial complex, with its high glandular activity, to accumulate radionuclides. Comparative radionuclide distribution data for winkles are difficult to find. MAFF and BNF plc provide data on radionuclide concentrations in Cumbrian winkles but, as for mussels, their results are for total soft parts only and are averaged over a year's monitoring.

The distribution of plutonium in winkle tissues has, however, been studied under laboratory conditions by Swift and Pentreath (1988). These authors report environmental concentrations of plutonium in the total soft tissues of the winkle for quarterly intervals in 1985. Concentrations range from 15.2Bqkg^{-1} (wet) to 29.4Bqkg^{-1}, comparable to the levels shown in Table 3.5 (using a wet:dry ratio of 2.8 determined in this study). Although the winkles studied by Swift and Pentreath were collected at St. Bees, 13km north of Sellafield (Ravenglass is 10km south of Sellafield), the quarterly figures are of more value than a single annual concentration in that they give an indication of within-year variability. In fact, their various laboratory experiments did not highlight the accumulative properties of the pallial complex. Although they split the pallial complex into (a) mantle with gill and osphradium and (b) mantle with rectum and hypobranchial

gland, the summed contributions to plutonium accumulation by these two components did not exceed that of the digestive gland plus stomach. In the studies reported here on both environmentally and laboratory labelled winkles (Section 3.2), the pallial complex consistently exhibited a high ability to accumulate radionuclides. The observations of Swift and Pentreath (1988) are therefore not consistent with those of this study.

Concentration factors of $^{239+240}Pu$ in the various winkle tissues are presented in Table 3.6 along with CFs determined by Swift and Pentreath for St. Bees winkles. All of the 'total soft tissue' CF estimates are again consistent with the range given by IAEA for mollusca. Between 1981 and 1985, reported CFs have ranged between 1500 to 9200, the highest value being given for 1984 samples (Swift and Pentreath, 1988). In this study, the total soft tissue CF is more similar to the 1984 CF value reported by Swift and Pentreath (1988) than to their 1985 data. Within the soft tissues (excluding the operculum) the pallial complex appear to concentrate plutonium twice as much as the next highest tissue, the digestive gland. During analysis the presence of silt in the pallial complex tissue may be responsible for the observed high CFs, Swift and Pentreath (1988) having found that silt contamination of food can lead to increased plutonium body burdens.

The distribution of plutonium in prawns (landed at Whitehaven) (Table 3.7) shows that the carapace contained the highest concentration of plutonium ($5.96 Bq kg^{-1}$), the hepatopancreas and abdomen muscle having similar but lower levels. Plutonium was not detected in the remaining tissues of the prawn (lower limit of detection 4mBq/sample). The ability of crustacean exoskeleta to accumulate transuranics effectively has been demonstrated by Ward (1966), Fowler *et al.* (1975) and Fowler and Guary (1977), as much as 90-100% of the total plutonium body burden being located there. Very little can be interpreted

TABLE 3.6

Concentration factors of $^{239+240}Pu$ in winkle tissues.

Sample	Wet:dry ratio	Year 1981	1982	1983	1984	1985	Comments
Total soft tissue		2721	1705	2628	9240	2022	Winkles collected at St. Bees 0.22 μm filtered sea water.
				1700	5257	4200	(Swift and Pentreath, 1988).
						1491	
						2533	
Total soft tissue	2.8				-	5700	Ravenglass winkles 0.45 μm filtered sea water.
Head	3.8				-	1400	This study
Foot	4.3				-	700	
Muscle	3.6				600	1100	
Pallial complex	2.9				15700	15800	
Operculum	1.3				15100	7400	
Digestive gland	2.5				9700	7100	
Shell	1.0				1800	1500	

TABLE 3.7

Distribution of plutonium in Whitehaven-landed prawns 1985.*
Concentrations in $Bqkg^{-1}$ dry weight ($\pm 2\sigma$ error).

Tissue	$^{239+240}Pu$	^{238}Pu	$\frac{^{239+240}Pu}{^{238}Pu}$
Hepatopancreas	0.81 ± 0.26	0.81 ± 0.22	1.00 ± 0.40
Carapace	5.96 ± 0.74	0.81 ± 0.26	7.32 ± 2.50
Abdomen muscle	0.85 ± 0.15	0.12 ± 0.06	7.19 ± 3.80

* Analyses were also carried out on Gill, Cardiac fore-gut, Abdomen shell and Legs (periopods) but the results were below detection limits for both $^{239+240}Pu$ and ^{238}Pu.

from the results on the remaining tissues since the plutonium levels are so low. Thus, although the hepatopancreas and abdomen muscle have similar plutonium levels, the high associated errors prevent any definitive comparisons.

The generally low plutonium levels in prawns are indicative of their greater distance of habitation from the Sellafield pipeline relative to the Ravenglass mussels and winkles. The observed $^{239+240}Pu/^{238}Pu$ activity quotient of the carapace indicates that the plutonium is derived from a combination of sources; from Sellafield (activity quotient ~ 4) and from nuclear weapons fallout (activity quotient ~25). Hence an activity quotient of 7.32 implies that ~ 84% of the plutonium is Sellafield-derived.

Reported levels of transuranic nuclides in Nephrops between 1977 and 1986 (Hunt, 1979-1987) have been 50-200 times less than those found in mussels and winkles along the Cumbrian coastline. These observations complement the relative findings of this study. Concentration factors for the edible part of prawns (abdomen muscle) cannot be as easily estimated as those of the mussel and winkle since details of the plutonium concentration in the sea water at the depth of habitation are unknown. In relating the CF range for plutonium reported by IAEA (1985) for crustaceans, to the plutonium concentrations measured in this study and by Hunt (1979-1987), a $^{239+240}Pu$ concentation of ~ $0.5mBql^{-1}$ in filtered sea water is required for consistency. This concentration of $^{239+240}Pu$ in sea water is not an unreasonable value in light of published data (Pentreath et al., 1984) suggesting that plutonium in the abdomen muscle of prawns is indeed behaving as predicted with regard to bioaccumulation.

3.1.2 Gamma-emitting nuclides

The distributions of artificial gamma-emitters (fission and neutron activation products) in mussels and winkles are summarised in Tables 3.8 to 3.13. The only natural gamma-emitter

regularly detected at significant levels in all the samples was ^{40}K, concentrations ranging from 10^2 to $10^3 Bqkg^{-1}$. Indeed this was the only nuclide of note in the prawns, there being no artificial gamma-emitters detectable in this species.

The most abundant gamma-emitter present in the mussels and winkles was ^{106}Ru. Caesium-137 and ^{95}Nb were regularly detected, although the 1985 winkles showed less consistency. The remaining nuclides (^{103}Ru, ^{95}Zr, ^{241}Am, ^{144}Ce, ^{85}Sr, ^{60}Co) were generally found only in the viscera of the organisms.

In comparing the ^{137}Cs, ^{106}Ru and ^{95}Nb activity trends within the soft tissues of the mussel (Tables 3.8, 3.9), the viscera consistently contains the highest concentrations, followed by gill. The remaining tissues all exhibit lower levels. These trends agree with those for plutonium, suggesting similar radionuclide uptake routes.

A ^{106}Ru concentration of $2856 Bqkg^{-1}$ and a ^{137}Cs concentration of $1180 Bqkg^{-1}$ were measured by Clifton et al. (1983) in Ravenglass mussels (total soft tissues) collected in January 1980. The ^{106}Ru concentration is of similar magnitude to those reported here, while the ^{137}Cs content is ~ 3 times greater. This latter large difference can be attributed to the decrease in radiocaesium discharged from Sellafield between 1980 and 1983-84 (2.5 - 7 fold), the ^{106}Ru discharges remaining relatively constant (340-553 $TBqy^{-1}$; 1980-84, (BNF, 1981-85)).

Concentration factors of ^{137}Cs in mussel tissues are given in Table 3.10, including some details of the concentrations used in the calculations. Of the gamma-emitters, ^{137}Cs was chosen for CF calculation because of i) its contribution to dose received by the critical group in the vicinity of Sellafield through the ingestion of seafood and ii) the abundance of ^{137}Cs data in Irish sea waters. Total soft tissue CF's are just below the respective IAEA range of mollusca CF data for caesium (10-50) (IAEA, 1985). Such a slight difference could easily be accounted for by the uncertainties in the ^{137}Cs data for 0.22μm filtered sea water, i.e. the average annual concentrations assumed here for the calculations

TABLE 3.8

Distribution of artificial gamma-emitters in Ravenglass mussels, November 1983.
Concentrations in $Bqkg^{-1}$ dry weight ($\pm 2\sigma$ error).

Sample	^{137}Cs	^{106}Ru	^{95}Nb	^{103}Ru	^{95}Zr	^{241}Am	^{144}Ce	^{85}Sr
Total soft tissue	328 ± 11	4750 ± 175	889 ± 53	120 ± 8	334 ± 14	B.D.L.	B.D.L.	B.D.L.
Viscera	685 ± 21	16000 ± 449	4710 ± 86	519 ± 25	1550 ± 42	312 ± 73	434 ± 59	B.D.L.
Gill	155 ± 18	7070 ± 282	434 ± 31	126 ± 24	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Mantle	143 ± 8	770 ± 58	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Mantle edge	123 ± 14	1800 ± 14	194 ± 26	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Muscle	166 ± 8	1670 ± 77	226 ± 13	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Foot	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Byssal threads	751 ± 87	8630 ± 1030	6110 ± 301	B.D.L.	76 ± 11	B.D.L.	B.D.L.	1407 ± 178
Periostracum	597 ± 29	2680 ± 238	1400 ± 86	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Shell	14 ± 1	B.D.L.	17 ± 2	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.

B.D.L. - Below Detection Limit

TABLE 3.9

Distribution of artificial gamma-emitters in Ravenglass mussels, September 1984.
Concentrations in Bqkg^{-1} dry weight ($\pm$ 2σ error).

Sample	^{137}Cs	^{106}Ru	^{95}Nb	^{103}Ru	^{95}Zr	^{241}Am	^{60}Co
Total soft tissue	254 $\pm$ 21	5370 $\pm$ 325	633 $\pm$ 50	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Viscera	411 $\pm$ 23	9660 $\pm$ 566	1760 $\pm$ 74	97 $\pm$ 26	488 $\pm$ 39	284 $\pm$ 104	57 $\pm$ 11
Gill	247 $\pm$ 23	7810 $\pm$ 444	307 $\pm$ 53	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Mantle	162 $\pm$ 16	2160 $\pm$ 178	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Mantle edge	151 $\pm$ 19	2760 $\pm$ 221	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Foot	227 $\pm$ 41	2010 $\pm$ 381	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Muscle	131 $\pm$ 16	1950 $\pm$ 179	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Byssal threads	1340 $\pm$ 94	14400 $\pm$ 984	8330 $\pm$ 385	B.D.L.	2520 $\pm$ 219	B.D.L.	B.D.L.
Shell	19 $\pm$ 2	156 $\pm$ 18	83 $\pm$ 8	B.D.L.	B.D.L.	B.D.L.	B.D.L.

B.D.L. - Below Detection Limit

TABLE 3.10

Concentration factors of ^{137}Cs in Ravenglass mussel tissues.

Tissue	Year 1983°	1984+
Total soft tissue	5	9
Viscera	10	15
Gill	1	4
Mantle	2	6
Muscle	2	4
Foot	-	5
Mantle edge	1	4
Byssal threads	9	40
Periostracum	7	-
Shell (scraped)	1	3

° ^{137}Cs in sea water $12.8 Bql^{-1}$ (Ellett, pers. comm.)

+ ^{137}Cs in sea water $5.36 Bql^{-1}$ (Ellett, pers. comm.)

are based on observed ranges of 7.4 - 19.9Bql^{-1} in 1983 and 2.50 - 8.52Bql^{-1} in 1984. Concentration factors for ^{137}Cs in mussel tissues are generally three orders of magnitude lower than the corresponding $^{239+240}$Pu CF values. Relative to the soft tissues, however, the byssal threads appear to be less efficient at accumulating ^{137}Cs compared to $^{239+240}$Pu. The conservative nature of ^{137}Cs is probably a major factor in explaining such differences. It is interesting, however, that, despite the differences in CF magnitudes between ^{137}Cs and $^{239+240}$Pu in mussels, the trends between tissues are similar for both nuclides, suggesting similar nuclide accumulation pathways. As for $^{239+240}$Pu, the viscera exhibits the highest levels of ^{137}Cs accumulation of all the soft tissues.

In comparing the 1983 and 1984 mussel data, the activities of the gamma-emitters in the viscera decreased by almost 50% (^{106}Ru 16000Bqkg^{-1} to 9660Bqkg^{-1}), whilst the remaining tissues all showed increases, particularly for the mantle (^{106}Ru 770Bqkg^{-1} to 2160Bqkg^{-1}). Total ^{106}Ru and ^{137}Cs contents of the mussels increased slightly, while ^{95}Nb concentrations decreased slightly. Many factors must be considered in attempting to interpret these contrasting observations, e.g. factors such as effluent composition, discharge frequencies, transit times, weather conditions and the physiological condition of the mussels (influenced by temperature, byssus production, gametogenesis and spawning (Pieters et al., 1979)) at time of sampling. Indeed, Clifton et al. (1983) suggest that radionuclide concentrations in mussels can be modulated by a factor of 2 simply through variation in total soft tissue weight during the year.

In Ravenglass winkles, there are marked differences in gamma-emitter concentrations between 1984 and 1985 (Tables 3.11 and 3.12). Fewer radionuclides were detected in 1985, ^{137}Cs proving to be more widespread than ^{106}Ru. In tissues containing both ^{137}Cs and ^{106}Ru, ^{106}Ru concentrations were consistently higher. The levels of ^{106}Ru in the digestive gland and pallial complex in 1985 were 82% lower than in the previous year,

TABLE 3.11

Distribution of artificial gamma-emitters in Ravenglass winkles, September 1984.

Concentrations in $Bqkg^{-1}$ dry weight ($\pm 2\sigma$ error).

Sample	^{137}Cs	^{106}Ru	^{95}Nb	^{103}Ru	^{95}Zr	^{60}Co
Digestive gland	740 ± 44	10064 ± 629	1965 ± 104	131 ± 35	485 ± 48	67 ± 12
Pallial Complex	1495 ± 82	5439 ± 451	4255 ± 221	B.D.L.	1025 ± 122	B.D.L.
Head	328 ± 40	1073 ± 321	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Foot	286 ± 41	1369 ± 349	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Muscle	279 ± 36	1450 ± 310	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Operculum	499 ± 100	2594 ± 884	1816 ± 347	B.D.L.	B.D.L.	B.D.L.
Shell	34 ± 2	154 ± 17	55 ± 6	B.D.L.	B.D.L.	B.D.L.

B.D.L. - Below Detection Limit

TABLE 3.12

Distribution of artificial gamma-emitters in Ravenglass winkles, September 1985. Concentrations in $Bqkg^{-1}$ dry weight ($\pm 2\sigma$ error).

Sample	^{137}Cs	^{106}Ru	^{60}Co
Digestive gland	260 ± 10	1746 ± 70	55 ± 6
Pallial complex	747 ± 27	995 ± 148	B.D.L.
Head	B.D.L.	B.D.L.	B.D.L.
Foot	103 ± 15	B.D.L.	B.D.L.
Muscle	122 ± 14	B.D.L.	B.D.L.
Operculum	232 ± 36	B.D.L.	B.D.L.
Shell	22 ± 2	B.D.L.	B.D.L.
Total soft parts	225 ± 13	955 - 93	B.D.L.

B.D.L. - Below Detection Limit.

whilst the ^{137}Cs levels decreased by 50-65% in these soft tissues. The ^{106}Ru trend between 1984 and 1985 can easily be explained by the four-fold drop in ^{106}Ru discharges between 1984 and 1985 (BNF, 1985; 1986). Decreases of 50-80% in ^{106}Ru concentrations have also been reported in various marine organisms, including winkles, collected along the Cumbrian coast (Hunt, 1985; 1986).

Concentration factors of ^{137}Cs in winkle tissues (Table 3.13) for the 1985 samples are generally half those for 1984. If this generalisation can be assumed to apply also for the total soft tissue ^{137}Cs CF value in 1984, when ^{137}Cs was not measured, then the results here are fully in agreement with the IAEA mollusca ^{137}Cs CF range. The tissues of highest accumulative ability are the pallial complex, operculum and digestive gland. Indeed, the pallial complex CF is three times higher than the total soft tissue CF. Complementing the mussel studies, CF tissue trends of ^{137}Cs in winkles are similar to those obtained for the CF's of $^{239+240}Pu$. The inclusion of silt was suggested as a possible cause for the pallial complex showing such high CF's of $^{239+240}Pu$. The respective ^{137}Cs CF's do not contradict such a possibility. It is noteworthy, however, that, in 1984, the ^{137}Cs contents of the winkles exceeded those in the mussels. Although the mussel encounters larger volumes of sea water, containing conservative ^{137}Cs, the sources of ^{137}Cs to the winkle (diatoms, particulates, algae) adequately supplement its activities emphasising the importance of the food pathway (and in turn giving credence to the presence of silt in some soft tissues being responsible for enhanced nuclide activity levels) to radionuclide uptake by winkles.

3.1.5 Polonium

Polonium analyses of the marine organisms studied in this project were performed primarily to compare the natural levels of polonium with the anthropogenic activities of plutonium in the same samples and therefore to define the contribution of polonium to the α-autoradiographic record (Section 3.2).

TABLE 3.13

Concentration factors of ^{137}Cs in Ravenglass winkle tissues.

Tissue	Year 1984°	1985+
Total soft tissue	-	16
Head	16	-
Foot	12	5
Muscle	15	6
Pallial complex	96	50
Operculum	71	34
Digestive gland	55	20
Shell	6	4

° ^{137}Cs in sea water 5.36 Bql^{-1} (Ellett, pers. comm.)

+ ^{137}Cs in sea water 5.12 Bql^{-1} (Ellett, pers. comm.)

The data in Table 3.14 indicate that in 1984 ^{210}Po concentrations in the tissues of Ravenglass mussels were systematically greater than those of $^{239+240}Pu$. The $^{210}Po/^{239+240}Pu$ activity quotients ranged from 1.9 in mantle to 3.9 in total soft tissue. Polonium activities ranged from 124Bqkg^{-1} in muscle to 596Bqkg^{-1} in viscera (respective plutonium values - 42.9Bqkg^{-1} and 219Bqkg^{-1}). The activity trends for both nuclides were identical; viscera > gill > mantle > muscle. This trend is in general agreement with radiotracer results for plutonium distributions in mussels, as observed in laboratory experiments by Guary and Fowler (1981) and by others as described in Section 3.1.1.

The polonium concentrations found in Ravenglass winkles are compared with the respective plutonium concentrations in Table 3.15. The ^{210}Po activities were consistently less than those of $^{239+240}Pu$ in the winkle tissues. Accordingly, the $^{210}Po/^{239+240}Pu$ activity quotients were all less than unity, ranging from 0.12 in pallial complex to 0.81 in viscera. Polonium values ranged from 12.2Bqkg^{-1} in the muscle to 145Bqkg^{-1} in the viscera. The assays on Whitehaven-landed prawns (Table 3.16) revealed ^{210}Po activities of similar magnitude to those in the winkles but the $^{239+240}Pu$ levels were orders of magnitude less than those in either mussels or winkles. The highest concentrations of ^{210}Po in the prawns were found to be associated with the cardiac fore-gut (144Bqkg^{-1}) and the hepatopancreas (115Bqkg^{-1}), with lower concentrations being found in the abdomen shell (9.10Bqkg^{-1}) and the periopods (6.11Bqkg^{-1}). The few calculable $^{210}Po/^{239+240}Pu$ activity quotients were in closer accordance with those in the mussels than with those in the winkles.

As will be shown later in this section, the activities of ^{210}Po detected in the Cumbrian mussels, winkles and prawns can be assumed to reflect natural concentrations. Beyond this study, very few ^{210}Po data on mussels or winkles were available. The results reported by Cherry and Heyraud (1981, 1982),

TABLE 3.14

Concentrations of ^{210}Po and $^{239+240}Pu$ in mussels collected from Ravenglass in September 1984 ($Bqkg^{-1}$ dry weight) ($\pm 2\sigma$ error).

Tissue	$^{239+240}Pu$	^{210}Po	$\frac{^{210}Po}{^{239+240}Pu}$
Total soft tissue	71 ± 2	279 ± 4	3.94 ± 0.20
Viscera	219 ± 8	596 ± 8	2.72 ± 0.13
Gill	107 ± 3	307 ± 5	2.88 ± 0.13
Mantle	65 ± 4	126 ± 2	1.92 ± 0.12
Muscle	43 ± 4	124 ± 2	2.88 ± 0.42

TABLE 3.15

Concentrations of ^{210}Po and $^{239+240}Pu$ in winkles collected from Ravenglass in October 1985 ($Bqkg^{-1}$ dry weight) ($\pm 2\sigma$ error).

Tissue	$^{239+240}Pu$	^{210}Po	$\frac{^{210}Po}{^{239+240}Pu}$
Total soft tissue	159 ± 7	31 ± 2	0.19 ± 0.01
Head	52 ± 4	14.2 ± 1.2	0.27 ± 0.03
Foot	29 ± 3	18.7 ± 1.5	0.64 ± 0.08
Muscle	39 ± 4	12.2 ± 1.1	0.31 ± 0.03
Pallial complex	457 ± 11	56 ± 3	0.12 ± 0.01
Operculum	96 ± 9	14 ± 1	0.15 ± 0.02
Digestive Gland	178 ± 5	145 ± 4	0.81 ± 0.03
Shell	15.1 ± 0.9	N.M.	-

N.M. - Not measured

TABLE 3.16

Distribution of ^{210}Po and $^{239+240}Pu$ in Whitehaven-landed prawns (October, 1985).

Concentrations in $Bqkg^{-1}$(dry) ($\pm$ 2σ error).

Tissue	$^{239+240}Pu$	^{210}Po	$\frac{^{210}Po}{^{239+240}Pu}$
Hepatopancreas	0.81 $\pm$ 0.26	115 $\pm$ 4	141 $\pm$ 45
Carapace	5.96 $\pm$ 0.74	28.8 $\pm$ 1.8	4.83 $\pm$ 0.67
Abdomen muscle	0.85 $\pm$ 0.15	2.67 $\pm$ 0.33	3.14 $\pm$ 0.68
Gill	N.D.	29.1 $\pm$ 3.95	-
Cardiac fore-gut	N.D.	144 $\pm$ 6	-
Abdomen shell	N.D.	9.10 $\pm$ 1.04	-
Legs (periopods)	N.D.	6.11 $\pm$ 0.70	-

however, include considerable information on ^{210}Po activity in a variety of crustaceans.Their data show that the ^{210}Po activity found here in Cumbrian prawn tissues lie at the lower end of the observed range. In fact, their highest ^{210}Po result, for the shrimp Gennadas valens, was 5100Bqkg^{-1} in the whole animal, 31700Bqkg^{-1} of which was located in the hepatopancreas (Cherry and Heyraud, 1982).

The ^{210}Po CFs in the tissues of mussels, winkles and prawns (Table 3.17) illustrate the great difference that exists between the ^{210}Po accumulative power of the mussel compared to the winkle or prawn. The IAEA estimates of CFs for polonium in mollusca are of the order of 10^4, a value which certainly holds well here for the mussel. The winkle values, however, require the lower end of the CF range to be defined at $\sim 5x10^3$. The CF for whole body accumulation of polonium by crustaceans ($5x10^4$; IAEA, 1985) is consistent with the CFs found here for the hepatopancreas and cardiac fore-gut. No whole body ^{210}Po CF estimate was possible for prawns in this study but the general similarity of the CFs for winkles and prawns suggests that the whole body CF of ^{210}Po in prawns should be 6000-10000. This range lies towards the lower end of the IAEA-recommended range of polonium CF values. The tissues and organs primarily associated with feeding and digestion in the three organisms consistently display the highest ^{210}Po CF values, the digestive gland of the winkle and the hepatopancreas and cardiac fore-gut of the prawn being of similar magnitude to the viscera of the mussel. In contrast to the trend shown by the ^{137}Cs and $^{239+240}Pu$ CF data, the ^{210}Po CF for the winkle's pallial complex is much less than that for the digestive gland, suggesting that the pallial complex can preferentially incorporate $^{239+240}Pu$ and ^{137}Cs in its tissues relative to ^{210}Po. Such preliminary observations, however, should be viewed with caution.

Interpretation of the differences in ^{210}Po accumulation exhibited by mussels, winkles and prawns requires consideration of

TABLE 3.17

Concentration factors of ^{210}Po in the tissues of mussels, winkles and prawns.

Mussel (1984)		Winkle (1985)		Prawn (1985)	wet:dry ratio	
Total soft tissue	25800	Total soft tissue	5500			
Viscera	58400	Head	1900	Hepatopancreas	2.6	22100
Gill	13100	Foot	2200	Carapace	2.9	5000
Mantle	11700	Muscle	1700	Abdomen muscle	3.9	300
Muscle	10500	Pallial complex	9700	Gill	3.8	3800
		Operculum	5400	Cardiac fore-gut	2.7	26700
		Digestive gland	29000	Abdomen shell	2.7	1700
				Legs (periopods)	2.6	1200

^{210}Po concentration in sea water 2mBql^{-1} (mean of range presented by Woodhead (1984)).

the ^{210}Po contents of the food and water in the environment of these organisms. The mussel feeds on phytoplankton and other suspended particles. Because of its ventilation rate ($1.5 l h^{-1}$ for an average 5cm mussel), particle retention ability (2-100 µm) and ingestion efficiency (approaching 100% before particle concentrations of between 25×10^6 to 2×10^8 particles l^{-1} are sufficiently high to induce production of pseudo-faeces) (Boyle, 1981), the mussel's filter-feeding mode is highly effective in collecting ambient food, especially in the marine environment where concentrations of food in the water column are normally high.

The eating habits of the winkle are such that its radular teeth scratch the surfaces of rocks or seaweed in a raking fashion to loosen diatoms, detrital particles or shreds of material from the weed thallus before pulling these into the buccal cavity. The passage of water through the winkle is obviously much less than in the mussel. Since the winkle is a littoral inhabitant, water can enter the mantle cavity. The water, likely to contain suspended matter, could damage the delicate tissue of the gill and conceivably block the whole mantle cavity. Ciliary currents, however, run over the epithelium of the walls in such a way as to clear the cavity of detrital material (Fretter and Graham, 1976).

The prawn is, in general, a varied feeder, regardless of sex or size, and indiscriminantly takes food from the benthic zone. The food supply includes polychaetes, crustacea, molluscs and echinoderms (de Figueirido and Thomas, 1967) seized by the great chelae or directly by the fourth or third pair of walking legs and passed to the maxillipeds which cover the more anterior mouth parts.

The ability to accumulate ^{210}Po via each food source can be compared by noting the respecitve ^{210}Po concentration factors (IAEA, 1985):

Phytoplankton	3×10^4
Zooplankton	3×10^4
Macro-algae	1×10^3
Mollusca	1×10^4
Crustacean	5×10^4
Fish	2×10^2
Coastal sediment K_d	2×10^7

These data in conjunction with different feeding patterns readily explain the mussel's relatively high ^{210}Po levels relative to those in winkles and prawns. A dominant source of ^{210}Po to the mussel, along with phytoplankton and sea water, is thus derived from suspended sedimentary material which has ~ 400 times the ability to accumulate ^{210}Po relative to the next most active source-term.

The concentrations of ^{210}Po found in the winkle indicate the greater restriction on entry of sediment particles and sea water to its body. Although relatively low levels of ^{210}Po were present in the prawns sampled in here, suggesting low activities in their food, high concentrations of ^{210}Po detected in various species of crustacea (Cherry and Heyraud, 1981; 1982) can be attained by selective ingestion of ^{210}Po-rich tissues, namely the hepatopancreas of crustacea (Cherry and Heyraud, 1981). (A similar situation involving a range of source term CF values for plutonium does not occur as the plutonium CF for coastal sediments is of similar magnitude and range to those for biological materials).

To ensure that the observed levels of ^{210}Po in the marine organisms were not artificially enhanced by local discharges, and in the absence of published data, total mussel soft parts from remote British and French coastal sites were analysed (Table 3.18). The selected sites provide a good range of coastal water conditions in Western Europe. Polonium concentrations ranged from 111Bqkg^{-1} at Hunterston on the Clyde estuary to 459Bqkg^{-1} in the north-west Mediterranean at Monaco. Concentrations

TABLE 3.18

Concentrations of ^{210}Po and ^{210}Pb ($Bqkg^{-1}$ dry weight) in total soft tissues of mussels collected from sites indicated in Figure 2.7. ($\pm$ 1σ error).

Sampling Site	Location	Date of Collection	Species Collected	^{210}Po	^{210}Pb	$\frac{^{210}Po}{^{210}Pb}$
Ravenglass	54°24'N 3°24'W	20. 9.84	M. edulis	279 ± 4		
Hunterston	55°45'N 4°25'W	10.12.84	M. edulis	111 ± 3		
Firth of Forth	55°58'N 3°18'W	21. 1.85	M. edulis	246 ± 17	24.6 ± 5.4	10 ± 1.2
Mont St. Michel, France	48°40'N 1°30'W	11. 2.85	M. edulis	258 ± 18	2.6 ± 4.9	32
Sete, France	43°23'N 3°42'E	14. 2.85	M. galloprovincialis	201 ± 16	7.0 ± 4.0	29 ± 23
Monaco	43°43'N 7°24'E	20. 6.84	M. galloprovincialis	442 ± 12	10.8 ± 1.4	41 ± 5
		19. 7.84	M. galloprovincialis	459 ± 18	13.9 ± 2.0	33 ± 5
		31. 7.84	M. galloprovincialis	428 ± 27	10.8 ± 1.6	40 ± 6

of ^{210}Pb were at much lower levels than its granddaughter ^{210}Po, levels ranging from 2.6 to 24.6Bqkg^{-1} and generating $^{210}Po/^{210}Pb$ activity quotients from 10 to 41. The notable difference in ^{210}Po concentrations between mussels from Monaco and elsewhere probably reflects a variety of factors (age, seasonal collection time, water throughput, sea water temperature) on which there is little published information.

The only previously available data on ^{210}Po levels in mussels were reported by Kauranen and Miettinen (1970) for the Gulf of Finland. Converting their results from a whole organism (total soft tissue plus shell) wet weight basis to total soft tissues dry weight gives an approximate activity of ~350 Bqkg^{-1} ^{210}Po, with a $^{210}Po/^{210}Pb$ activity quotient of ~31. These values are thus consistent with the levels and quotients presented in Table 3.18.

The general similarity of the ^{210}Po concentrations in mussels from a variety of sites (Table 3.18) suggests that these are representative of natural background levels. The high $^{210}Po/^{210}Pb$ activity quotients show that polonium is largely unsupported by its lead grandparent and indeed the elevated natural dose received by most marine organisms is caused in most cases by selective incorporation of naturally occurring ^{210}Po by the organisms themselves (Cherry and Shannon, 1974; Heyraud and Cherry, 1979; Cherry and Heyraud, 1981, 1982). Essentially, the mussel's mechanism for concentration of ^{210}Po from sea water is much more effective than that for ^{210}Pb.

The data here show that the activities of natural polonium in mussel tissues are significantly in excess of the present plutonium activities found in mussels in the vicinity of Sellafield. There is no significant enhancement of ^{210}Po levels in Cumbrian mussels, in apparent agreement with BNF plc's statement that the Sellafield plant does not discharge ^{210}Po into the Irish Sea (Atherton, pers. comm.). It is not in theory impossible, because of the volatility of ^{210}Po,

that atmospheric releases could occur. Indeed such releases have been recorded in 1952 (1.8×10^{11}Bq) and 1957 (8.8×10^{11}Bq) (Stather et al., 1986). Despite the possibility of a Sellafield effect and the existence of other potential polonium sources along the Cumbrian coats, e.g. uranium discharges from Sellafield (Hamilton and Stevens, 1985), uranium mobilisation from minerals, local industrial wastes containing considerable quantities of Ra and Po (Hamilton, pers. comm.), it is still evident that the ^{210}Po levels in Ravenglass mussels can reasonably be considered natural. This observation is thus also assumed to apply to the winkle and Dublin Bay prawn data.

^{210}Po in mussel faecal pellets.

The ^{210}Po concentrations obtained from this short experiment are shown in Table 3.19. Since fifteen mussels were used to produce the faecal pellets, the polonium contents of the mussels before and after defaecation were calculated to provide an inventory of the polonium throughout the experiment. Initially there was a total of 4.05Bq ^{210}Po present between 15 mussels (total soft parts) and 6 litres of 0.22 µm-filtered sea water. At the end of the experiment, there was 4.02Bq ^{210}Po present in the experimental system distributed between the mussels, the sea water and the faecal pellets. Thus the ^{210}Po inventory of the experiment was closed and accounted for. Although small levels of ^{210}Po activity were encountered in the faecal pellets (0.0106Bq) and sea water (0.0337Bq after subtraction of background ^{210}Po), it is evident that only a small amount of ^{210}Po was lost from the mussel via its faeces. Only 0.26% of the total ^{210}Po body burden was lost in the faecal pellets, 0.83% being lost directly to the water, resulting in 1.1% of the total ^{210}Po activity of the mussel being lost when it was left to defaecate.

In commercial molluscan fisheries, mussels are usually allowed to purge their gut contents before being made available for sale to the public. From this short experiment performed on defaecating mussels, this practice appears to have little

TABLE 3.19

^{210}Po concentrations in Mediterranean mussels and sea water ($\pm$ 1σ error).

Sample	Total dry weight	Size of sample used	^{210}Po $Bqkg^{-1}$ (dry)
Before loss of faecal pellets: total soft parts of 5 mussels	1.9171g	0.5285g	704 $\pm$ 36
After loss of faecal pellets: total soft parts of 5 mussels	2.2941g	0.5292g	577 $\pm$ 31
Faecal pellets (from 15 mussels)	0.0168g	0.0146g	631 $\pm$ 35
* Sea water (0.22 μm filtered) (6 litres used)	-	1.5 litres	6.55 $\pm$ 0.48 x 10^{-3} Bql^{-1}

* Natural level of ^{210}Po in 0.22 μm filtered Mediterranean sea water is 9.25 x 10^{-4} Bql^{-1} (Heyraud, pers. comm.)

effect in lowering the ^{210}Po content of the edible parts of the mussel.

The need to establish the uptake route of radionuclides by marine organisms is driven by the importance assigned to assessing the radiological impact of any marine-based nuclear waste disposal practice. Koide et al. (1981) suggested, on the basis of Am/Pu activity quotients in sea water, particulate matter and mussels, that ingestion of contaminated particles represent the principal route for plutonium (and americium) accumulation in mussels. On the other hand, Hamilton and Clifton (1980) found, using the plastic α-track detector CR-39, that the distribution of alpha-particle activity in mussel tissues was homogeneous and, on this basis, they proposed that direct uptake of plutonium (whether active or passive) was from a conservative species in sea water. Bjerregaard et al. (1985) performed laboratory experiments in which mussels were exposed to plutonium-labelled food and water. They concluded that both these routes contributed significantly to the body burdens and, extrapolating their experimental results to natural environments, suggested that the mussels used by Goldberg et al. (1978, 1983) in the US Mussel Watch programme accumulated most of their radionuclides from the dissolved phase.

Nuclide activity quotients, as used by Koide et al. (1982) can also be included in the interpretation of the data for Ravenglass mussels and winkles. Thus Mackenzie et al. (1987) defined $^{137}Cs/^{239+240}Pu$ activity quotients for particle-associated Sellafield waste, soluble Sellafield waste and atmospheric fallout under Sellafield discharge conditions of 1984. Assumptions invoked in such definitions can be extrapolated to give a series of nuclide activity quotients relevant to the periods of sampling in this project. From Table 3.20, it appears then that the quotients in tissues record a dominant signature of particle-associated material. This approach, however, does not allow for the bioaccumulative properties of the organisms since the approach of Mackenzie et al. (1987) is strictly for comparison of sedimentary material. Consideration

TABLE 3.20

Nuclide activity quotients in Ravenglass mussel and winkle tissues.

Mussel	$\frac{^{137}Cs}{^{239+240}Pu}$		Winkle	$\frac{^{137}Cs}{^{239+240}Pu}$	
	1983	1984		1984	1985
Total soft tissue	2.13	3.58	Total soft tissue	-	1.41
Viscera	1.82	1.88	Operculum	2.83	2.42
Gill	0.50	2.31	Viscera	3.42	1.63
Mantle	2.27	2.49	Pallial complex	3.67	1.63
Muscle	2.72	3.05	Muscle	15.08	3.13
Byssal threads	0.66	0.81	Head	-	-
Periostracum	1.10	-	Foot	-	3.55
Shell	0.64	-	Shell	2.02	1.46
Foot	-	11.35			
Mantle edge	-	3.14			

	$\frac{^{137}Cs}{^{239+240}Pu}$		
	1983	1984	1985
Particle-associated Sellafield waste	2.00	1.91	1.47
Soluble Sellafield waste	96.2	36.6	87.5
Atmospheric fallout	49	48	47

Tissue quotient errors $\pm$ 4-14% based on 2σ counting errors.

of ^{137}Cs and $^{239+240}Pu$ concentrations in sea water and sediment in conjunction with concentration factors and transfer factors should provide a more realistic comparison with respect to determining source terms for marine organisms. Details of ^{137}Cs and $^{239+240}Pu$ concentrations in sea water in the vicinity of Ravenglass have previously been presented. For sediments, levels of ^{137}Cs and $^{239+240}Pu$ have not been determined in Ravenglass intertidal sediment but MAFF Annual Reports (Hunt, 1985-86) include such concentrations in nearby Newbiggin silt. Transfer factor of $^{239+240}Pu$ for mussels is taken as 0.006 (based on work on the clam Venerupis decussata by Aston and Fowler (1984)) and for winkles as 0.004 (Swift and Pentreath, 1988). Similar transfer factor data for ^{137}Cs have not been reported to date but, in this instance, it is assumed to be the same as for plutonium. Such an assumption is not unreasonable as Aston and Stanners (1982) and McKay and Baxter (1985) have demonstrated ^{137}Cs to be associated with non-exchangeable sites particularly in aged sediments. Estimates of the expected $^{137}Cs/^{239+240}Pu$ activity quotients in the total soft tissues of mussels and winkles from sea water or sediment particles only are given in Table 3.21. From these data and bearing in mind the major assumption inherent in their derivation, it is evident that either source could be responsible for the observed Cs/Pu quotients in mussel and winkle tissues. If the most uncertain assumption (i.e. the TF of ^{137}Cs is the same as that for $^{239+240}Pu$) could be tested and resolved, then it might be possible to resolve which nuclide source is dominant.

TABLE 3.21

Calculated $^{137}Cs/^{239+240}Pu$ activity quotients in mussel and winkle total soft parts from sea water or sediment sources.

		1984	1985
Mussel	Ravenglass	3.6	-
	Sea water	3.9	-
	Sediment	1.9	-
Winkle	Ravenglass	-	1.4
	Sea water	-	1.4
	Sediment	-	1.5

3.2 ALPHA-AUTORADIOGRAPHIC STUDIES OF MARINE ORGANISMS.

3.2.1 Laboratory studies: Tissue distributions of ^{237}Np, ^{239}Pu and ^{241}Am in marine organisms after periods of radionuclide accumulation and depuration.

3.2.1.1. The common mussel (Mytilus edulis)

Initial radiolabelling experiments exposed the mussel to the tracer ^{241}Am. Of the tracers used, ^{241}Am was always the first radionuclide to be administered to each species because the 59.7keV γ-emission of ^{241}Am could easily be monitored for the duration of the experiments. With the onus of these experiments being on producing suitably labelled tissues appropriate for α-autoradiography, the rigorous monitoring schedules required to obtain accumulation and depuration biokinetic patterns of transuranic nuclides in the marine organisms (Fowler et al., 1975; Guary and Fowler, 1981; Aston and Fowler, 1984; Bjerregaard et al., 1985) were not a prerequisite for this study.

After an accumulation period of 13 days in ^{241}Am-labelled sea water, the ^{241}Am concentration in the whole mussel ($Bqkg^{-1}$ wet) was 90 times that of the ^{241}Am concentration in the surrounding sea water (Bql^{-1}) (cf. Bjerregaard et al. (1985), CF ~30 after a 5 day exposure period), with 94% of the ^{241}Am activity contained on the shell and 55% of the total soft tissue activity present in the viscera. After depuration periods of 13 days and 48 days, mussels contained, respectively, 70% and 48% of the maximum body burden.

From the α-autoradiographs, tissue activity trends can be determined (Table 3.22). These are based on comparing the nuclide activity present in a tissue (represented by its

α-track density (tracks cm^{-2} sec^{-1})) with the nuclide activity present in the least active tissue. In general, the α-track densities used depict the homogeneous α-track distributions of the tissue in question, although in heterogeneous distributions, present usually in the more active tissues (viscera of the mussel, pallial complex of the winkle), the dominant track density is considered. "Hot" regions in tissues (areas of relatively more intense α-track distributions) were noted but not used in the above tissue trend calculations. Detailed comparison of tissue trend activities within a single uptake and depuration experiment, i.e. 13 day uptake against 13 day depuration against 48d depuration, is not practical because different individual organisms are used to provide such trends. It has been observed that differences can exist between the radionuclide contents of the tissues of organisms exposed to the same experimental conditions. Presented here are the generalised observations of the experiments. Subsequently, treatment of tissue activity quotients between uptake and loss periods within the same experimental run are restricted to relative comparisons only. In some experiments less active tissues show track densities slightly greater but comparable to background levels. As all the tissue activity quotients are calculated from the least active tissue,the errors involved can be as high as 50% and thus several tissues are grouped together within error in some tissue trends.

Tissue α-track distributions, whether of high or low activity, can be described as being either homogeneous or heterogeneous. Homogeneous α-track distributions in tissue indicate that, whatever the dominant labelling process may be, and whether uptake is active or passive, the α -emitting nuclide is distributed evenly throughout the tissue. This signifies that accumulation or retention conditions are uniform throughout the tissue in question. Conversely, heterogeneous distributions

imply that accumulation or retention conditions are not constant throughout the tissue under study as regions of higher or lower activity are present. The major common feature of heterogeneous distributions is the presence of hot areas (of relatively more intense α-track distributions), either through the inclusion of labelled particulate material (i.e. sediment, food or faecal fragments) or because specific tissue cells are more efficient at accumulating and/or retaining the nuclide than neighbouring tissues (i.e. digestive tubules, pallial complex glands).

The distribution of radionuclides is dependent on several factors including the physiological and biochemical functions of the tissue and the speciation and hence the bioavailability of the nuclide in question. The presence of heterogeneous α-track distributions within tissues is a feature which would have passed unnoticed if the tissues were analysed for radionuclide content using conventional radioanalytical techniques.

Of the mussel tissues, after uptake in the ^{241}Am labelling experiment, the viscera showed a heterogeneous distribution of α -tracks, with higher track densities located over the digestive tubules. The extent of heterogeneity decreased after 13 days of depuration until a homogeneous α -track distribution was found after 48 days. Generally, the remaining tissues exhibited varying degrees of homogeneous distributions, although random "hot" areas were observed in the mantle (Figure 3.1) and mantle edge (Figure 3.2) after uptake. The hot area of the mantly edge could be related to the inclusion of a piece of periostracum in the tissue section but the hot area of the mantle remains a random occurrence.

TABLE 3.22

Transuranic activity trends and quotients in mussel tissues relative to the least active tissue after exposure of mussels to radiolabelled sea water.

^{241}Am

13 day uptake:	Viscera	> Mantle	> Mantle edge,	Gill	> Foot,	Muscle	
	1055	127	20	14	1.1	1	
13 day depuration:	Viscera	> Gill,	Mantle	> Mantle edge,	Foot	> Muscle	
	1243	21	20	9	7	1	
48 day depuration:	Viscera	> Mantle,	Foot,	Mantle edge,	Gill	> Muscle	
	18	5.5	2.5	2.4	2.2	1	

^{237}Np

13 day uptake:	Viscera	> Gill	> Mantle edge,	Mantle	> Muscle,	Foot	
	96	12	5.3	3.4	1.5	1	
14 day depuration:	Viscera	> Foot,	Mantle,	Gill	> Muscle,	Mantle edge	
	12	4.7	4.1	3.1	1.6	1	

^{239}Pu

13 day uptake:	Viscera	> Mantle edge	> Gill	> Mantle,	Foot,	Muscle	
	5790	30	6.1	1.8	1.4	1	
14 day depuration:	Viscera	> Gill,	Mantle	> Foot	> Muscle	> Mantle edge	
	1724	64	48	16	3.3	1	
50 day depuration:	Gill	> Viscera,	Foot,	Mantle	> Mantle edge,	Muscle	
	12	7.7	4.2	3.2	1.3	1	

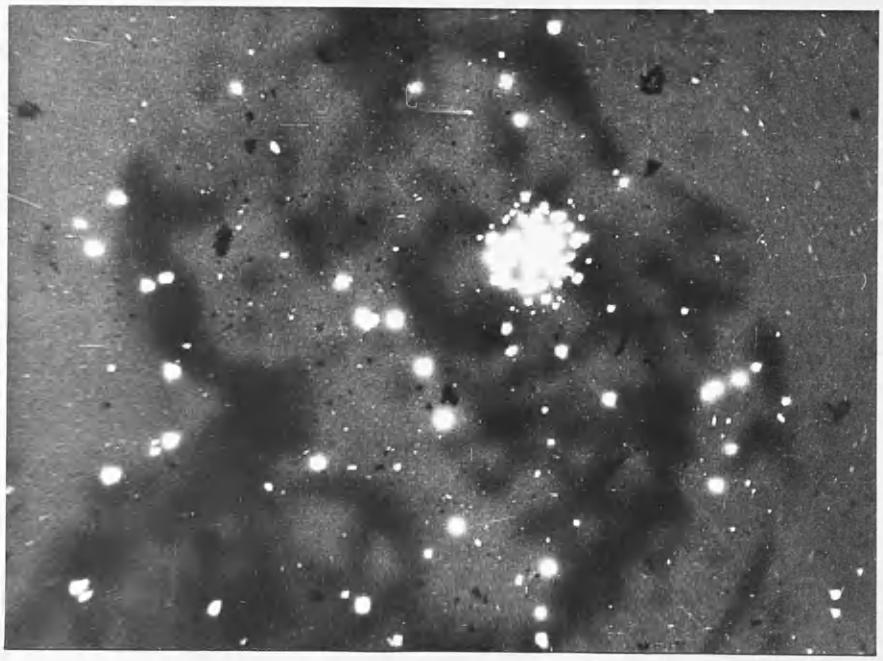


Figure 3.1. 'Hot' area present in the mussel's mantle after a 13 day uptake period of ^{241}Am from labelled sea water. 18 day exposure. 3cm = 200 µm.

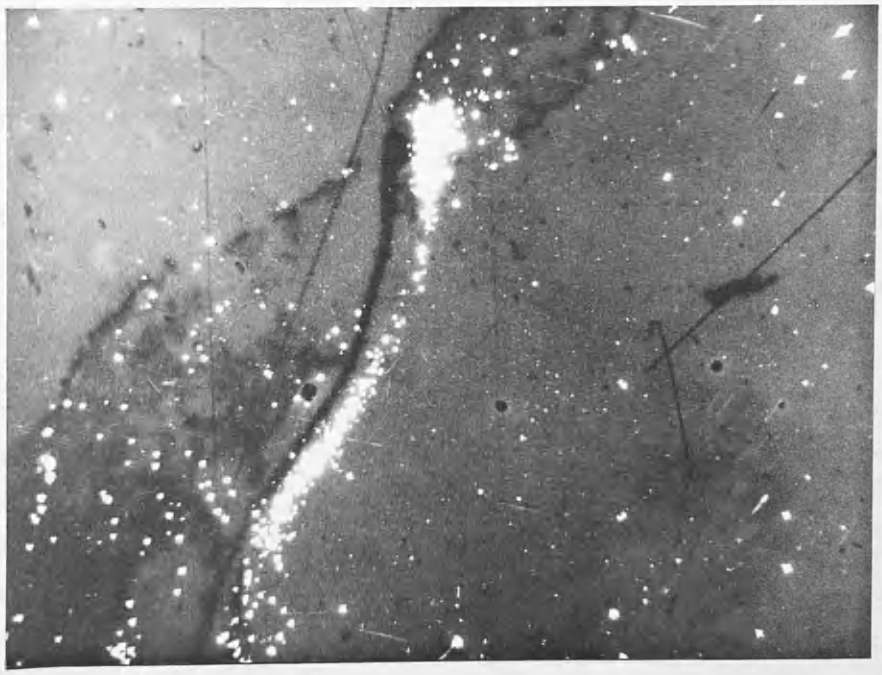


Figure 3.2. 'Hot' area present in the mussel's mantle edge after a 13 day uptake period of ^{241}Am from labelled sea water. 58 day exposure. 3cm = 200 µm.

Activity quotients clearly indicate the affinity of the visceral tissues for ^{241}Am. The ^{241}Am content of this tissue is at least an order of magnitude greater than those of other mussel tissues after uptake and initial depuration periods. On the other hand, muscle tissue consistently displayed the lowest ^{241}Am content of the mussel's tissues. After 48 days, the viscera had shown the most significant loss. Although it remained the most active tissue, its dominance had decreased. The substantial loss of activity occurring from the gill, mantle and mantle edge resulted in the previously less active tissues, such as muscle and foot, becoming of comparable activity.

Results from ^{237}Np and ^{239}Pu tracer experiments (Figure 3.3) reinforced the ^{241}Am data by showing that, after uptake, the viscera contained the highest activity, this activity being primarily associated with the digestive tubules. The only other consistency between the three tracers in mussel tissues is that muscle tissue displayed low nuclide activities throughout. Activity quotients of ^{237}Np are comparable to those of ^{241}Am (and ^{239}Pu) except in viscera after uptake. This is due to the combination of relatively lower activity in the viscera and relatively higher activity in the foot (and subsequently in the remaining tissues), suggesting that the conservative ^{237}Np is more evenly distributed than ^{239}Pu or ^{241}Am in mussel tissues.

During depuration of ^{237}Np, the tissue activity trend changed almost completely, Promotion of the foot within the activity sequence during depuration periods is observed for both ^{237}Np and ^{239}Pu tracers. This phenomenon, although insignificant in terms of activity quotients, reflects a higher retention capability for the foot relative to the remaining less active tissues. As the actual α-track distribution (for ^{237}Np and ^{239}Pu) changes from a homogeneous diffuse pattern throughout the tissue after uptake to one tending to exhibit preferential peripheral activity, it may be implied that transport of these nuclides occurs during depuration via metabolic processes.

Alternatively, in depurating the radiotracer, the form of the nuclide may be altered becoming more available for uptake by the foot. Since an epidermal preference is shown, surface incorporation of ^{237}Np and ^{239}Pu seems highly feasible as glandular secretions are present especially during the formation of byssal threads.

From the observed activity trends during the mussel/^{239}Pu experiment, the gill retains ^{239}Pu most efficiently after 50 day depuration. The α-track distributions show, however, that the viscera loses nuclide heterogeneity and hence activity, resulting in the gill being the most active tissue. This result suggests that ^{239}Pu has a shorter turnover time in the viscera relative to ^{237}Np or ^{241}Am.

Conversely, the ^{239}Pu uptake activity quotient in the viscera is high due to the relatively low ^{239}Pu activity in the muscle (and hence in the remaining soft tissues). This observation contrasts with those for ^{237}Np accumulation in that, whereas the ^{239}Pu tissue distribution is heavily biased towards the viscera, that of ^{237}Np is more uniform.

As described in Section 2.6.2., only ^{241}Am could be used as a tracer for mussel labelling experiments via food. The activity trends and quotients obtained after feeding mussels with the marine centric diatom Thalassiorsira pseudonana (clone 3H) are presented in Table 3.23. As in labelling from sea water, the viscera displayed a heterogeneous α-track distribution for all three conditions studied. Again, assimilation of ^{241}Am within the viscera occurred in the digestive tubules. Clusters of high activity were observed in the lumen of the digestive gland through the presence of food material in the section (Figure 3.4). Hot regions detected in the mantle, mantle edge and foot following uptake were not present after any of the depuration periods. This could be due to the presence of diatom-like material being included in the tissue at the time of sectioning. Subsequently the food

TABLE 3.23

Activity trends and quotients in mussel tissues relative to the least active tissue after exposure of mussels to ^{241}Am-labelled food.

^{241}Am

5 day uptake:	Viscera >	Gill,	Mantle edge,	Muscle,	Mantle,	Foot
	5045	4.3	2.3	2.0	1.5	1
13 day depuration:	Viscera >	Gill >	Mantle >	Muscle,	Foot >	Mantle edge
	11524	27	14	4.0	2.3	1
42 day depuration:	Viscera >	Mantle,	Muscle,	Foot,	Mantle edge,	Gill
	21	1.9	1.7	1.4	1.4	1

Figure 3.3. Heterogeneous alpha-track distribution obtained from the mussel's viscera after a 13 day uptake period from labelled sea water. 8 day exposure. 3cm = 500 μm.

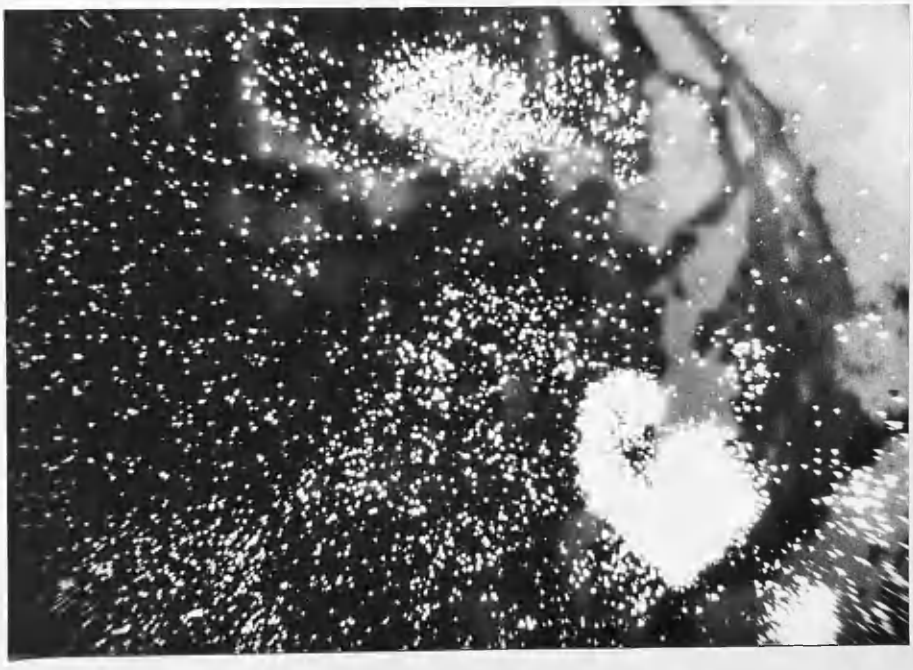


Figure 3.4. 'Hot' areas present in the mussel's viscera after a 5 day uptake period of ^{241}Am from labelled food. 1 day exposure. 3cm = 500 μm.

particles have been removed from these tissues during loss periods. The depuration pattern of the gill in which, in effect, it loses all of its accumulated activity within 42 days, implies that the gill has a more rapid ^{241}Am turnover than do neighbouring tissues. This is suggested in the tissue trends obtained in the ^{241}Am sea water experiment although it is not so clearly indicated there.

The activity quotients show a similar trend to that observed during the ^{239}Pu sea water experiment in that the viscera readily accumulates the radiotracer whilst the remaining tissues show a lesser degree of assimilation. As in previous experiments, the relative nuclide activity in the viscera has after a 42 day depuration period been greatly reduced to only one order of magnitude above other tissues.

Under all experimental conditions, the mussel's digestive tubules in the viscera were the sites at which accumulation of ^{237}Np, ^{239}Pu and ^{241}Am was most efficient by at least an order of magnitude greater than the other tissues. The digestive processes in the mussel are therefore most influential in radionuclide assimilation and excretion. The gill is of interest in its ability to retain ^{239}Pu more efficiently than any other mussel tissue. Such behaviour contrasts with ^{237}Np and ^{241}Am retention in the gill where turnover rates are more rapid, particularly when labelled with ^{241}Am in food. Why the gill preferentially retains ^{239}Pu is currently unclear but may require the oxidation states of ^{239}Pu to be studied more closely. Muscle tissue exhibited the lowest activities in all the sea water labelling experiments, reflecting its relative non-involvement in short-term metal assimilation in mussels. During uptake of all three tracers from sea water, the foot behaved similarly to muscle but, during loss periods of ^{237}Np and ^{239}Pu, glandular activity in conjunction with altered nuclide availability, is proposed to explain the observed heterogeneous distributions. Hot areas detected in the mantle and mantle edge did not follow any specific pattern and their occurrence appeared to be quite random.

The food-labelling experiment with ^{241}Am demonstrated a regular occurrence of hot areas after uptake, in contrast to the less common observation of heterogeneity in the water labelling experiments. The food source thus provides a more uneven distribution of radionuclides, presumably reflecting higher particulate contents.

During all loss experiments, the frequency of hot areas and heterogeneous distributions decreased through time. The loss of activity from viscera (clearly demonstrated by the activity quotients in Tables 3.22 and 3.23) is probably by active excretion ((Coombs and George, 1978) and will be discussed further in Section 3.3), where loss over a 50 day depuration period can result in remaining visceral activity being approximately two orders of magnitdue lower than activity present after uptake. Furthermore, the activity quotients show that, after accumulation, ^{237}Np is more evenly distributed amongst the tissues than ^{239}Pu or ^{241}Am. This may be due to the more conservative nature of ^{237}Np but such a hypothesis requires further investigation.

From the present study, then, the mussel has clearly exhibited the ability to accumulate radionuclides from both food and water, with no obvious discrimination between sources being shown by the individual tissues.

As these α-autoradiographic experiments on mussels are unique caution must be exercised in comparing the results with those from other approaches. Miramand and Germain (1985) studied the uptake and distribution of ^{239}Pu and ^{241}Am in the edible cockle (Cerastoderma edule). They reported that ^{241}Am was accumulated from labelled sea water to a higher level than ^{239}Pu ($\sim$8 times), an observation which was not as clearly demonstrated in the experiment described earlier here. Of the activity accumulated, 80% of ^{239}Pu and only 36% of ^{241}Am were contained in the shell. Within the soft tissue (figures only given for ^{241}Am), 96% of ^{241}Am was found in the viscera. Not surprisingly, their α -autoradiographic studies revealed

^{239}Pu and ^{241}Am principally localised in the digestive tract wall and in the wall of the digestive tubules.

Other research on the uptake and distribution of transuranic nuclides in mussels under laboratory conditions report tissue concentrations but no further α-autoradiographic work has been performed. The previous observation that the shell contains the bulk of the transuranic nuclide load of the whole mussel, whilst the viscera contains the bulk of the soft tissue activity (~ 70%) has been reported on several occasions (Guary and Fowler, 1981; Bjerregaard et al., 1985; Fisher and Teyssie, 1986). The apparent more rapid depuration rate of ^{239}Pu over ^{241}Am observed in visceral tissue in this research is supported by Guary and Fowler (1981) and Bjerregaard et al. (1985). Guary and Fowler (1981) remark that, although the short-lived compartment of plutonium (1-2 days and 2 weeks) may turnover more rapidly than those of ^{241}Am (2 and 3 weeks), the long-lived compartments (20-30% of total activity accumulated) may be similar. The similarity between the tissue distributions observed from food and water labelling media has also been noted by Bjerregaard et al. (1985).

Past biokinetic studies involving molluscs and neptunium demonstrate the capacity of the shell for accumulation of the bulk of the nuclide body burden. Low concentration factors for the whole body were found for Mytilus galloprovincialis (~ 20) (Guary and Fowler, 1977) and Cerastoderma edule (~ 40) (Germain et al., 1987) when exposed to neptunium in sea water. Only values for shell and total soft parts were given.

3.2.1.2 The Dublin Bay Prawn (Nephrops norvegicus)

The difficulty encountered in obtaining and maintaining live Nephrops had a strong bearing on the strategy adopted for this set of radiolabelling experiments. Thus only uptake experiments were performed using the three transuranic tracers under both labelling conditions. Tissue activity trends

and quotients are presented in Table 3.24. Initial experiments using ^{241}Am revealed the ^{241}Am concentration in the whole prawn ($Bqkg^{-1}$ wet) to be 360 times greater than the concentration of ^{241}Am in the surrounding sea water (Bql^{-1}), after a 5 day uptake period. Of this accumulated activity, 92% was associated with the exoskeleton and 56% of the activity of the total soft parts was localised in the gills. From labelled food (pieces of sand smelt (Atherina presbyter) injected with ^{241}Am), an 8 day uptake period revealed 43% of the total soft tissue activity to be contained in the hepatopancreas and 28% in the cardiac fore-gut. (Unfortunately the heart was overlooked during initial dissections of the prawn after being labelled with ^{241}Am and ^{239}Pu from sea water, resulting in the omission of heart tissue from these tissue activity trends in Table 3.24).

Although all activity quotients are relative to the least active tissue, for ^{237}Np uptake from sea water the activities in claw muscle and abdomen muscle were comparable to background levels, in effect, having no enhanced activity for calculations. From sea water, Nephrops gills accumulated ^{241}Am (Figure 3.5 and ^{239}Pu more efficiently than the digestion-associated tissues of the hepatopancreas and cardiac fore-gut, whereas ^{237}Np was not accumulated so efficiently, perhaps reflecting the relative bioavailability of these nuclides to the gill. This observation contrasts the previous general conclusions of the mussel experiments where the mussel's gill did not concentrate the radiotracers to a higher level than the viscera (which contains the digestive gland).

The relatively high and homogeneous activity of Nephrops gill reflects its different function relative to the gill of the mussel. Whereas the latter is used for both respiration and filtration-feeding, the Nephrops gill is solely used for the purpose of respiration. Consequently the mussel's gill has mucous secretions which are used to trap particulate material which in turn is transported to the digestive tract

TABLE 3.24

Transuranic activity trends and quotients in Dublin Bay prawn tissues relative to the least active tissue after exposure of Dublin Bay prawns to radiolabelled sea water and food.

^{241}Am, 5 day uptake from sea water:

Gill	>	Hepatopancreas, Cardiac fore-gut	>	Abdomen muscle	>	Claw muscle
5780		137		130		6.2		1

^{241}Am, 8 day uptake from food:

Hepatopancreas	>	Cardiac fore-gut, Gill	>	Heart	>	Claw muscle	>	Abdomen muscl
1460		115		112	18	8.9		1

^{237}Np, 5 day uptake from sea water:

Cardiac fore-gut	>	Hepatopancreas, Gill	>	Heart	>	Claw muscle, Abdomen muscle
21		9.7	5.9	1	-	-

^{237}Np, 7 day uptake from food:

Cardiac fore-gut	>	Hepatopancreas, Heart	>	Abdomen muscle, Gill	>	Claw muscle
687		31	21	6.8	4.5	1

^{239}Pu, 5 day uptake from sea water:

Gill	>	Hepatopancreas	>	Cardiac fore-gut, Claw muscle	>	Abdomen muscle
235		17		6.8	3.2	1

^{239}Pu, 9 day uptake from food:

Hepatopancreas	>	Heart	>	Gill	>	Cardiac fore-gut	>	Abdomen muscle, Claw muscl
228		60	30		8.1		1.1	1

via the palps and oesophagus by cilliated currents. Any tracer contained in these secretions subsequently enhances the visceral nuclide content and reduces the gill content. Mucous transport processes of this kind are not associated with functions of Nephrops gill.

The hepatopancreas exhibited homogeneous distributions irrespective of nuclide activity or source, higher nuclide concentrations (^{239}Pu and ^{241}Am) being located in the digestive tubules following food ingestion. The cardiac fore-gut showed consistent α-track distributions from both food and sea water media using ^{237}Np and ^{241}Am tracers, hot areas being numerous. ^{239}Pu, however, did not provide as high an incidence of hot areas. This may in some way reflect the condition of the test prawn at the time of study rather than show a specific nuclide selection of the tissue. The hot areas were attributed to the hard chitinous tissue present in the tissue section (Figure 3.6). As chitinous material has been associated with highly efficient radionuclide accumulation properties (cf. the mussel's periostracum (Hamilton and Clifton, 1981) and this study, Section 3.1), it is to be expected that some enhanced activity would be present in the cardiac fore-gut. Metal binding in chitinous-type material is discussed later in Section 3.3. The abdomen and claw muscle tissues complement the mussel's muscle tissue in hosting the lowest radiotracer concentrations within the organism.

After labelling Nephrops with ^{241}Am via food the hind gut still contained material for excretion. Sections of this material provided the highest α-track densities found in the prawn (Figure 3.7). Relatively large quantities of ^{241}Am are therefore excreted.

Heart tissue when labelled with ^{239}Pu via food showed a high α-track density second only to that of the hepatopancreas (Figure 3.8). Such accumulation behaviour in prawn heart tissue may be unique to this study but similar accumulative

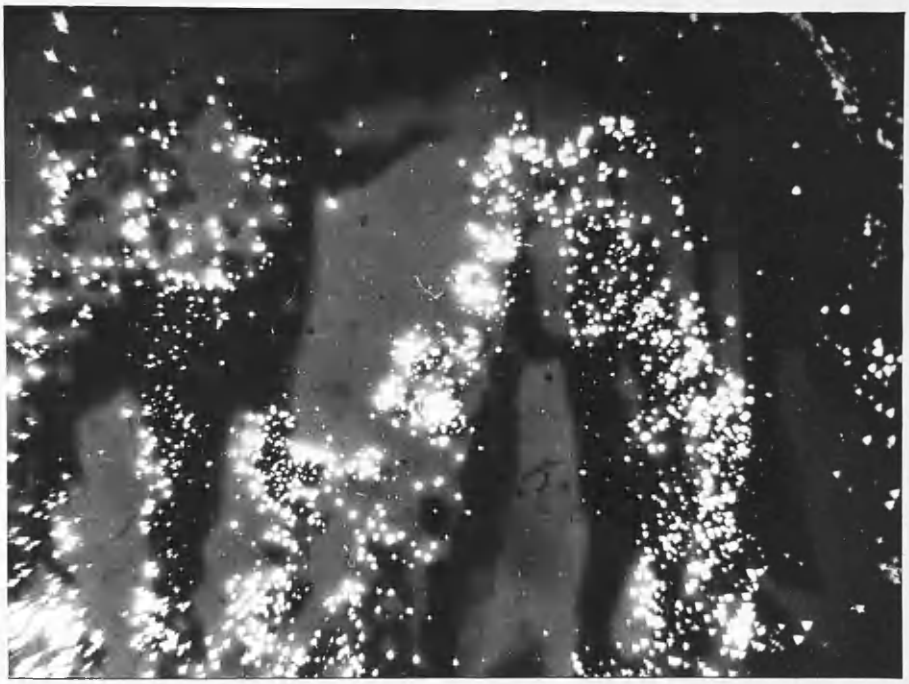


Figure 3.5. Alpha-track distribution present in the Dublin Bay prawn's gills after a 5 day uptake period of ^{241}Am from labelled sea water. 38 day exposure. 3cm = 500 μm.

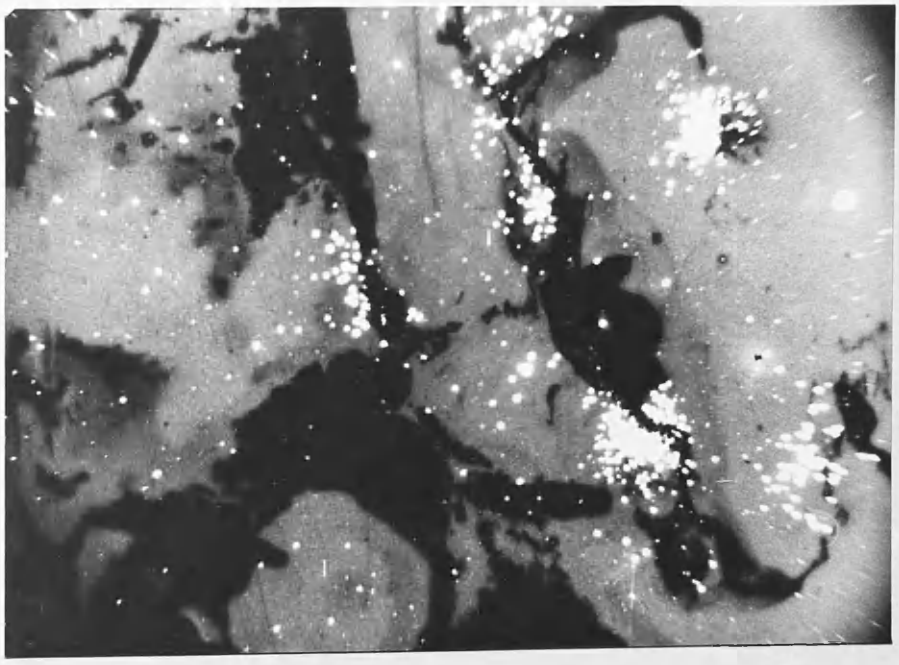


Figure 3.6. 'Hot' areas present in the Dublin Bay prawn's cardiac fore-gut after a 5 day uptake period of ^{241}Am from labelled sea water. 85 day exposure. 3cm = 500 μm.

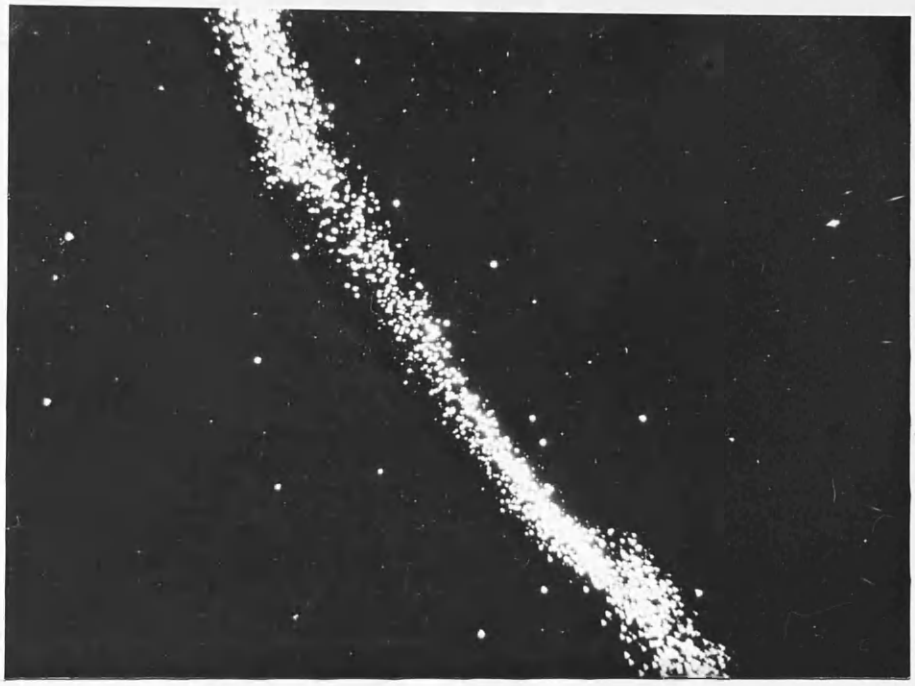


Figure 3.7. 'Hot' area present in the Dublin Bay prawn's hind gut after an 8 day uptake period of ^{241}Am from labelled food. 22 day exposure. 3cm = 500 µ m.

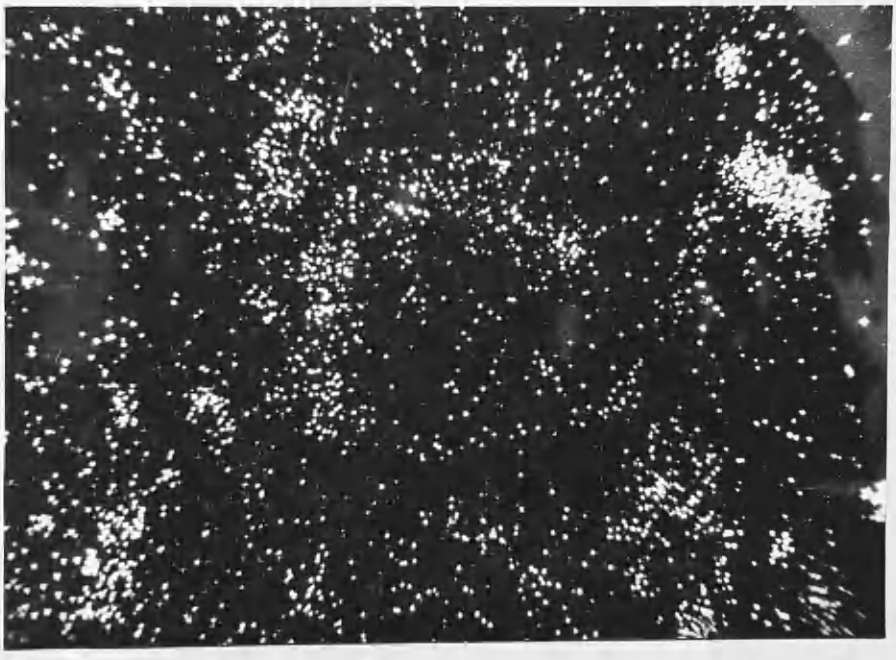


Figure 3.8. Alpha-track distribution present in the Dublin Bay prawn's heart tissue after a 9 day uptake period of ^{239}Pu from labelled food. 148 day exposure. 3cm = 500 µm.

powers have been observed in the heart tissue of the octopus (Octopus vulgaris) by Miramand and Guary (1981). Although the physiological and morphological characteristics between prawn and octopus heart tissues may not be the same since here we are comparing between a crustacean and a mollusc, it is interesting that such tissues should exhibit enchanced activity. In the octopus, the association of ^{241}Am was shown to be with the adenochromes, cells probably engaged in metal detoxification processes (Miramand and Guary, 1981). Such a process may be occurring in the prawn with ^{239}Pu implying then that, relative to ^{237}Np or ^{241}Am, ^{239}Pu is preferentially transported to the heart. This proposal, however, should be considered with caution as the heart tissues compared could be fundamentally different.

The activity quotients show that the most active tissue after each experimental run is an order of magnitude greater than the next most active tissue. Typically, the gill and the hepatropancreas are the most active tissues although the cardiac fore-gut exhibits an affinity for ^{237}Np under both labelling conditions. The muscle tissues, as in the mussel, consistently contained the lowest levels of radiotracer throughout the tissues studied.

The Dublin Bay prawn, as found with the mussel, is capable of accumulating ^{237}Np, ^{239}Pu and ^{241}Am from food or sea water sources. The gill clearly exhibits a preference for ^{239}Pu and ^{241}Am from the aqueous phase whereas the remaining tissues do not. The hepatopancreas consistently exhibits high activities whilst hot areas are abundant in the cardiac fore-gut particularly when labelled with either ^{237}Np or ^{241}Am. Heart tissue accumulated ^{239}Pu from food more efficiently than any other nuclide from any other source. Although the explanation for this is unclear the role of detoxifying granules in heart tissue could be significant. Whenever present, the faecal material in the hind gut exhibits very hot regions of activity indicating that large amounts of consumed activity are excreted.

Comparative work on the distribution of transuranic nuclide in crustacean species reveal complementary observations. Ward (1966) found that, from labelled sea water, 90% of plutonium in the lobster (Homarus vulgaris) was contained in the calcified exoskeleton. Fowler and Guary (1977) reported that the crab (Cancer pagurus), when fed ^{237}Pu via polychaete worms (Nereis diversicolor), concentrated the largest fraction of plutonium in the hepatopancreas, with less in the gill, stomach and muscle. Alpha-autoradiographic studies on the lobster (Homarus gammarus) and crab (Cancer pagurus) by Miramand (1984), revealed ^{241}Am accumulation to be dominantly associated with the hepatic tubules in the hepatopancreas, either from labelled food or sea water. Calcium or phosphate granules within these tubules were thought to provide the final target of the accumulated ^{241}Am in the tissues of these crustaceans, a suggestion which, in the light of the Nephrops experiment, could easily apply here to other observations on Dublin Bay prawn.

A study of the tissue distribution of $^{239+240}Pu$ and ^{241}Am in Nephrops from the Irish Sea (Pentreath, 1980) revealed a very different trend for plutonium compared to those obtained here under laboratory conditions. The stomach and contents and the gills contained similar levels of plutonium, the digestive gland (hepatopancreas) having levels ten times lower. For ^{241}Am, however, activities in the digestive gland were similar to those in the gills and stomach. (Plutonium levels in prawns discussed in Section 3.1.1 were so low that a reasonable tissue trend could not be derived). Pentreath (1980) reported that, of the muscle tissues of the lobster Homarus gammurus, the claw muscle showed the greatest preference for $^{239+240}Pu$, whilst the abdomen muscle exhibited a preference for ^{241}Am. None of these observations was evident under the experimental conditions reported here.

3.2.1.3 The winkle (Littorina littorea)

This species proved to be convenient for laboratory tracer experiments - easily handled, with feeding (using radiolabelled seaweed) presenting none of the problems encountered in feeding mussels. Indeed the winkle's compatability with tank studies made it the most successful of the test organisms here because the widest range of conditions could be applied to it.

Preliminary experiments exposed the winkle to ^{241}Am from sea water. The ^{241}Am concentration in the whole winkle ($Bqkg^{-1}$ wet) was 5 times greater than the ^{241}Am activity in the surrounding sea water (Bql^{-1}) after a 14 day exposure period. The shell contained 78% of the winkles total ^{241}Am activity. Of the soft tissue activity, 56% was localised in the digestive gland and 26% in the pallial complex.

In all the experimental conditions presented above, the operculum (a cuticular secretion at the base of the foot) accumulated radioactivity to the extent of providing the highest α-track densities encountered in this study regardless of the radiotracer used. The operculum belongs to the group of scleroproteins found in invertebrate organisms. Other tissues in this group are the periostracum and byssal threads in mussels. All possess the ability to accumulate radionuclides to much higher levels than neighbouring soft tissues. As the surface of the operculum is not perfectly flat, patterns of the operculum whorl are depicted in the α-autoradiograph (Figure 3.9).

The dominance of the operculum in winkle tissue activity trends is clearly demonstrated by the activity quotients presented in Table 3.25 where α-track densities found in the operculum are usually 1 to 2 orders of magnitude greater than in the next most active soft tissue. For all three radiotracers used, the digestive gland consistently exhibited radionuclide assimilation in the digestive tubules. The α-track distributions, in conjunction with the ranking

TABLE 3.25

Transuranic activity trends and quotients in winkle tissues relative to the least active tissue after exposure of winkles to radiolabelled sea water.

^{241}Am

14 day uptake:	Operculum	> Digestive gland	> Pallial complex	> Muscle, Foot, Head		
	5500	455	16	1.8	1.2	1
13 day depuration:	Operculum	> Pallial complex	> Digestive gland	> Foot	> Muscle, Head	
	14800	7380	2710	5	1	-
48 day depuration:	Operculum	> Pallial complex	> Digestive gland, Head, Foot, Muscle			
	581	14	4.4	1.5	1	-

^{237}Np

14 day uptake:	Operculum	> Pallial complex	> Digestive gland, Muscle, Head, Foot			
	52	8.1	1.2	1.2	1	1
14 day depuration:	Operculum	> Pallial complex, Digestive gland	> Head, Foot, Muscle			
	23	4.7	4.7	2.7	1.2	1

^{239}Pu

13 day uptake:	Operculum	> Pallial complex	> Digestive gland	> Muscle, Head, Foot		
	3640	45	6.8	2.7	1.5	1
14 day depuration:	Operculum	> Pallial complex	> Muscle, Digestive gland	> Foot, Head		
	1110	30	7.6	5.0	2.9	1
50 day depuration:	Operculum	> Pallial complex	> Head, Foot, Digestive gland, Muscle			
	371	22	1.5	1.5	1.4	1

of the digestive gland in the tissue activity trend and its respective activity quotients show that uptake of ^{241}Am from sea water did not truly occur from the aqueous phase but that particulate material was present in the experimental system. Hot regions occurred in the digestive gland after ^{241}Am uptake (but were not present after loss periods), whereas, when exposed to ^{237}Np and ^{239}Pu, hot areas were absent throughout. The activity trends and quotients for ^{241}Am, after uptake and initial loss periods, demonstrate that the digestive gland is, after the operculum, one of the most active tissues, whilst for ^{237}Np and ^{239}Pu, it is ranked in mid-range.

Alternatively it can be deduced that, in the winkle, ^{237}Np and ^{239}Pu behave differently from ^{241}Am. As similar behaviour of ^{237}Np, ^{239}Pu and ^{241}Am uptake is exhibited in the viscera of the mussel and in the hapatopancreas of the prawn, it seems unlikely that there would be exceptional behaviour in the winkle's digestive gland. Hence the evidence leans strongly towards the presence of inadvertant particulate material in the labelling medium. While this perhaps reduces the usefulness of ^{241}Am in this section of the research, it is of use for comparison with the specific food-labelling experiments.

The other soft tissue of note which contains high α-track densities is the pallial complex which, except in the ^{241}Am uptake experiment, showed higher levels of radioactivity than the digestive gland (see activity in Table 3.25). The α-track distribution in the pallial complex was strongly influenced by the presence or otherwise of faecal material in a given tissue section (Figure 3.10). This material was responsible for many hot areas observed in the pallial complex tissue sections. Elsewhere in the sections strong heterogeneous distributions were present especially with ^{239}Pu and ^{241}Am tracers. The pallial complex contains various glands and apertures. Some glandular activity is involved in keeping the mantle cavity relatively free from damaging

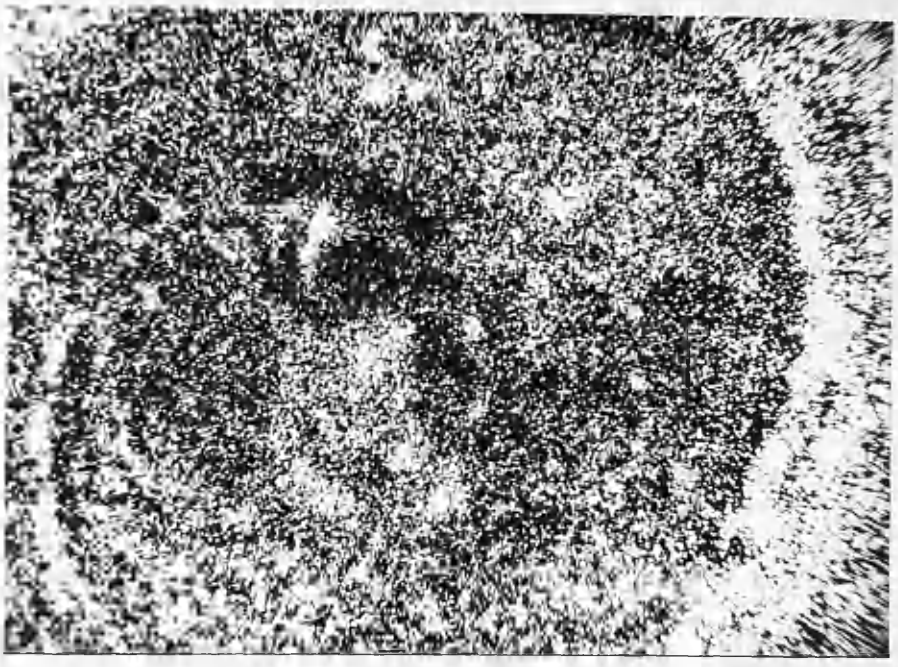


Figure 3.9. Alpha-autoradiograph of the winkle's operculum obtained after a 14 day uptake period of ^{237}Np from labelled sea water. 13 day exposure. 3cm = 500 μm.

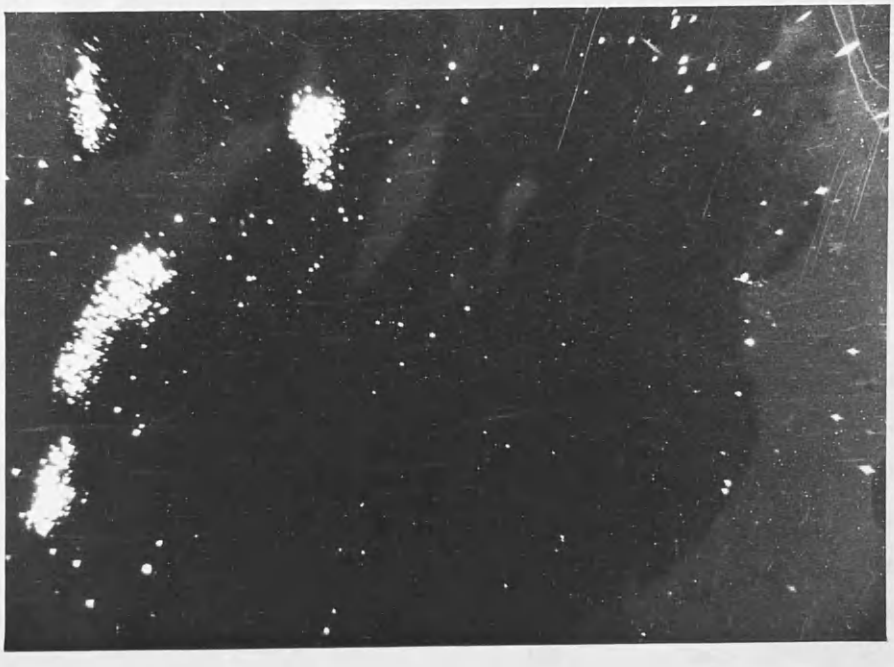


Figure 3.10. Alpha-track distribution present in the winkle's pallial complex after a 13 day loss period of ^{241}Am initially accumulated from labelled sea water. 40 day exposure. 3cm = 500 μm.

particulate material by ensnaring the latter in mucous secretions. Excretory and genital openings are present within the pallial complex. These bodily functions provide exposure routes for the tracers to the pallial complex via the associated high glandular activities. The heterogeneous α-track distributions found in the pallial complex after uptake of all three tracers were maintained throughout loss periods, although clearly α-track densities became decreased with time.

After the uptake experiments, the remaining winkle tissues studied were generally of markedly lower activity than the operculum and pallial complex. The foot, when labelled with ^{241}Am, showed homegeneous distributions throughout uptake and loss, while, with ^{237}Np and ^{239}Pu, a definite peripheral uptake pattern was observed. These latter regions, however, diminished in intensity during nuclide loss. A similar nuclide preference was exhibited by the mussel's foot discussed earlier in section 3.2.1.1. The lack of ^{241}Am at the periphery of the foot could reflect binding of ^{241}Am to particulate material in such a manner that its bioavailability to the foot is reduced.

This lack of peripheral preference for ^{241}Am is also observed in the head, in which surface activity was observed only with ^{237}Np and ^{239}Pu (Figure 3.11). The buccal mass region of the head section, however, displayed slightly enhanced activities of all three tracers. Present in the buccal mass is chitinous material similar histologically to that found in the prawn's cardiac fore-gut. Hence the presence of chitinous material appears to enhance radionuclide accumulation within the head tissue. In the winkle's buccal mass, however, levels of accumulated radioactivity were lower than those observed in the cardiac fore-gut of the prawn. Enhanced levels of activity were maintained in the head section during loss periods of all three tracers, levels decreasing of course through time.

From the activity quotients in Table 3.25, the ranges calculated for ^{237}Np are narrower than those for ^{239}Pu and ^{241}Am. This trend, also present in the data from the sea water experiments on the mussels is due to a combination of a relatively lower activity in the operculum and a higher activity in the muscle head and foot tissues.

Having exposed winkles to ^{241}Am-labelled food in the form of seaweed (Fucus vesiculosus) for a 22 day uptake period, 71% of the accumulated activity was observed in the shell. Of the soft tissue activity, 74% was contained in the digestive gland, 7% in the pallial complex and 9% in the operculum. After a 28 day loss period, 82% of the whole body activity of ^{241}Am was located in the shell, with 54%, 12% and 7% of the total soft tissue activity being present in the digestive gland, pallial complex and operculum respectively. Tissue activity trends and quotients are presented in Table 3.26.

The α-track distribution patterns of the three tracers were very similar. All displayed (a) high accumulative properties in the operculum, (b) heterogeneous distributions in the digestive gland (Figure 3.12), the site of uptake being in the digestive tubules, (c) hot areas in the pallial complex even after loss periods and (d) enhanced activities at the edges of head and foot tissue sections, the head also exhibiting some enrichment of radiotracers in the buccal region. The digestive gland, not surprisingly, assumes a higher ranking in the tissue activity trends when labelled via food than when labelled via sea water. In fact, only after a 49 day depuration period with ^{237}Np was there a distinct difference between activities of digestive gland and pallial complex tissues. After all three food uptake experiments, a consistent tissue trend can be derived, as follows:

TABLE 3.26

Transuranic activity trends and quotients in winkle tissues relative to the least active tissue after exposure of winkles to radiolabelled food.

^{241}Am

22 day uptake:	Operculum	>	Pallial complex, Digestive gland	>	Foot, Head, Muscle		
	4350		105		76	1	- -
28 day depuration:	Operculum	>	Pallial complex, Digestive gland, Head	>	Foot, Muscle		
	19650		531		419	339	1 -

^{237}Np

13 day uptake:	Operculum	>	Pallial complex, Digestive gland	>	Foot	>	Head, Muscle		
	1310		328		281	5	2.1	1	
22 day depuration:	Operculum	>	Digestive gland, Pallial complex	>	Head, Foot, Muscle				
	357		11		9	1.9	1 -		
49 day depuration:	Operculum	>	Digestive gland	>	Head	>	Pallial complex, Foot	>	Muscle
	3830		121		34	13	9		1

^{239}Pu

13 day uptake:	Operculum	>	Digestive gland, Pallial complex	>	Foot	>	Head	>	Muscle
	4170		262		150	65	6		1
21 day depuration:	Operculum	>	Digestive gland	>	Pallial complex, Head	>	Foot, Muscle		
	439		48		19	12	1 -		
43 day depuration:	Operculum	>	Head	>	Pallial complex, Digestive gland, Foot, Muscle				
	54		4.2		1.8	1.3	1 -		

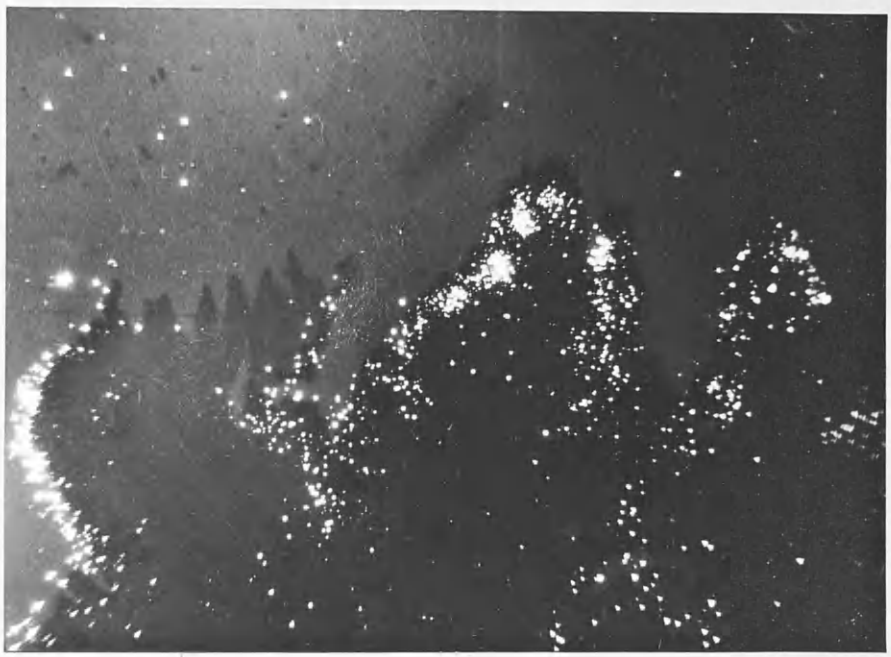


Figure 3.11. Alpha-track distribution present in the winkle's head after a 14 day loss period of ^{239}Pu initially accumulated from labelled sea water. 78 day exposure. 3cm = 500 µm.

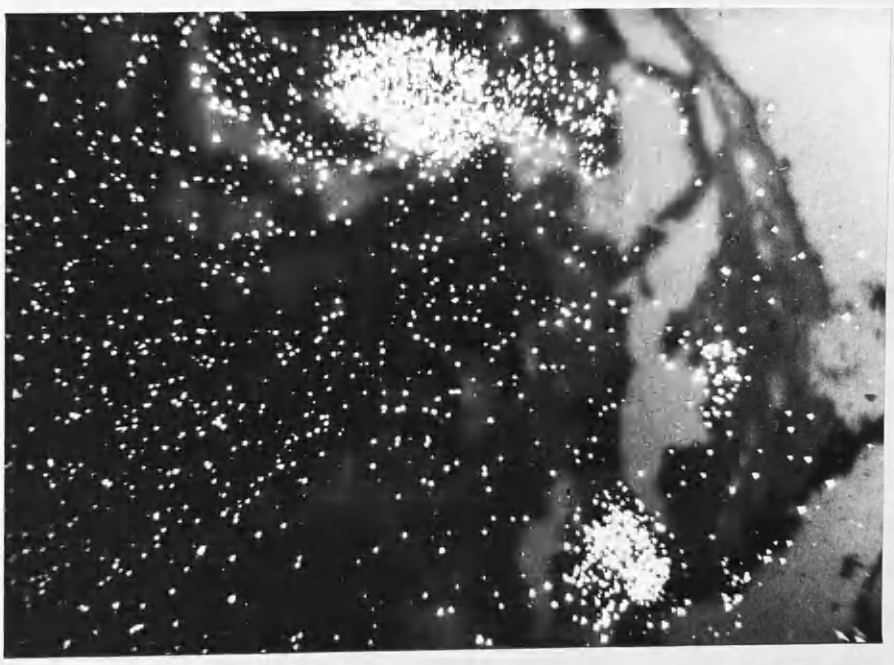


Figure 3.12. Heterogeneous alpha-track distribution present in the winkle's digestive gland after a 13 day uptake period of ^{239}Pu from labelled food. 19 day exposure. 3cm = 500 µm.

Operculum > Pallial complex, Digestive gland > Foot > Head, Muscle. As previously mentioned, there was a notable loss of ^{237}Np from the pallial complex relative to the digestive gland after a 49 day loss period. This loss feature coincides with an absence of hot areas in the tissue. However, the explanation of this behaviour is not apparent. On the other hand, the head, after each loss period for each nuclide, increases its position in the relative order of activity. This may be due to a relative preferential redistribution of the nuclides to the head or more feasibly is due to the greater nuclide retention by the head relative to some soft tissues.

In reviewing the tissue activity trends obtained from both food and water labelling media, many points of interest arise. The operculum demonstrated the highest α-track densities under all experimental conditions. Although the digestive tubules in the digestive gland were the sites of nuclide accumulation, the differences in α-track distributions observed between food and water labelling media suggest that radionuclides are more readily assimilated from food than from sea water. The occurrence of hot areas in the pallial complex was dependent on the inclusion of faecal material in the tissue section, no discrimination being shown between radiotracer sources. Besides these hot areas, strong heterogeneous α-track distributions were consistently observed under all experimental conditions, reflecting the different accumulative properties of the wide range of glands in the pallial complex.

Although the tissue trends for ^{241}Am-labelled food and sea water are not identical, the α-track distributions observed in the digestive gland after feeding support the view that particulate material was present in the ^{241}Am spiked sea water. The α-track densities observed in the digestive gland and pallial complex after feeding were greater than those found in other soft tissues, although, after accumulation

from sea water, the α-activity of the digestive gland was more like those observed in several tissue types of lower activity.

Of the remaining soft tissues, the head and foot demonstrated surface absorption of all the radiotracers, particularly after the labelled food experiments. Such behaviour is principally due to the mucous secretions of the surface squamous epithelium cells. Within the head, the buccal apparatus regularly produced areas of enhanced activity because of its chitinous nature. As in other organisms, the muscle tissue consistently held the lowest activity present in any of the soft tissues studied. This finding indicates the absence of surface absorptive processes in muscle tissue and demonstrates that, on the timescale of these experiments, radionuclide transport from the major uptake sites of the pallial complex and the digestive gland is slow.

Studies of the distribution of transuranic nuclides in the winkle have recently been reported by Swift and Pentreath (1988). As their results have been discussed in Section 3.1.1, they will not be repeated here. However, the α-autoradiographic data for the winkle provide further evidence on plutonium distributions in winkles (Section 3.1.1) and, in particular, demonstrate the role of the pallial complex in radionuclide accumulation a factor not supported by the laboratory observations of Swift and Pentreath (1988).

3.2.2 Environmental studies: Tissue distributions of α-emitters in Ravenglass mussels and winkles.

Levels of radioactivity in environmental samples are many orders of magnitude less than those encountered in the laboratory test organisms. Because of the relatively low sensitivity of the technique, however, samples with high levels of environmental radioactivity are required for successful

autoradiography. The most likely source of organisms of sufficiently high activity is again in the vicinity of the BNF plc nuclear reprocessing plant at Sellafield, Cumbria. As described earlier, mussels and winkles from the Esk estuary at Ravenglass have been exposed to enhanced levels of artificial radioactivity throughout their lifespan. Nevertheless, as levels of radioactivity in Ravenglass mussels and winkles are still relatively low compared to the activities generated in the laboratory experiments, longer exposure times between sample and plastic detector were employed here, namely ~2 years. Hamilton and Clifton (1980) exposed their plastic detector for only 166 days; however, since their study period between 1977 and 1979, levels of α-emitting waste discharged from Sellafield have decreased by a factor of four. The low levels of radioactivity contained in mussel and winkle tissues are illustrated by the finding of activities in several of the tissues at levels very close to background. From Table 3.27, the activity trend for the mussel tissues are compatible with any of the tissue trends determined either from laboratory conditions or from the plutonium distributions discussed in Section 3.1.1. The activity quotients, however, are of a narrow range relative to the ratios encountered in the laboratory, probably a reflection of the magnitude of radioactivity present in each of the systems studied. As both experimental food and water uptake activity trends are reminiscent of the observed environmental trend, no further evidence is provided on the main nuclide source for the mussel. Of note, though is the fact that the more active mussel tissues, the viscera, gill and mantle, are clearly assigned to be so under both laboratory and environmental studies. This observation lends support to the validity of laboratory studies in a complementary role to environmental research.

The winkle tissue activity trend is interesting in that the activities detected in the digestive gland and pallial complex can be grouped with the tissues usually considered to contain the lowest activities within the winkle. The anomalous observation could be a reflection of the specific condition of the winkles

TABLE 3.27

Alpha activity trends and quotients in Ravenglass mussel and winkle tissues relative to the respective least active tissue

Mussel:

Viscera,	Gill,	Mantle >	Mantle edge,	Foot,	Muscle
18	12	11	1	1	-

Winkle:

Operculum	> Digestive gland,	Head,	Pallial complex,	Muscle,	Foot
129	3	2	1	1	-

at the time of processing for α-autoradiographic study, serving as a reminder of the possible nuclide fluctuations that can exist within a collection of winkles from a selected area. Consideration of the Ravenglass winkles' tissue activity trend, without reference to the activity quotients, could lead to the belief (because of the track dominance of the digestive gland over the pallial complex) that the food pathway is the major source of radionuclides to the winkle. The small difference in relative activity between the digestive gland and the pallial complex, as indicated by the activity quotients shows that the food pathway is not clearly dominant.

Homogeneous α-track distributions were consistently exhibited throughout all of the tissues of Ravenglass mussels and winkles except for the winkle's operculum (Figure 3.13). Here, a semblance of a heterogeneous distribution was present, most probably caused by uneven contact between the plastic detector and the whorl on the surface of the operculum. No hot areas were observed in any of the environmental tissues studied. Hamilton and Clifton (1980) found hot spots in the viscera of mussels collected in 1979 but, since then, the decrease in discharged activities has been accompanied by a marked reduction in hot particle release. Although the observations here might imply that hot particles do not now occur in the Ravenglass environment, this should not be assumed to be the case. Rather, we can only conclude that the environmental abundance of particles has declined to a level at which our organisms failed to sample any.

The environmental tissue activity trends discussed here are of course a result of uptake of a cocktail of α-emitters, including natural ^{210}Po and artificial transuranic nuclides. The different nuclide sources of α-tracks within a tissue section cannot readily be resolved using α-autoradiography. Potentially, the track analysis technique used by Fews and Henshaw of Bristol University (Fews and Henshaw, 1984) to resolve α-particle energies using the CR-39 plastic track

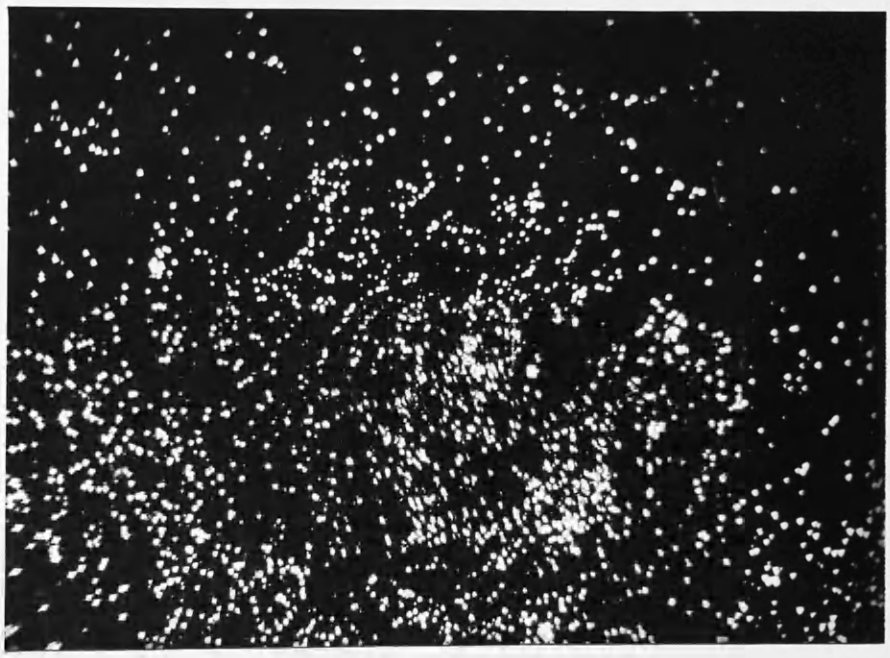


Figure 3.13. Alpha-track distribution present in the winkle's operculum after being exposed to environmental conditions at Ravenglass, Cumbria. 695 day exposure. 3cm = 500 μm.

detector may provide a solution to this problem. This method, however, is slow, laborious and has many associated problems, and, to date, high resolution studies have been performed only on samples which are more ideal than the Ravenglass mussels and winkles studied here.

(It would have been worthwhile to compare the alpha activities of the tissue sections, calculated from the α-track data, with the activity concentrations of plutonium and polonium measured previously and presented in sections 3.1.1 and 3.1.3. As a result of a variety of factors, however, such as defining exact tissue dimensions and the relatively high background of α-tracks generated during long exposure periods, the necessary assumptions and approximations involve too many major uncertainties to make the exercise valid).

3.3 DISCUSSION

The objective of performing laboratory experiments which can be considered as accurately duplicating environmental conditions is a somewhat idealised one. Presently, the application of laboratory-derived data to natural environment conditions is generally accompanied by a degree of caution. At most, laboratory data are used to indicate expected order of magnitude values when extrapolating the process under investigation to natural environmental conditions (Phillips, 1980). This project can contribute to the above discussion on the validity of laboratory data since radionuclide distributions in marine organisms were obtained under both laboratory and field conditions.

In support of laboratory/environmental comparisons, good agreement is obtained here between the laboratory and environmental studies in identification of the tissues and organs of the marine organisms which exhibit efficient bioaccumulation of radionuclides. This agreement, however, is derived from general considerations. If studied in more detail, the environmental α-autoradiographs do not show the winkle's digestive

gland and pallial complex as being tissues of enhanced radioactivity, as was observed in the respective laboratory studies. This difference partly reflects the low activities present in the winkle, these being comparable to background levels encountered in the plastic detector. Despite this, plutonium, polonium and γ -emitter analysis of Ravenglass mussels and winkles provided similar soft tissue activity trends to those obtained in the laboratory. The exception to this is the ranking of the operculum. All α -autoradiographic studies showed the operculum to be the most active tissue in the winkle, whereas in the Ravenglass samples the radioactivity of the operculum is seen to be lower than that in digestive gland and pallial complex. In the Ravenglass samples, the total tissues are analysed for radionuclide content. In the α-autoradiographic studies, the total operculum is still used, whilst only a fraction of the other tissues and organs are actually studied, resulting in the differences described above. Although not conclusively demonstrated here, this project does show that observations from laboratory experiments can successfully be extrapolated to environmental conditions at least at the 'order of magnitude' level mentioned previously.

Elucidation of the major source of transuranic radionuclides to marine benthic organisms is presently unclear. Arguments for nuclide accumulation occurring principally from the soluble phase have been presented by Hamilton and Clifton (1980) (based on the detection of homogeneous α-track distributions in mussel tissues) and Koide et al. (1982) (based on the behaviour of uranium in byssal threads). Alternatively, the importance of the particulate/food phase has been described by Koide et al. (1981) (based on Am/Pu quotients determined in mussel soft tissue), Swift and Pentreath (1988) (based on the influence on total activity of the inclusion of silt winkle tissues) and McKay and Pattenden (in press) (based on comparable nuclide activity quotients being present between suspended particulate matter and winkle tissue). From laboratory experiments, Bjerregaard et al. (1985) noted similarities in the activity distributions in mussels after labelling via both food and water.

The observations made during this project tend to agree with those of Bjerregaard et al. (1985) in that both labelling pathways seem important to radionuclide accumulation. Consideration of the $^{137}Cs/^{239+240}Pu$ quotients in Ravenglass samples could not distinguish any dominant pathway, although the levels of ^{210}Po found in mussel tissues suggested the inclusion of sediment material to account for the ^{210}Po levels encountered. The α-autoradiographic studies could not provide any clear indication of the relative importance of food versus sea water although tissues associated with feeding and digestion were generally of greater activity after feeding experiments. The only tissue which differed markedly in activity depending on the nuclide source was the prawn's gill. Extrapolation of this laboratory observation to environmental prawn samples implies that the major source of radionuclides to the prawn (see Table 3.16) is from the particulate/food phase. Such a preliminary comparison should, however, be approached with caution.

A perspective between artificial and natural α-emitting radiation was maintained by analysing environmental samples for ^{210}Po. Relatively high levels of ^{210}Po were detected in mussel tissues compared to winkle tissues. $^{210}Po/^{239+240}Pu$ quotients of the mussel tissue were ~ 4, whilst respective quotients for winkle tissues were below unity. Prawn $^{210}Po/^{239+240}Pu$ quotients were greater than unity principally due to the very low levels of $^{239+240}Pu$ present. These quotients imply that natural α-emitters provide an important contribution to the total α-activity of the organism especially in the mussel and prawn where the natural contribution dominated the anthropogenic component. Such ^{210}Po activities in mussels, winkles and prawns were shown in this study to be consistent with natural concentrations and are not enhanced in the Ravenglass region.

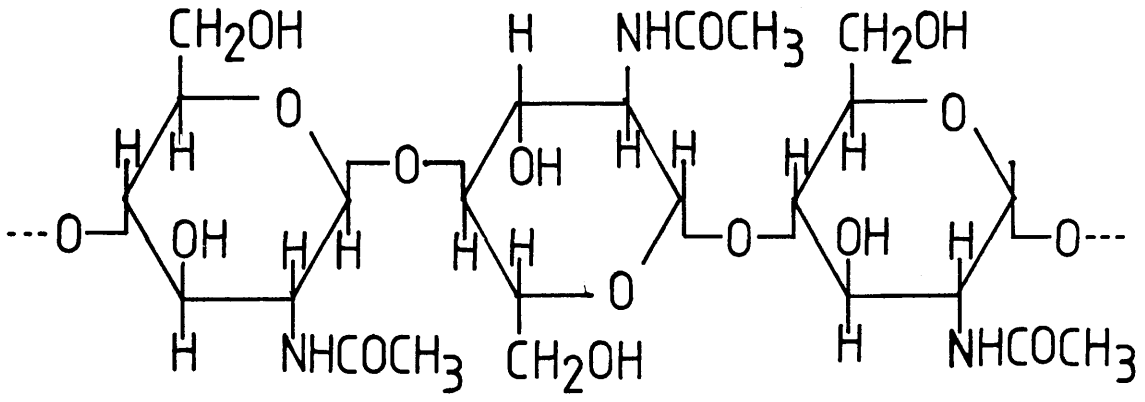
In studying environmental levels of artificial α-activity using α-autoradiographic techniques, the interference from ^{210}Po would have to be overcome. Countermeasures involving storage of the tissue sections over a period of time (when decay of ^{210}Po ($t_{½}$ = 138 days) is significant) prior to exposing the plastic detector to the section would reduce the ^{210}Po contribution to the α-tracks obtained. A period of ~2 years would be necessary to reduce the ^{210}Po α-activity from 50% of the total α-activity to 1-2%. Such delays in sample processing, however, are seldom practicable. The observed levels of α-activity in the environmental samples are presently so low that α-autoradiographs can provide only extremely limited information. It thus appears that a definitive study of environmental transuranic element distributions via α-autoradiography of marine organisms is at present an impractical proposition not only because of potential counter-measures required to reduce intereference by ^{210}Po but also because present day levels of transuranics are generally too low to generate significant track densities on useful timescales.

The process of heavy metal (e.g. transuranic nuclide) accumulation in marine organisms is extremely complex. A large number of variables such as age, weight, size, sex, season, site of sampling, temperature and diet, of the organisms all influence the accumulated inventory in an organism and it is often difficult therefore to interpret such data in terms of uptake mechanisms (Phillips, 1980).

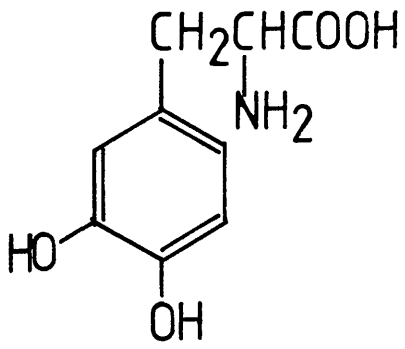
From the laboratory studies here, the principal sites of transuranic accumulation were shown to be in chitinous-type tissues (winkle's operculum and prawn's cardiac fore-gut), digestive glands of the mussel and winkle and the hepatopancreas of the prawn. The chitinous-type tissues are not of pure chitin (a tough but pliable polysaccharide and protein) but possess similar structural and histological properties to it. (Chitin is a polymer of the monomer N-acetylglucosamine (NAG) which contains linkages similar to cellulose (Figure 3.14)).

Figure 3.14. Molecular structures of a) Chitin, b) DOPA and c) DOPA - protein.

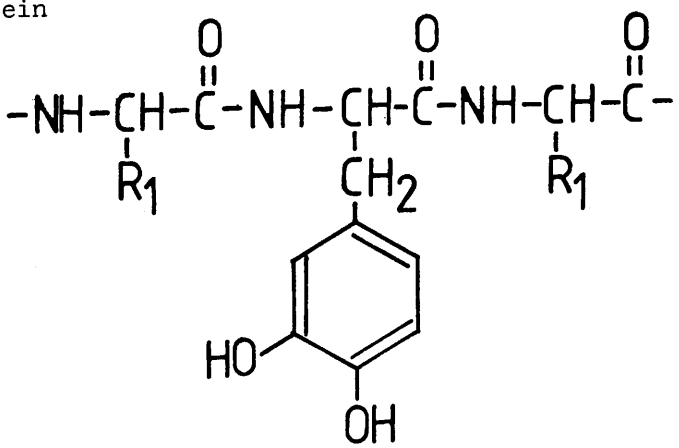
a) Chitin



b) DOPA



c) DOPA - protein



The winkle's operculum (as well as the mussel's periostracum and byssal threads) can be described as a quinone-tanned sclero-protein. Scleroproteins in general, contribute mechanical strength to supporting structures in organisms and can be based on collagen, elastin, fibrin or keratin (Waite, 1983). The accumulation properties of molluscan scleroproteins have been recorded in several instances (e.g. Fowler et al., 1975; Hamilton and Clifton, 1980). Waite (1983) proposed that quinone tanning and sclerotisation of molluscan scleroproteins revolve around the concept of the DOPA protein (3, 4-dihydroxy-phenylalanine) (Figure 3.14). DOPA is an o-diphenol and readily forms quinones and semiquinones by photolysis, autoxidation and enzyme catalysis. The ability of o-diphenols to chelate various metals with their vicinal aromatic hydroxyls may contribute to sclerotisation of molluscan proteins by fostering a passive mineralisation resulting from a selective sequestration of metals from sea water. This uptake mechanism of selective sequestration of metals from any source in the vicinity of the scleroproteins is particularly appealing when attempting to interpret the efficiency of the winkle's operculum and the mussel's periostracum and byssal threads in accumulating transuranics so readily. Although the involvement of o-diphenols is described only in terms of formation of scleroproteins, it appears from the α-autoradiographic studies that sequestration of heavy metals, in this instance of transuranic nuclides, continues quite effectively from both aqueous and solid phases.

To help explain the tissue activity trends obtained in the laboratory studies, an understanding of metal transport in soft tissues is required. Within soft tissues, metals are taken up by a process of endocytosis, i.e. engulfment of the metal by the epithelial cell membrane, which then pinches off to form the membrane-bound vesicle inside the cell (Coombs and George, 1978). After endocytosis, the vesicle migrates to the basal end of the cell and is then excreted by a reverse process of exocytosis into the circulatory fluid. Here, in turn, the metal is reabsorbed by the circulating amoebocytes

(amoeboid haemocytes) by a similar endocytosis for subsequent transfer to tissues and organs for storage and eventual excretion. By this means, organisms can tolerate extremely high concentrations of metals within their tissues by isolating the potentially toxic metal within a membrane and thereby immobilizing and detoxifying it.

Uptake of metal contaminents by mussels studied by Pirie (1982) was reported to occur via the gills, mantle and gut, tissues which have already been identified as major uptake sites in this study. Pirie found that the metals were transported from the gills and gut, via the amoebocytes or as a high molecular weight complex in the cell-free haemolymph, to the kidney (contained in the viscera), the major storage organ for various metal pollutants. In the latter metals are stored in membrane-bound insoluble granules which can occupy ~20% of the cell volume. These metal containing granules are known to occur in the foot, mantle and digestive gland of many molluscs. Grahame (1973) has shown that up to 21% by weight of winkle faeces can be comprised of these granules. Miramand and Guary (1981) demonstrated the association of ^{241}Am with granular deposits in the branchial heart of the octopus. These granules or adenochromes act as natural complexing agents, have a high affinity for iron and are probably engaged in the heavy metal detoxification process. Unfortunately, because of the characteristics and limitations of the α-autoradiographic technique employed in this project, the assignment of α-tracks to intracellular granules could not be performed.

Since the chemistry of ionic species in aquatic, particularly marine, systems is extremely complex, the form of the ions and their ligand complexes in the environment are difficult to define but are critical in controlling the rate of uptake. Simkiss et al. (1982) suggested that various types of ligands may bind metals in mussels and that these ligands may well vary amongst the different tissues. Thus, they indicated that

hydroxyl groups may be operative in the intestinal epithelium and byssal threads, metallothioneins in the gills, urates in the kidneys and phosphates in the digestive gland. It is possible that mucous binding may provide a ligand source for enhancing metal ion uptake (Simkiss and Mason, 1983) in a form which is then transferrable to the alimentary tract. Mucous secretions can be induced by the presence of a variety of salts. As a consequence, binding of metals onto this layer occurs irrespective of the metal's possible involvement in uptake systems. Other work suggests, however, that intracellular transport of metals involves metallothioneins, copper chelatin or low molecular weight compounds as alternative mediating moleculues (Roesidjadi, 1980).

Previous studies on metal accumulation from sea water of food by molluscs (Pentreath, 1973; Young, 1977) suggested that uptake of metals from sea water is normally minimal relative to that from food or particulate sources, concluding that dietary inputs are much more important than those from sea water. Metals used in these studies were Mn, Co, Fe and Zn. Studies using Pb (Schulz-Baldes, 1974), however, concluded the Pb uptake could equally occur from either medium, It is difficult therefore to extrapolate a general consensus view to the present study on radionuclides.

The mechanistic information and observed distributions of transuranic nuclides obtained in this study conform, in general, with the above review of metal uptake in that the soft tissues of particular activity and interest here were the digestive glands, gills and excretory organs of the organisms. Other organs of interest were the pallial complex of the winkle and the cardiac fore-gut of the prawn. The role of mucous secretions in radionuclide accumulation (also observed by Germain et al., 1987) is evident in the pallial complex, a tissue of high glandular activity and subsequently one of the more radioactive soft tissues of the winkle. In possessing a chitinous lining, the cardiac fore-gut displays transuranic accumulative powers similar to other chitin-related tissues (e.g. operculum, byssal threads). Tissues exhibiting lower levels of radionuclide accumulation in the mussel and winkle

can be linked with the presence of mucous secretion (head, food) or chitinous material (buccal mass).

The environmental concentrations of radioactivity found in the seafood samples here can be used to assess the radiological implications to man, in particular, the internal radiation exposure via their ingestion. Only the nuclide contents of the edible parts of the organisms have to be considered. In the mussel, these are the viscera, gill, mantle, mantle edge, foot and muscle; in the winkle, pallial complex, digestive gland, head, foot and muscle and, in the prawn, the abdomen muscle and hepatopancreas. It is of interest that some of the previously discussed 'active' tissues (e.g. mussel's byssal threads and periostracum; winkle's operculum and prawn's cardiac fore-gut) are excluded by exercising some simple and obvious procedures. Prior to ingestion of the edible tissues the marine organisms are cooked (usually boiled) for some minutes. Although the extent of nuclide loss from the tissue during cooking has not been recorded in the scientific literature, the assumption of some nuclide loss occurring at this stage is not unreasonable. Once ingested, a fraction of the transuranic radionuclides is absorbed from the gastro-intestinal tract into the bloodstream. For radiological protection purposes, this fraction is expressed as a gut transfer factor. Presently the value used in public exposure rate calculations for transuranic nuclides is 1×10^{-3} (NRPB, 1987). This value, however, is frequently reviewed to ensure the validity of such calculations. Of the transuranic activity entering the bloodstream, 80% of this activity is deposited in the liver and skeleton where retention half-times of 20 years and 50 years respectively are experienced (NRPB, 1987). From these considerations, it is evident that, of the activities of environmental radioactivity expressed in Section 3.1, only a small fraction will be assimilated by the body.

The combination of radionuclide content of edible tissues, nuclide loss during cooking and nuclide metabolic behaviour are all examined before critical group dosages (see Table 1.11) can be calculated. To interpret the observed nuclide activities in the Ravenglass mussels and winkles in terms of exposure levels due to ingestion, the relevant Annual Limits on Intake (ALI) for the nuclide(s) of interest must be considered. In 1979, ICRP produced ALI data on a wide range of radionuclides relating rates of ingestion (and inhalation) with radiation exposure levels (ICRP, 1979). This information enables straightforward calculations to be made between nuclide activities present in seafood and the expected doses received through seafood ingestion. Of particular interest in this project are the anthropogenic nuclides of ^{238}Pu and $^{239+240}Pu$ and the natural α-emitter ^{210}Po. Nuclide activities considered are those determined in total soft parts (Section 3.1) of the organism, activities having been converted to wet weight using the appropriate wet/dry ratio of the organism. The ALI's provided by ICRP (ICRP, 1979) refer to intake by radiation workers and hence are relevant to the old $50mSvy^{-1}$ dose limit for workers. In this study, appropriate modifications have to be made to convert the ALI's for application to the critical group subsidiary dose limit of $5mSvy^{-1}$. This entails reducing the quoted ICRP ALI values by a factor of 10. Calculated doses received by the critical group, using the mollusc consumption data of Hunt (1985, 1986) are given in Table 3.28. (Similar considerations for member of the public (principal dose limit of $1mSvy^{-1}$) would affect Table 3.28 by reducing all ALI data by a factor of 5 and by increasing the neighbouring % dose rate columns also by a factor of 5. All other data would remain unaltered). The assumed consumption rates of molluscs are, in effect, those of winkles. The consumption rates of mussels, however, have been assumed to equal the mollusc consumption rate for that year to allow comparisons.

TABLE 3.28

Exposure rates to critical group from ingestion of Ravenglass mussels (1984) and winkles (1985).

		$Bqkg^{-1}$ (wet)	Critical Group ALI (Bq)	Dose (as % of $5mSvy^{-1}$)	x5	Dose (mSv)	x5
Mussel	^{210}Po	51.7	1×10^4	3.0	-	0.15	-
	^{238}Pu	3.5	3×10^4	0.07	0.35	0.003	0.017
	$^{239+240}Pu$	13.1	2×10^4	0.38	1.14	0.02	0.057
Winkle	^{210}Po	11.1	1×10^4	1.05	-	0.05	-
	^{238}Pu	13.6	3×10^4	0.43	2.1	0.02	0.10
	$^{239+240}Pu$	56.8	2×10^4	2.70	13.5	0.13	0.67

Radiation exposures from naturally occurring radionuclides (or medical procedures) are not subject to the ICRP system of dose limitation. The ^{210}Po data in Table 3.28, however, has been included to provide a perspective between the radiological implications of natural and artificial radiation. Although in Table 3.28, all of the nuclide exposure levels are comfortably below the subsidiary dose limit of $5mSvy^{-1}$, the ^{210}Po contribution to the exposure rate is ~3 times greater than the $^{239+240}Pu$ contribution (after the plutonium gut transfer enhancement factor has been applied). In the winkles, however, plutonium activities are greater than ^{210}Po activities (x5), with the effect, especially after applying the plutonium gut transfer enhancement factor, that plutonium dominates the delivery of dose. It is of note that the doses calculated are all within the principal dose limit for members of the public ($1mSvy^{-1}$).

Modifications to eating habits and gut transfer factors etc. can significantly modify the radiation dose estimates for the critical group. The decrease in these doses in Cumbria since 1981 (Hunt, 1983-87) however, is a direct result of the decrease in marine discharges of radionuclides from the Sellafield plant (Figure 1.3). As the present policy at Sellafield is to reduce discharges even further critical group exposure rates can be expected to decrease further from the most recent reported levels (1987) of $0.3-0.4mSvy^{-1}$. The principal dose limit to the UK public is likely to be further reduced to $0.5mSvy^{-1}$ (NRPB, 1987).

3.4 OVERVIEW

The environmental section of this study (Section 3.1) shows that natural and artificial radionuclides are readily detectable in Ravenglass mussels and winkles, while artificial nuclide levels in Whitehaven-landed prawns are close to detection limits. Nuclide distributions exhibited by the mussel revealed that the highest levels of plutonium isotopes and gamma-emitters were contained in the periostracum, the byssal threads and,

of the soft tissues, the viscera. Highest ^{210}Po concentrations were found in the viscera (periostracum and byssal threads were not analysed).

In the winkle, the operculum is the tissue most analogous to that of the mussel's periostracum or byssal threads. Its role in radionuclide accumulation under environmental conditions is, however, secondary to the soft tissues of the digestive gland and pallial complex. Whereas plutonium concentrations are similar in mussels and winkles, the latter accumulate gamma-emitters more effectively and mussels accumulate ^{210}Po more readily. The ^{210}Po inventories of the organism's immediate environment of food, water and sediment can explain the ^{210}Po concentrations observed in the total soft parts of the organism. Gamma-emitter accumulations, however, are not so easily accounted for.

The CFs of ^{137}Cs, ^{210}Po and $^{239+240}Pu$ in the total soft tissues of the species studied here are consistent with the respective CF values recommended by IAEA (IAEA, 1985). In mussel tissues, ^{210}Po CF values were $\sim 10^4$, the viscera exhibiting the highest CF encountered in this study (58400), $^{239+240}Pu$ CFs were $\sim 10^3$ although the scleroprotein tissues were of a similar magnitude to the ^{210}Po CFs and ^{137}Cs CFs were $\sim 10^1$. The winkle exhibited similar $^{239+240}Pu$ CF values to the mussel although the pallial complex rather than the operculum accumulated plutonium most effectively. In general, ^{137}Cs CF values for winkle tissues were marginally greater than those for the mussel. ^{210}Po CF data, however, were ten times lower in the winkle, with the exception of the digestive gland. In the prawn, ^{210}Po CF data ranged from 10^2 to 10^4, tissues associated directly with feeding and digestion (cardiac fore-gut and hepatopancreas) showing the higher CF values.

Radionuclide activity quotients in the tissues of the marine organisms could not clarify the major transport medium responsible for nuclide uptake. This failure, however, was based on the assumption that the ^{137}Cs transfer factor is similar to that for $^{239+240}Pu$, an assumption open to verification.

The radiolabelling experiments demonstrated that mussels, winkles and Dublin Bay prawns all readily accumulate ^{237}Np, ^{239}Pu and ^{241}Am from both food and sea water media. The shell/periostracum of the mussel and winkle and the carapace of the prawn accumulate 80-90% of the radionuclide inventory. In the mussel's soft tissues, the site of most efficient nuclide accumulation is in the digestive tubules of the viscera. No definitive indication of the dominant tracer source, however, was provided by these mussel experiments.

The Dublin Bay prawn, on the other hand, did provide a tissue exhibiting a definite preference between food and water - namely the gill, which accumulated ^{239}Pu and ^{241}Am more effectively from sea water relative to food. As for the mussel, the prawn's digestive organs dominate those tissues containing enhanced radionuclide activities - the cardiac fore-gut, the hepatopancreas and the hind-gut. One unusual observation was that the prawn heart accumulates ^{239}Pu to a much higher level than ^{237}Np or ^{241}Am, an observation probably linked with detoxification processes.

In the winkle, the soft tissues of greatest bioaccumulative ability and interest were the digestive gland and the pallial complex, although the operculum showed the highest α-activities of all the tissues studied in these experiments. As in the mussel, the digestive tubules were the site of uptake in the winkle's digestive gland. Some surface adsorption due to mucous secretions in the foot were observed, activity in the head being associated with similar epidermal adsorption (especially from labelled food) or with the chitinous buccal apparatus.

The environmental α-autoradiographs showed that the tissue activity trends were in general agreement with those from the laboratory studies, lending some support to the validity and value of laboratory tank experiments. No hot areas, however, were observed in the environmental samples.

The uptake of transuranic elements by marine organisms is influenced greatly by the presence of scleroproteins, chitinous-type tissues and mucous secretions (mucopolysaccharide based). Once adsorbed in the soft tissues, principally in the digestive gland, the metal is transported through the organism via circulatory fluids to its tissues and glands for storage and secretion. In order to eliminate or reduce toxic effects, the metal is stored in membrane-bound vesicles (granules) before excretion. Absorption of the metal from either food or water source-term depends on its speciation and on its compatibility with the available binding ligands in the mucous sheets or digestive secretions.

Radiological assessment of the observed radionuclide levels in the Ravenglass mussels and winkles shows that the critical group receives only a few per cent of the ICRP-recommended dose limit through ingestion of such seafoods. The observed natural ^{210}Po levels in these organisms provide a realistic perspective to the radiation exposure levels received from natural and artificial sources in ingestion of these marine organisms.

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APPENDIX A : PROCEDURE USED IN CALCULATING ^{210}Po and ^{210}Pb CONCENTRATIONS IN MARINE ORGANISMS

APPENDIX A

PROCEDURE USED IN CALCULATING ^{210}Po and ^{210}Pb CONCENTRATIONS IN MARINE ORGANISMS

(after Heyraud, pers. comm.)

Details of the appropriate laboratory techniques are described in section 2.4.2.

Initially we have,

Po concentration at time of collection ($t_o = 0$) = $(C_{Po})_o$ and
Pb concentration at time of collection ($t_o = 0$) = $(C_{Pb})_o$.

Let time for first plating be t_1. Then,

1. Po concentration at t_1, $(C_{Po})_1 = (C_{Po})_o \exp(-\lambda_{Po} t_1) + (C_{Pb})_o (1-\exp(-\lambda_{Po} t_1))$

and 2. Pb concentration at t_1, $(C_{Pb})_1 = (C_{Pb})_o \exp(-\lambda_{Pb} t_1)$.

Assume that at time of first plating all Po is removed. Let time of counting for for first plating be t_2. Then,

3. Po concentration on disc at t_2, $(C_{Po})_2 = (C_{Po})_1 \exp(-\lambda_{Po}(t_2-t_1))$.

Let time of second plating be t_3. Then,

4. Po concentration at t_3, $(C_{Po})_3 = (C_{Pb})_1 (1-\exp(-\lambda_{Po}(t_3-t_1)))$.

Assume that at time of second plating all Po is removed.
Let time of counting second plating be t_4. Then,

5. Po concentration on disc at t_4, $(C_{Po})_4 = (C_{Po})_3 \exp(-\lambda_{Po}(t_4-t_3))$, hence,

6. $$(C_{Po})_o = \frac{(C_{Po})_1 - (C_{Pb})_o(1-\exp(-\lambda_{Po}t_1))}{\exp(-\lambda_{Po}t_1)}$$ (from 1)

7. $$= \frac{(C_{Po})_1 - (C_{Pb})_1\left(\frac{1-\exp(-\lambda_{Po}t_1)}{\exp(-\lambda_{Pb}t_1)}\right)}{\exp(-\lambda_{Po}t_1)}$$ (from 2 and 6)

8. $$= \frac{\frac{(C_{Po})_2}{\exp(-\lambda_{Po}(t_2-t_1))} - \frac{(C_{Po})_3(1-\exp(-\lambda_{Po}t_1))}{(1-\exp(-\lambda_{Po}(t_3-t_1)))(\exp(-\lambda_{Pb}t_1))}}{\exp(-\lambda_{Po}t_1)}$$ (from 3,4 and 7)

9. $$= \frac{\frac{(C_{Po})_2}{\exp(-\lambda_{Po}(t_2-t_1))} - \frac{(C_{Po})_4(1-\exp(-\lambda_{Po}t_1))}{(1-\exp(-\lambda_{Po}(t_3-t_1)))(\exp(-\lambda_{Po}(t_4-t_3)))(\exp(-\lambda_{Pb}t_1))}}{\exp(-\lambda_{Po}t_1)}$$ (from 5 and 8)

The Po concentration at the time of collection is now expressed in terms of the Po concentrations of the two plated discs.

Similarly for Pb,

10. $$(C_{Pb})_o = \frac{(C_{Pb})_1}{\exp(-\lambda_{Pb}t_1)}$$ (from 2)

11. $$= \frac{(C_{Po})_3}{\exp(-\lambda_{Pb}t_1)\ (1-\exp(-\lambda_{Po}(t_3-t_1)))}$$ (from 4 and 10)

12. $$= \frac{(C_{Po})_4}{\exp(-\lambda_{Pb}t_1)(1-\exp(-\lambda_{Po}(t_3-t_1)))(\exp(-\lambda_{Po}(t_4-t_3))}$$

Notice that the expression for $(C_{Pb})_o$ is the same as the second term in the numerator of the expression for $(C_{Po})_o$ apart from the factor $(1-\exp(-\lambda_{Po}t_1))$.

To ease Po and Pb calculations a computer program, incorporating expressions 1 to 12, has been written, details of which are given in Appendix B.

APPENDIX B : BASIC COMPUTER PROGRAMME FOR ^{210}Po and ^{210}Pb CALCULATIONS

APPENDIX B

BASIC COMPUTER PROGRAMME FOR ^{210}Po AND ^{210}Pb CALCULATIONS

```
     C     PO/PB-210 PROGRAM
0001       BYTE AS(20)
0002 20    TYPE 5000
0003 5000  FORMAT(1H1 ,1X,'PROGRAMME TO CALCULATE 210-PO AND 210-PB
          X CONCENTRATION IN SAMPLES WHICH HAVE BEEN DEPOSITED
          X TWICE ON SILVER DISCS')
0004 55    TYPE 5020
0005 5020  FORMAT(1H ,1X,'WEIGHT OF SAMPLE IN GRAMS=    ',$)
0006       ACCEPT *,W1
0007       TYPE 5030
0008 5030  FORMAT(1H ,1X,'NUMBER OF DAYS TO FIRST PLATING=    ',$)
           ACCEPT *,T1
0010       Z=0
0011       TYPE 5040
0012 5040  FORMAT(1H ,1X,'NUMBER OF DAYS TO FIRST COUNTING=    ',$)
0013       ACCEPT *,T2
0014       TYPE 5050
0015 5050  FORMAT(1H ,1X,'ACTIVITY OF SPIKE USED-IN DPM/ML=    ',$)
0016       ACCEPT *,PB
0017       TYPE 5056
0018 5056  FORMAT(1H ,1X,'VOLUME OF SPIKE ADDED-IN ML=    ',$)
0019       ACCEPT *,PC
0020       TYPE 5060
0021 5060  FORMAT(1H ,1X,'NUMBER OF DAYS SPIKE DECAYED TO COUNTING=
          X    ',$)
0022       ACCEPT *,T5
0023       TYPE 5070
0024 5070  FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION A=    ',$)
0025       ACCEPT *,A
0026       TYPE 5080
0027 5080  FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION B=    ',$)
0028       ACCEPT *,B
0029       TYPE 5090
0030 5090  FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION C=    ',$)
0031       ACCEPT *,C
0032       TYPE 5100
0033 5100  FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION D=    ',$)
0034       ACCEPT *,D
0035       TYPE 5110
0036 5110  FORMAT(1H ,1X,'COUNTING TIME IN SECONDS=    ',$)
0037       ACCEPT *,T6
0038       TYPE 5120
0039 5120  FORMAT(1H ,1X,'HAS THE SAMPLE BEEN COUNTED TWICE? 1 OR 0 ',$)
0040       ACCEPT *,I
0041       GOTO 83
0042 50    Z=1
0043       TYPE 5130
0044 5130  FORMAT(1H ,1X,'SECOND COUNTING DATA )
0045       TYPE 5140
0046 5140  FORMAT(1H ,1X,'NUMBER OF DAYS TO SECOND PLATING=    ',$)
```

```
0047        ACCEPT *,T3
0048        TYPE 5150
0049 5150   FORMAT(1H ,1X,'NUMBER OF DAYS TO SECOND COUNTING=    ',$)
0050        ACCEPT *,T4
0051        TYPE 5160
0052 5160   FORMAT(1H ,1X,'ACTIVITY OF SPIKE USED-IN DPM/ML=    ',$)
0053        ACCEPT *,PB
0054        TYPE 5165
0055 5165   FORMAT(1H ,1X,'VOLUME OF SPIKE ADDED-IN ML=    ',$)
0056        ACCEPT *,PC
0057        TYPE 5170
0058 5170   FORMAT(1H ,1X,'NUMBER OF DAYS SPIKE DECAYED TO COUNTING=
           X  ',$)
0059        ACCEPT *,T5
0060        TYPE 5180
0061 5180   FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION A=    ',$)
0062        ACCEPT *,A
0063        TYPE 5190
0064 5190   FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION B=    ',$)
0065        ACCEPT *,B
0066        TYPE 5200
0067 5200   FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION C=    ',$)
0068        ACCEPT *,C
0069        TYPE 5210
0070 5210   FORMAT(1H ,1X,'NUMBER OF COUNTS IN REGION D=    ',$)
0071        ACCEPT *,D
0072        TYPE 5220
0073 5220   FORMAT(1H ,1X,'COUNTING TIME IN SECONDS=    ',$)
0074        ACCEPT *,T6
0075 83     E=(A*C)/B
0076        F=(A*D)/B
0077        E1=0
0078        F1=0
0079 95     E1=(A*(C-F))/(B-E)
0080        F1=(A*D)/(B-C)
0081        IF((E1-E).LT.0.1.AND.(F1-F).LT.0.1) GOTO 87
0083 88     E=E1
0084        F=F1
0085        GOTO 95
0086 87     S3=0.693147/(24*60*365.25*2.8976)
0087        PS=INT(B-E1-F1+D+C+0.5)
0088        PO=INT(A+E1+F1+0.5)
0089        WRITE(5,5230)PS,PO
0090 5230   FORMAT(1H ,1X,T10,2F10.3)
0091        ES=SQRT(PS)/T6
0092        EO=((SQRT(PO)/T6)*60)/2.22
0093        PS=(PS/T6)*60
0094        PS=PS*EXP(S3*T5*24*60)
0095        PA=PB*PC
0096        G=PS/PA
0097        WRITE(5,5235)G*100
0098 5235   FORMAT(1H ,1X,'OVERALL EFF IS    ',F9.5)
0099        TYPE 5236
0100 5236   FORMAT(1H ,1X,'DETECTOR EFF IS-IN DECIMAL=    ',$)
```

```
0101        ACCEPT *,DE
0102        PE=(G/DE)*100
0103        WRITE(5,5237)PE
0104        FORMAT(1H ,1X,'PLATING EFF IS',F9.5,'%')
0105        PO=((PO/T6)*60)/(G*W1*2.22)
0106        EO=(EO/W1)/G
0107        WRITE(5,5240)PO,EO
0108 5240  FORMAT(1H ,1X,'CONCENTRATION OF PO-210 ON DATE OF COUNTING
           X IS',F9.5,'PCI/G +/-',F9.5)
0109        WRITE(5,5250)PO*37,EO*37
0110 5250  FORMAT(1H ,1X,T10,F9.5,'+/-',F9.5,'BQ/KG')
0111        IF(I.EQ.0.AND.Z.EQ.0) GOTO 55
0113 60    IF(Z.EQ.0) GOTO 70
0115        GOTO 75
0116 70    C1=PO
0117        C3=EO
0118        GOTO 50
0119 75    C2=PO
0120        C4=EO
0121        SO=0.0052
0122        S1=0.00085
0123        A=EXP(-S1*T1)*(1-EXP(-SO*(T3-T1)))*(EXP(-SO*(T4-T3)))
0124        B=C2*(1-EXP(-SO*T1))
0125        C=EXP(-SO*T1)
0126        D=C1/EXP(-SO*(T2-T1))
0127        PO=(D-(B/A))/C
0128        P1=C2/A
0129        P3=C4/A
0130        P4=(((EXP(SO*T1)/EXP(-SO*(T2-T1)))*C3)**2)
0131        P4=SQRT(P4+((((1-(EXP(-SO*T1)))*(EXP(SO*T1)))/A)*C4)**2)
0132        WRITE(5,5255)A,B,C,D
0133 5255  FORMAT(1H ,1X,'A=',F9.5,'B=',F9.5,'C=',F9.5,'D=',F9.5)
0134        TYPE 5280
0135 5280  FORMAT(1H ,1X,'==================================')
0136        WRITE(5,5270)P1,P3
0137 5270  FORMAT(1H ,1X,'PB=',F9.5,'+/- ',F9.5,'PCI/G')
0138        WRITE (5,5275)P1*37,P3*37
0139 5275  FORMAT(1H ,1X,T10,F9.5,'+/-',F9.5,'BQ/KG')
0140        WRITE(5,5290)PO,P4
0141 5290  FORMAT(1H ,1X,'PO=',F9.5,'+/- ',F9.5,'PCI/G')
0142        WRITE(5,5295)PO*37,P4*37
0143 5295  FORMAT(1H ,1X,T10,F9.5,'+/- ',F9.5,'BQ/KG')
0144        P5=PO/P1
0145        P6=P5*SQRT((P4/PO)**2+(P3/P1)**2)
0146        WRITE(5,5300)P5,P6
0147 5300  FORMAT(1H ,1X,'RATIO PO/PB=',F9.5,'+/-',F9.5)
0148        TYPE 5310
0149 5310  FORMAT(1H ,1X,'DO YOU WANT TO CALCULATE ANOTHER SAMPLE?
           XANSWER 1/0   ',$)
0150        ACCEPT *,J
0151        IF(J.EQ.1) GOTO 20
0153 5500  STOP
0154        END
```