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SEDIMENTATION STUDIES RELEVANT TO LOW-LEVEL RADIOACTIVE EFFLUENT DISPERSAL IN THE IRISH SEA

T J SMITH, W R PARKER and R KIRBY

Part I
Radionuclides in Marine Sediments

Report No 110

1980

NATURAL ENVIRONMENT RESEARCH COUNCIL

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INSTITUTE OF OCEANOGRAPHIC SCIENCES

Wormley, Godalming,
Surrey, GU8 5UB.
(0428 - 79 - 4141)

(Director: Dr. A.S. Laughton)

Bidston Observatory,
Birkenhead,
Merseyside, L43 7RA.
(051 - 653 - 8633)

(Assistant Director: Dr. D.E. Cartwright)

Crossway,
Taunton,
Somerset, TA1 2DW.
(0823 - 86211)

(Assistant Director: M.J. Tucker)

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Department of the Environment

Institute of Oceanographic Sciences
Crossway
Taunton
Somerset
TA1 2DW

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SUMMARY

Certain elements, particularly plutonium and americium, small quantities of which are routinely discharged into the marine environment from nuclear fuel reprocessing plants rapidly became associated with the sea bed sediments. Hence the fate of these radionuclides is intricately linked to the fate of the local sea bed sediments.

This report examines the discharge of various radionuclides into the Irish Sea with particular reference to the interaction between the radionuclides and the sediments. A review of the relevant literature has revealed a variety of possible interaction mechanisms which are sensitive to many environmental parameters. It is concluded that the particular mechanism and any potential for remobilisation are dependent on the unique conditions existing at a particular site. The precise nature of the interaction in the Irish Sea and the remobilisation potential of the various radionuclides are poorly known.

Measurements of radionuclide distributions have previously been used to infer rates of sedimentary processes. The assumptions underlying these interpretations are considered and it is shown that a large amount of information on the sedimentological regime of a given area is required before confident interpretations of radionuclide distributions can be made. This background material is only partially available for the Irish Sea.

It is concluded that considerably more information than is presently available concerning:

(a) the sedimentological regime of the Irish Sea
(b) the interaction between radionuclides and marine sediments in the marine environment

is required before any estimate of the long term fate of the radionuclides can be made.

CHAPTER 1

INTRODUCTION

Low-level radioactive effluent is being discharged under authorisation into the marine environment from a number of nuclear facilities throughout the world. Considerable worldwide concern has been expressed about the public health consequences of radioactive discharges in view of the high radiotoxicity of many of the radionuclides they contain. More recently, attention has been focussed on the transuranic elements because of their very long half lives and consequent retention in the enviornment for many thousands of years.

In the UK, the majority of the radioactive waste dischargedinto the environment comes from the nuclear fuel reprocessing plant at Windscale in Cumbria. Research by the Fisheries Radiobiological Laboratory (FRL) of the Ministry of Agriculture, Fisheries and Food (MAFF) has established that some of those radionuclides of long-term significance become associated with the indigenous fine sediment population in the vicinity of the discharge point within a few days of being released. For the discharges from Windscale into the Irish Sea, a preliminary budget for plutonium has revealed that the majority of this radionuclide is being retained in the local seabed sediments which are thus acting as a reservoir and potential future source of activity, (Hetherington, 1976a). Therefore, it is evident that the indigenous fine sediment population greatly influences the fate and transport pathways of some radionuclides, although the ultimate fate of the radionuclides may not necessarily be that of the fine sediment.

In view of the potential importance of fine sediment in determining the fate of certain radionuclides in the marine environment, a detailed study of the sedimentological regime in the vicinity of any discharge point is desirable. This report describes the preliminary finding of an investigation of the sedimentology and fine sediment dynamics of the north-eastern Irish Sea with reference to the dispersal of the low-level radioactive effluent discharged from the Windscale nuclear fuel reprocessing plant (Figure 1).

This report has three main aims:

(i) to review the existing literature on the sedimentology of the north-east Irish Sea and hence to define both the short term and the long term areas of research required to develop an understanding of the fine sediment dynamics in the area,

(ii) to review the existing literature on the present distribution of radionuclides in the Irish Sea and on the interaction between radionuclides and sediments. This will enable the physical and chemical parameters important in governing this interaction to be identified and hence provide initial information on the potential importance of the various sedimentary processes on the dispersal of radionuclides,

(iii) to assess the use of radioactive discharges as sediment tracers and to assess the potential of the observed distributions of radionuclides in sea bed sediments as a means of dating sediment layers in sea bed core samples. This assessment will be mainly based on the reviews of the environmental behaviour of radionuclides.

The interaction between radionuclides and soils and sediments is discussed in Chapter 2 which reviews this interaction in terms of the mechanisms and factors controlling the retention and release of radionuclides in sediments. A review of the observed environmental behaviour of radionuclides, with special reference to the Irish Sea is considered.

Chapter 3 reviews the sedimentology of the Irish Sea with particular emphasis on the north-east basin. The surface sediment distribution in the vicinity of the Windscale outfall is also examined in detail. Chapter 4 describes the history of low-level discharges into the Irish Sea; the important elements in the discharge are discussed and the major contributors to the alpha, beta and gamma activities are identified. Chapter 5 reviews the present distribution of the important radionuclides in both the seawater and sediments of the Irish Sea. Particular attention is paid to the transuranic elements and a comparison of the distribution of these and other more abundant radionuclides is made.

Chapter 6 examines the feasibility of using existing radioactive discharges as tracers for sedimentological studies and also considers the interpretation of the vertical distribution of radionuclide concentrations in sea bed sediments as a means of establishing sediment chronology. Finally, Chapter 7 concludes the report by defining those areas of sedimentological research which are required to provide a better understanding of the dispersal of low-level radioactive effluent.

The context of this study is the Irish Sea and since it is impossible to divorce the evaluation of data from its site, many of the results and conclusions will be only applicable to the Irish Sea. However, it is anticipated that some of the remarks will be generally applicable to studies of the dispersal of low-level radioactive elements in the marine environment.

CHAPTER 2

RADIONUCLIDES IN SOILS AND SEDIMENT

2.1 Introduction

The ability of sediments to retain radionuclides is usually described in terms of a partition coefficient, Kd, defined as the ratio of the activity in the sediment sample to the activity in the adjacent seawater. Values of Kd are known for all the radionuclides of environmental significance. However, the mechanisms by which radionuclides are retained by soils and sediments is not fully understood under the variety of environmental conditions encountered.

The chemistry of the sediments and the overlying waters is complex and biological factors play an important role both directly and also indirectly by such processes as bioturbation. Consequently, the chemical state of the sediment and the adjacent pore water can vary rapidly in the vertical and more slowly in the horizontal while the chemical properties of the overlying water can change over time scales between a tidal cycle, as in estuaries, and several years.

It is difficult for the non-chemist to understand the details of the interactions in this complex system but an attempt must be made to understand the broad picture if the role played by sediment dynamics is to be understood and sedimentological evidence interpreted. This chapter is an attempt to achieve this.

Many possible relevant parameters have been identified from the considerable amount of data which exists on the mechanisms and factors controlling the sorption* of principally fallout radionuclides on soils and marine sediments. In general, these data indicate that, for marine sediments, a number of sorption mechanisms are in operation. These can include direct retention by surface adsorptionor ion exchange and indirect retention in the thin films of water and hydrated oxide or humus on particle surfaces. In particular, the adsorption of the transuranic elements is strongly associated with manganese or iron oxide films on the sediment particles (Means et al, 1978; Muller, 1978).

In addition, there appear to be four over-riding parameters which influence the uptake and retention of radionuclides by sediments:

(i) the salinity of the water phase;
(ii) the state of acidity: the pH;
(iii) the oxidising power of the system, described by the redox potential, Eh;
(iv) the ionic sorption capacity of the solid particles.

However, other factors, including the concentration of competing ions, chelating agents and other chemicals which could form complexes with the radionuclides have also been identifiied as being potentially important. The role of organic material in radionuclide retention is uncertain although many radionuclides, particularly plutonium can form strong complexes with organic matter (Bondietti et al, 1976). However, organic material appears to be far less important than clay minerals in the retention of the non-transuranic elements. Finally, some of the transuranic elements, particularly plutonium, have a number of oxidation states which can coexist in the environment and which exhibit different chemical properties. Consequently, plutonium for example, distributes itself between the water and particulate phases in a manner dependent on the mixture of the oxidation states which itself is governed by the local chemistry of the sediments.

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* The term sorption is used to denote any reaction between the sediments and a radioactive solution whereby activity is transferred to the sediment and thus includes both adsorption and absorption reactions.

A review of the literature on the interaction of radionuclides with solids and sediments published prior to 1980 is presented in Appendix A. Further results were presented at the IAEA Symposium on the Impacts of Radionuclide Releases into the Marine Environment, Vienna, October 1980, the proceedings of which are currently in press and should be consulted for up to date details on this topic.

2.2 The Environmental Behaviour of Radionuclides

Much of the data on the retention and migration of radionuclides in soils and sediments have been obtained using techniques which may not simulate conditions found in the field. Caution is required when using these data as laboratory studies may not allow sufficient time for radionuclides to reach equilibrium with the soil or sediment and extraction procedures usually rely on leaching with a strong extractant. In the field, the extractant is usually dilute and weak while radionuclides can be available for sorption over periods of months or even years. Consequently, verification of laboratory results by field observations is necessary,

One of the major environmental questions concerns the remobilisation and migration of the radionuclides after their initial incorportion in the soil or sediments. Edgington et al (1976b) compared measurements of the plutonium distribution due to atmospheric fallout in Great Lakes sediments with the results of a least squares fit of a three parameter model (sedimentation rate, mixing scale and surface flux) to the measured profiles. A discrepancy in the measured and fitted plutonium profiles in the near surface region of the sediment cores was interpreted as evidence for the significant resuspension of previously sedimented material. Thus particle associated activity may migrate with the suspended load. However, it was noted that, as Lake Michigan sediments remain aerobic, little plutonium was available for chemical remobilisation from the hydrous oxide or organic phases of this resuspended material (Edgington et al, 1976a). Measurements between 1964 and 1973 of the vertical distribution of fallout plutonium in North Atlantic shelf sediments were also interpreted as showing subsequent upwards movement of activity previously incorporated into the sediments by biological activity (Bowen et al, 1976). This interpretation was primarily based on the elimination by 1970 of a subsurface maximum concentration observed in 1964. Bowen et al (1976) also noted an apparent discrepancy between the depth distribution of plutonium and caesium beneath unit area of the sediment surface which developed over a number of years. This was interpreted as an apparent loss of plutonium activity with no equivalent loss from the caesium inventory in the same cores and was taken to be definite evidence for the chemical remobilisation of sedimented plutonium back into the water column although this interpretation has recently been questioned by Edgington (R J Pentreath, personal communication). The precise mechanism for remobilisation was unknown although complexation with microbially generated dicarboxylic or polyhydroxy acids diffusing upward through the sediment was suggested. The chemical form of the plutonium was unknown, but Jakubick (1976) has observed migration of PuO_2 and $Pu(NO_3)_4$ in natural soils. However, results from a freshwater aquatic ecosystem has indicated that both plutonium and americium were relatively immobile (Emergy and Klopfer, 1976) while Hetherington et al (1976) concluded that there was no detectable remobilisation of plutonium after its incorporation within stable sedimentary deposits in the Irish Sea for periods of up to twenty years. The latter conclusion was based on the goodness of fit between the known discharge history of plutonium and the measured depth distribution of activity within the core rather than on measurements of plutonium inventory. However, it is understood that more detailed and unpublished measurements of plutonium, americium and curium inventory have been made (R J Pentreath, personal communication).

Finally, desorption of radiocaesium has been proposed as the primary mechanism for the observed removal of caesium from the bottom sediments of the Hudson River Estuary (Jinks and Wrenn, 1976). This phenonen occurs during the intrusion of saline water at times of low river flow and hence salinity was proposed as the primary environmental factor influening the accumulation of caesium. Patel et al (1978) also observed desorption of caesium from sediments in Bombay Harbour where again, of the various environmental factors effecting desorption, salinity was found to be the most important. These results were in accordance with the laboratory results of Graham and Killion (1962).

These apparently conflicting results indicate that, because of the many and varied parameters influencing the retention and migration of radionuclides, each partiular study area must be considered as an individual site with data from other sites used with extreme caution.

The role of organic material in the retention and migration of radionuclides is not fully understood although Hetherington (1978) showed that only a small fraction of the total alpha activity in Irish Sea sediments was associated with the organic fraction. Stephens (1975) emphasised the effect of burrowing organisms on the Eh regime and bacterial biochemistry of marine sediments. For example, large, fast moving worms such as Arenicola or Nereis actively draw seawater deep into their burrows to support their own respiration zone between aerobic and anerobic sediment extending this zone deeper into the sediments. Any activity associated with the seawater drawn into the burrows might be immobilised there by ion exchange onto the clay minerals or by absorption on the mucopolysaccaride linings of the burrows (Bowen et al, 1976). In either case, the Eh regime in the sediments, particularly in the transition zone between aerobic and anerobic sediments would be particularly important.

Plankton have been shown to concentrate plutonium (Edgington et al, 1976b), a phenomenon which was postulated as being the reason for the seasonal variation in the observed concentration factor for surface water in the Great Lakes. Indeed, a transport mechanism for plutonium via the settling of phytodetritus and zooplankton faecal pellets has been proposed (Wahlgren and Marshall, 1975; Nunny, 1978). However, it should be noted that, as most of the plutonium discharged into the aquatic environment is associated with the sediments, the amounts of plutonium remaining to be transported and deposited by this mechanism is only a small percentage of the total plutonium budget.

2.3 Conclusions

A number of physical parameters have been shown to affect the uptake, retention and remobilisation of radionuclides by sediments. These include chemical form, salinity, pH, Eh, sediment mineralogy and the availability of various organic and inorganic complexing and leaching agents. In addition, the potentially important role of benthic organisms in determining conditions within the sediments was noted.

An understanding of the transport of radionuclides within the Irish Sea sediments requires an evaluation of all these parameters. It is convenient to split the above parameter list into two sections:

(i) those concerned with the chemical conditions within the sediments;
(ii) those concerned with the physical condition of the sediment.

The latter group contains parameters such as the distribution of sediment size and mineralogy, the abundance, distribution and type of benthic organisms and the processes involved with physical changes in the sediment. It is this second group of parameters which has received least attention in studies of radionuclide distribution in the Irish Sea and elsewhere and consequently should be a focal point of future research. Results from a study of these parameters could then be linked with data on the radionuclide distribution to assist in the interpretation of sedimentological data in terms of those sedimentological processes which may yield some information on the potential residence times of radionuclides in sea bed sediments.

CHAPTER 3

THE SEDIMENTOLOLOGY OF THE NORTHERN IRISH SEA

3.1 Introduction

The northern Irish Sea is part of a virtually enclosed sea only connecting to the ocean through the narrow North Channel in the north-west and the restricted St Georges Channel in the south. The region has an area of approximately 900 km^2 and is shown in Figure (1).

This chapter briefly summarises the distribution of present day surface sediments in the north-eastern Irish Sea with a view to presenting sufficient information to enable an appreciation of the present distribution of radionuclides to be made. Particular emphasis is placed on the fine sediment fraction in view of its importance in the retention of many radionuclides. The factors influencing the present sediment distribution are discussed and some preliminary observations on the potential sources, transport paths and sinks of fine sediment are made. A comprehensive study of the Quaternary sediments of the Irish Sea is in preparation (Williams et al, in press).

The geological structure of the Irish Sea has been extensively studied using geophysical and drilling techniques; summaries of which are provided by Mitchell (1960, 1972), Bott (1968) and Dobson (1977). Briefly, the area consists of a number of sedimentary basins formed by subsidence due to faulting and containing Carboniferous and Permo-Triassic rocks. There is some evidence that the faulting is of Hercynian age and hence the bed rock is no younger than the Permo-Triassic "red beds" upon which superficial sediments have been laid down since the Pleistocene. The Quaternary sediments of the area have been extensively studied by Cronan (1969) and Pantin (1977, 1978). Boulder clays (tills) of varying thicknesses are found over the whole region underlying highly stratified proglacial lagoon sediments and marine deposits. These marine deposits are generally devoid of any primary sedimentary fabric, a feature which has been attributed to extensive sediment reworking by benthic infauna (Pantin, 1977, 1978). A more detailed discussion of the Quaternary sediments in the Irish Sea is presented in Appendix B.

3.2 Size Distribution of Surface Sediments

Early work on sea bed, surface sediment distribution in the Irish Sea was reported by Stride (1963) and Belderson (1964) and that in the vicinity of the Windscale outfall by Jones (1952) and Templeton and Preston (1966). However, the major reconnaisance survey of the area was undertaken by the Institute of Geological Sciences between 1967 and 1973. Data were obtained in the form of grab samples, long gravity cores and vibrocores on a fairly dense network of sample stations. Additional data on the deeper sediments were obtained from pinger records and occasional borings down to bedrock. Three authoritative accounts of this work have been published by Cronan (1969) and Pantin (1977, 1978) from which most of the information in this section is taken.

The distribution of surface sediment is considered in terms of its partition between the silt/clay fraction (< 62.5 μm e.s.d., 4ϕ) and the sand/gravel fraction (> 62.5 μm e.s.d., 4ϕ). Figure (2) shows the distribution of the silt/clay fraction in surface sediments as a percentage dry weight of bulk sediment. This diagram was compiled by Nunny (1978) from data in Pantin (1977, 1978). The large area of predominantly silt/clay sediments off the Windscale outfall and the southerly trend of these muddy sediments parallel to the coast are major features. The low silt/clay content outside this zone is apparent. Gravels are predominant over much of the western part of the area and are associated with subordinate proportions of sand which increase towards the centre of the area where almost unimodal sands occur. Near the English coast the sediments become locally coarser (Cronan, 1969). Outcrops of firm clay and glacial boulder clay occur to the north with the tills overlain by a thin layer of sandy sediments in some areas. A second, much larger area of very muddy sediments exists to the west of the Isle of Man (Belderson, 1964).

Detailed information on the cumulative sediment size distribution is scare although Hetherington and Jefferies (1974) obtained size distributions of intertidal sediments in the Ravenglass Estuary at 3 monthly intervals from 1970-72. These results are shown in Table (1) with an example plotted in Figure (3). The size distribution varied little during this period and was predominantly silt with little clay and an appreciable proportion of sand. This distribution is also said to be typical of sediments from other estuaries in the area (Hetherington and Jefferies, 1974).

Little information is available on the vertical distribution of grain size although Hetherington and Jefferies (1974) found that there was little change of sediment size distribution with depth on intertidal mud flats in the Ravenglass Estuary. This result is not unexpected in view of the heavily bioturbated nature of these sediments. Figure (4) shows two views of these intertidal mud flats and the sampling stations while Figure (5) shows X-radiographs of two rectangular box cores taken by the authors in January 1979 from the sites shown in Figure (4). The lack of primary sedimentary structure in both cores is apparent as are the numerous animal burrows.

3.3 Factors Influencing Sediment Distribution

The belt of muddy sediments running parallel to the Cumbrian coast appears to be the latest stages of the infilling of a depression. However, there appears to be very little correlation between those areas having a high mud content and current topographic depressions (see Figures 2 and B.1). This suggests that the present surface sediment distribution in the Irish Sea is primarily controlled by horizontal energy gradients in bottom tidal currents (McQuillan et al, 1968). Indeed, the two areas of muddy sediments do coincide with regions of minimum M_2 tidal current amplitudes (Robinson, 1979). However, geophysical evidence suggests that the eastern Irish Sea is currently an area of non-deposition including the shallow coastal areas between St Bees Head and Morecambe Bay but with the exception of the various estuaries which appear to be still experiencing deposition (Williams et al, in press).

A general source of fine sediment in an exposure of Keuper Marl to the north of the Isle of Man has been tentatively identified by Pantin (1978) although this has yet to be confirmed. A secondary source has also been suggested in an outcrop of boulder clay and lag deposits to the south-east of the Isle of Man (Pantin, 1978). These are supported by the bedform analysis of Belderson and Stride (1969) who concluded that there is a net eastward movement of sand to the north and south of the Isle of Man with the resulting transport paths seeming to converge off Windscale. This interpretation has recently been reported by Pingree and Griffiths (1979) on the basis of calculations of the amplitude of the bottom stress vectors due to M_2 and M_4 tidal interactions. However, it should be noted that much of the evidence concerning the sources, transport paths and sinks of fine sediment in the Irish Sea remains circumstantial.

3.4 Concluding Remarks

The general sediment distribution shown in Figure (2) is based on widely spaced grab samples and consequently will not represent the detailed distribution patterns. Thus, if the transport paths of the radionuclides are to be determined it is essential that the sedimentation regime is carefully documented and a detailed investigation carried out to identify the sources and sinks of fine sediment. Similarly, the occurrence of widespread bioturbation of the surficial sediments implies that benthic organisms may contribute to the mechanisms incorporating radionuclides into Irish Sea sediments and hence this contribution should also be investigated.

CHAPTER 4

LOW LEVEL RADIOACTIVE EFFLUENT DISCHARGES INTO THE IRISH SEA

4.1 Introduction

Most of the fuel from the United Kingdom's civil and military nuclear programme is reprocessed by British Nuclear Fuels Limited (BNFL) at Windscale in Cumbria; a plant which has been in operation for over thirty years.

A variety of wastes are produced in the reprocessing of spent nuclear fuels; some are discharged into the environment under authorisation from MAFF and DOE while others are stored on site. The wastes of interest in this report are those discharged to sea via two contiguous mild steel pipes 25 cm in diameter and extending 2500 m seawards beyond the mean high water mark, ending in approximately 20 m depth of water. Some of these liquid effluent streams arise from the processing of nuclear fuel and these are treated before reaching low active waste storage tanks. The waste in these tanks is strongly acid (pH 2-3) but is neutralised by the addition of ammonium hydroxide before discharge to sea (Hetherington et al, 1975). Liquid effluents also arise from purge water from the ponds in which spent fuel is stored prior to reprocessing. The pond water has become contaminated because of corrosion of the cladding of the magnox fuel elements caused by delays in reprocessing although ion exchange materials placed in skips in the pond have reduced the activity discharged from this source.

4.2 Nature of the Discharges

The major radionuclides in the liquid effluent discharged into the Irish Sea are listed in Table (2) which was compiled from British Nuclear Fuels Limited (1979). The annual discharges of the more important radionuclides (in terms of the amount of activity discharged) from 1957 until 1978 are shown in Table (3) which was compiled from a number of published sources from BNFL and FRL. The apparent discrepancy in the discharges of total alpha activity and those of plutonium-238 + 239 + 240 between 1960 and 1964 inclusive is due to the errors incurred in interpolating plutonium discharges from a plotted discharge history (Hetherington, 1976a) rather than obtaining them from tabulated values. Hence, these figures should not be taken as a disagreement between different published sources.

The relative proportions of the various radionuclides in the low-level effluent depend on the particular chemical separation techniques used in the reprocessing as well as the prorportions in the irradiated fuel. The processing of the irradiated fuel and the treatment of the liquid waste at the Windscale plant originally gave rise to a discharge in which a high proportion of the gamma activity was due to ruthenium-106 (^{106}Ru). However, a new chemical reprocessing plant was commissioned in 1964 which has a much higher efficiency in fission product extraction. This new process considerably improved the extraction of ^{106}Ru such that its contribution to the gamma activity in the discharge was considerably reduced (Figure 6). However, discharges of zirconium-95 (^{95}Zr) and niobium-95 (^{95}Nb) increased some 20 times (Figure 7). In recent years, further alterations in the extraction process and the increasing amounts of more highly irradiated fuel reprocessed have led to the discharges of ^{95}Zr and ^{95}Nb returning to their low, pre-1964 values.

Discharges of caesium-137 (^{137}Cs) and caesium-134 (^{134}Cs) increased dramatically after 1969 (Figure 8) due to the commencement of reprocessing more highly irradiated fuel but mainly as a result of corrosion of the magnox fuel elements in the ponds and subsequent leaching of caesium into the pond water, such that caesium is currently the major contributor to the beta activity released into the Irish Sea. The measurement of total beta activity in the discharge is required under the terms of the authorisation but the measurement techique used is such that low energy beta emmitters such as tritium (^{3}H) and plutonium-241 (^{241}Pu) are not included. The amount of ^{241}Pu beta activity in the discharge is many times the amount of activity from the alpha emitting plutonium nuclides. However, ^{241}Pu has a relatively short half life and a much lower radiotoxicity than plutonium alpha activity although it decays to the alpha emitter americium-241 (^{241}Am). Consequently, the environmental impact and the ultimate radiological effect of the discharges of ^{241}Pu (at 1974 levels) is similar to that of the associated discharge of alpha active plutonium (Hetherington et al, 1976).

The total alpha activity in the discharge is mainly due to plutonium isotopes and ^{241}Am (Figure 9). Until 1972 the majority of the alpha activity was due to alpha active plutonium isotopes but the processing of more highly irradiated fuel led to significant increases in the discharge of ^{241}Am such that in 1974 it was responsible for over 70% of the alpha activity discharged (Figure 9). However, since 1974 the amount of ^{241}Am in the discharge has been dramatically reduced. The annual discharges of plutonium shown in Table (3) and Figure (9) are the total discharges of alpha active plutonium which comprises the isotopes ^{238}Pu, ^{239}Pu, ^{240}Pu and ^{242}Pu, as precise details of the discharges of the individual isotopes are not available for most of the time prior to the late 1970's.

The measurement of isotope ratios in sediments is potentially important as a means of sediment dating providing the history of isotope ratio in the discharge is known. For plutonium, it is known that the quantities of ^{242}Pu are almost negligible while the ratio of ^{239}Pu + ^{240}Pu to ^{238}Pu has decreased from approximately 70:1 in the early 1960's to approximately 5:1 in the early 1970's (Hetherington, 1978) and more recently to 4:1. This ratio is a function of the irradiation time of the fuel elements and its decrease reflects the increased irradiation time of modern reactor fuels. It is not possible to differentiate between ^{239}Pu and ^{240}Pu by radiometric methods. However, mass spectrometric measurements on samples obtained after discharge revealed that the ratio of ^{239}Pu to ^{240}Pu was not less than 10:1 (Hetherington et al, 1975). Consequently, where activities of ^{239}Pu are quoted in this report it will usually include a contribution from ^{240}Pu. The remainder of the alpha activity not due to plutonium or americium is made up of curium isotopes and traces of other transuranic elements including neptunium.

4.3 Concluding Remarks

This chapter presents the discharge history of the major radionuclides from the Windscale low-level radioactive waste disposal site. It is important to note that limits on these discharges are set by MAFF and DOE and that all the discharges quoted in this report represent values less than the authorised limits. No attempt has been made to put these discharges in the context of the limits as this is outside the scope of this report. However, full details can be obtained from Hetherington(1976b),Hunt(1979),Mitchell (1973, 1975, 1977a, 1977b, 1978) and British Nuclear Fuels Limited (1979, 1980). It should also be noted that the Windscale authorisation is currently under review (R J Pentreath, personal communication).

CHAPTER 5

THE DISTRIBUTION OF RADIONUCLIDES IN THE IRISH SEA

5.1 Introduction

A considerable amount of data on the distribution of artificial radionuclides in the Irish Sea have been assembled by MAFF as part of their monitoring and research programmes into the public health consequences of low-level radioactive discharges from the Windscale plant. In principle, these data can be used in sedimentological studies in two ways:

(i) the horizontal distribution of radionuclides in the sea bed can yield information on the sediment transport paths in the area and

(ii) the vertical distribution of radionuclides in sediment cores can be used to date sediment horizons within the core when correlated with the known discharge history of the effluent.

Care must be taken when making sedimentological interpretations from radiochemical distributions as many factors influence the incorporation of radionuclides into seabed sediments. In addition, the distribution of radionuclides within the water mass can reveal information on residual water movements which is vital if transport paths of suspended sediment are being considered.

This chapter examines the distribution of radionuclides in the Irish Sea, both in the seawater and the sediments. The majority of the transuranic elements discharged into the Irish Sea currently reside in the local seabed sediments whereas the affinity of the other fission products for the sediments is considerably less (Hetherington et al, 1975). Consequently, the discussion of the distribution of activity in the Irish Sea considers these two groups separately.

5.2 The Distribution of the Transuranic Elements

5.2.1 Seawater

The distribution of ^{239}Pu in surface seawater in the Irish Sea in July 1973 and July 1974 is shown in Figure (10) (taken from Hetherington, 1976a). The contours were interpolated from thirty sampling points. The samples were passed through a 0.22 μm millipore filter before analysis to remove any fine particulate matter. The distribution of ^{238}Pu was found to follow an almost identical distribution to ^{239}Pu with the ratio ^{239}Pu:^{238}Pu being virtually constant with a value of 5.5. The concentration of plutonium on the suspended load was found to be between 11% and 150% of the plutonium concentration in filtered seawater with a mean value over 15 samples of 39%. No correlation was found between the magnitude of the suspended load and the fraction of the water-borne plutonium associated with it (Hetherington, 1976a).

Estimates of the total plutonium inventory in filtered seawater in the area between the North Channel and a line drawn between Holyhead and Dublin (Figure 10) for the years 1973 and 1974 have been made (Hetherington, 1976a). The results showed that, despite the input of 1800 Ci of plutonium activity during the year, the amount of plutonium in the seawater was a constant. Estimates of the amount of plutonium activity in the seawater and suspended load leaving the Irish Sea via the North Channel were at least an order of magnitude less than the total discharged during the year. This is taken as evidence that the major proportion (> 90%) of the plutonium discharged is retained within the Irish Sea and is associated with the seabed sediments (Hetherington, 1976a). However, it should be noted that the partition coefficient* for plutonium depends on the oxidation state of the element (Nelson and Lovett, 1978) and hence the proportion of the plutonium which becomes associated with the sediment is dependent on the ratios of oxidation states in the discharge or, more likely,on the states formed in sea water after discharge.

5.2.2 Sediments

Sediment samples have been obtained from both intertidal and subtidal sites by FRL. The sediment cores in the intertidal zone were collected by driving a 10 cm diameter, thin-walled PVC tube directly into the sediment. The subtidal cores were obtained as sub-samples of large Reineck box core samples. All sediment cores were deep frozen immediately after collection.

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* The partition coefficient is defined as the ratio of the activity in the sediment sample to the activity in the adjacent water.

Preliminary analysis of intertidal cores from Newbiggin in the Ravenglass Estuary had revealed that the alpha activity per unit dry weight of sediment associated with a particular grain size increased steadily with a decrease in grain size from sands to clays (Hetherington et al, 1975). Later analysis for ^{239}Pu (Hetherington, 1978) and ^{241}Am (James et al, 1978) revealed similar trends. These data are summarised in Tables (4) and (9).

The plutonium activity in surface sediments at Newbiggin has been determined annually since 1966 (Hetherington, 1976a) and a summary of these results is presented in Figure (11). Also shown is the variation of surface activity per unit discharge with time. This shows that there has been no increase in the plutonium activity per unit discharge in surface sediments at Newbiggin during the period 1966 to 1973 despite a four-fold increase in the discharge rate.

The plutonium and americium activity has also been determined in the top 20 cm of a number of subtidal and intertidal sediment cores taken at varying distances from the Windscale outfall (Hetherington, 1976a; Hetherington et al, 1976). No apparent correlation of activity with distance from the outfall was observed for either plutonium or americium. There was also no correlation between the partition coefficient (Kd) for plutonium and distance from the outfall. These correlations relate to the activity on a bulk sediment sample with no account being taken of the varying sediment composition at the sample sites. However, it was found that the higher values of Kd were obtained at the muddier stations while the low values tended to be associated with sandier sediments (Hetherington, 1976a). No significant difference between the Kd values at stations near to the outfall and those at a distance was found when sites of a similar mineralogical composition were compared (Hetherington et al, 1975).

The vertical distribution of ^{239}Pu and ^{238}Pu in sediment cores from a number of selected stations has been determined (Hetherington, 1976a). These results are reproduced in Table (5). The concentration of ^{239}Pu was found to decrease approximately exponentially with depth in both the intertidal and subtidal cores. The results also showed an increase in the ratio of $^{239}Pu:^{238}Pu$ with depth. However, the results from a long gravity core at one of the subtidal stations revealed no increase in the plutonium isotope ratio with depth down to the limit of analysis at 55 cm (Table 6). The discrepancy between the two cores (from the same site) could be due to disturbance by one or other of the corers.

No estimate of the errors induced by the coring process is available although some plutonium transfer within the sediment during the coring is conceivable and when the very small masses of the isotopes in the sample are considered this may be significant. The vertical distribution of ^{241}Am in one of the subtidal cores was also determined and the results are shown in Table (5).

Subsequent analysis of two further intertidal cores taken from the Ravenglass Estuary revealed that the majority of the plutonium in the sediment was associated with the mineral fraction having a density greater than 2 g cm^{-3} although the concentration on the light fraction (density < 2 g cm^{-3}), taken to be representative of the organic fraction, was twice that on the heavy fraction, (Hetherington, 1978). The depth distribution of ^{239}Pu and the plutonium isotope ratio on the sediments in the two cores resembled the distribution in other cores. These profiles are reproduced in Table (7).

The distribution of ^{239}Pu concentration and plutonium isotope ratio in the interstitial water of the cores was also examined (Hetherington, 1978). The results, also shown in Table (7), reveal an almost constant concentration with depth, except for an enhanced layer near the surface. The plutonium isotope ratio was relatively constant with depth having a value similar to that in the overlying water column.

The results for the interstitial water are not surprising in view of the intertidal nature of the sampling site which remains uncovered for part of the tide. This allows partial draining of the interstitial water which is replaced, from above, on the next tide. Thus over the course of several tidal cycles the interstitial water in the top 30 cm of the core can be completely replaced. As the variation of ^{238}Pu and ^{239}Pu concentration in seawater is negligible over this time scale, it would be expected that the interstitial water had values similar to the overlying water column. The difference in distribution of plutonium activity between the interstitial water and the sediment is interesting although it does not imply that the plutonium is irreversibly sorbed onto the sediment, as any plutonium leached from the sediment will be carried away by the interstitial water. It should also be noted that both the physical and chemical conditions at an intertidal site are significantly different from those at a subtidal site. Consequently, it is not possible to extrapolate results from one type of site to the other.

The distribution of plutonium activity and oxidation state on the solid phase and in the interstitial water of subtidal cores has now been obtained (Pentreath et al, 1980) in order to seek a possible mechanism by which long lived radionuclides could return to the sediment surface. These results clearly show that, while the plutonium in the overlying seawater is predominantly Pu(V + VI), that below 5 cm in the interstitial water is predominantly Pu (III + IV), the less mobile of the two oxidation states. Further cores have also been examined to determine the distribution of Eh, pH and stable elements to improve current understanding of the potential for isotope mobilisation in sediments.

A study of plutonium and americium in estuarine and river sediments near Windscale and Morecambe Bay has also been published by the National Radiological Protection Board (James et al, 1978). The results of this survey are shown in Table (8) with the sampling stations shown in Figure (12). The activities quoted are those detected in the top 5 cm of sediment cores taken at each site. It should be noted that the activities obtained in sediments from the Ravenglass Estuary do not represent average values but were selected from areas of high activity detected during a survey of the background gamma radiation. The ratio of americium to plutonium compares well with the values obtained by Hetherington et al (1976) for subtidal surface sediments. James et al (1978) also examined the fractionation of americium in both the Ravenglass and sea shore sediments. These results are presented in Table (9) and show that the concentration per unit dry weight of sediment (hereinafter referred to as concentration) increases with a decrease in grain size in accordance with earlier results for plutonium (Hetherington, 1978). This was interpreted as suggesting that much of the americium may be ion-exchange into the lattice of aluminosilicate particles rather than being associated with the available surface area. These data also show that the combination of this phenomenon and the particle size distribution in the sediments makes the silt size fraction the major carrier of activity in the areas investigated.

James et al (1978) defined a concentration factor as the ratio of the concentration in a given size fraction of the sediment to the concentration in the bulk sample. The concentration factor for the organic residue of 0.6 obtained by James et al (1978) appears to disagree with the value of 1.74 obtained from Hetherington's (1978) data for the fraction of the sediment with a density less than 2 g cm^{-3}.

However, only 66% by weight of this light fraction was lost on ignition and it may be that the remainder of the light fraction was made up of very fine clay particles adhering to the organic fraction. If it is assumed that the percentage of Hetherington's (1978) light fraction not lost on ignition is made up of clay particles and it is further assumed that the concentration factors for the organic fraction and clay fraction obtained by James et al (1978) are representative of the value in Hetherington's (1978) sample then combining these values with the bulk sample concentration gives an activity in the light fraction of 159 pCi/g. This compares favourably with the value of 135 pCi/g quoted by Hetherington (1978) for the activity in the light fraction and offers some explanation of the apparent discrepancy between the two sets of results.

James et al (1978) also examined the characteristics of the actinide particles within the sediment and concluded that, in the sample examined, 10% of the alpha activity was present as particulates with alpha activities in the range 0.2 to 1.2 fCi with the remaining 90% being diffusely distributed.

5.3 Distribution of Elements other than the Transuranides

5.3.1 Seawater

The concentrations of ^{137}Cs in filtered surface seawater in the Irish Sea for September 1968, May/June 1972, July 1973, July 1974 and January 1976 are shown in Figures (13), (14), (15), (16) and (17). The increase in activity over the seven year period can be clearly seen, particularly that between 1972 and 1974, corresponding to the four fold increase in caesium discharge during this period. However, in spite of the large changes in concentration that have taken place between 1968 and 1976, the pattern of the activity contours has remained much the same. The southerly trend of the activity in the vicinity of the outfall should be noted.

It should also be noted that caesium budgets for the northern Irish Sea have shown that most of the caesium discharged is retained in the water phase (Hetherington et al, 1975).

Measurements of the distribution of other radionuclides, including ^{106}Pu and ^{95}Zr/^{95}Nb shown in Figure (18), show a similar pattern of activity contours although the magnitudes vary considerably (Hetherington and Jefferies, 1974).

The activity of ^{95}Zr and ^{95}Nb, ^{106}Ru and ^{137}Cs in shoreline filtered seawater samples taken between 1964 and 1966 as a function of the distance from the outfall are shown in Figure (19) (Preston et al, 1971). The southerly trend of the radionuclides can again be clearly seen.

5.3.2 Sediments

Annual surface sediment samples from the Ravenglass Estuary (Eskmeals) have been analysed for the radionuclides ^{137}Cs, ^{106}Ru, ^{95}Zr/^{95}Nb and ^{144}Ce by FRL (Hetherington and Jefferies, 1974). The samples were obtained from the top centimetre at ten sample stations within a ten metre diameter cirle. The results are shown in Table (10) together with their mean annual activities per Ci/day discharged. The results show that an almost steady state exists between the activity discharged and the surface activity at Eskmeals. These results are consistent with those obtained for plutonium discussed earlier. A good correlation between surface sedient activity in estuarine sediments and distance from Windscale was also found for ^{144}Ce, ^{106}Ru and ^{95}Zr/^{95}Nb (Preston et al, 1971).

The relationship between discharge rate and concentration in surface sediments at Eskmeals has been examined using serial correlation techniques. This revealed a lag period of one month for both ^{144}Ce and ^{106}Ru. However for ^{95}Zr/^{95}Nb a lag of two or three months was obtained albeit with a much smaller degree of significance than for ^{144}Ce and ^{106}Ru. This is believed to be due to the regular cyclic pattern of discharge of ^{95}Zr/^{95}Nb due to the method of operating the processing plant (Hetherington and Jefferies, 1974) which gives high discharges of these radionuclides at times of the year when onshore transport due to waves and wind is more likely. Surface sediment samples were also taken at Walney Island and Whitehaven between 1966 and 1971 and analysed for ^{144}Ce, ^{106}Ru and ^{95}Zr/^{95}Nb. The results showed that the peak concentrations of each nuclide at these sites and at Eskmeals were most frequent between November and March. A regular variation was observed with activities at Eskmeals and Walney, to the south of the discharge, fluctuating out of phase with the activities at Whitehaven in the north (Hetherington and Jefferies, 1974).

Seabed surface sediment concentration between 1968 and 1971 related to unit mean annual daily discharge are shown in Figure (20) (Hetherington and Jefferies, 1974). The northward drift of the activity in the sediments should be noted and contrasted with the southerly drift observed in seawater concentrations. This difference is emphasised in the distribution of the partition coefficient shown in Figure (21) (Hetherington and Jefferies, 1974). In view of the apparent preference of ^{95}Zr/^{95}Nb, ^{106}Ru and ^{137}Cs for the fine sediment fraction (Hetherington and Jefferies, 1974) the radionuclide distributions shown in Figure (20) should be interpreted in conjunction with the sediment distribution in the area, Figure (2) which shows that the major proportion of the fine sediment is in a band extending south to the outfall. Thus the concentrations of the non-transuranic radionuclides do not appear to be correlated with percentages of fine sediment in the seabed surface unlike the results obtained for plutonium discussed earlier.

Sediment cores from an intertidal mud flat at Eskmeals on the Ravenglass Estuary were taken regularly during the period 1967 to 1973 by FRL. The sampling technique was similar to that described previously. The depth distribution of ^{95}Zr/^{95}Nb, ^{106}Ru, ^{144}Ce, ^{137}Cs and ^{134}Cs were said to be in a steady state when related to unit annually averaged daily discharge of the relevant element from the reprocessing plant (Hetherington and Jefferies, 1974). The vertical distribution of the radionuclides was found to be very nearly exponential. The typical distribution are reproduced in Figure (22) (Hetherington and Jefferies, 1974).

5.4 Concluding Remarks

The above discussion contains a number of significant results. The partition of plutonium, americium and total alpha activity between the various grain sizes has been shown to follow earlier results for other radionuclides with the activity favouring the fine sediment fraction. In addition, organic matter has been shown to play a negligible part in the retention of sea bed activity. For example, in one intertidal sample the organic fraction which comprised 2% of the mass of the sample, carried 1.5% of the activity whereas the clay fraction, which accounted for 6% of the mass carried 25% of the activity. It also appears that the concentration of a number of radionuclides (including plutonium) in surface sediment samples from the Ravenglass Estuary is directly proportional to the annually averaged daily discharge of that radionuclide, although for each radionuclide there is considerable scatter of the constant of proportionality on a year to year basis! This relationship has important implications in the prediction of radionuclide concentrations at Newbiggin.

Another major result in the above data is the apparent discrepancy between the near field distributions of certain radionuclides in the sea bed sediments and in the overlying seawater. The non-transuranic radionuclides in the surface seawater show a southerly trend while those in the sediment show a northerly trend. This latter result is even more significant when it is considered that the major area of fine sediment is to the south of the outfall. This discrepancy has yet to be explained. Insufficient data have been published to deduce whether the same discrepancy also occurs for the transuranic elements. However, if it does then this implies that considerable attention will have to be given to the sediment transport paths in the immediate vicinity of the Windscale outfall.

In conclusion, published measurements of plutonium activity on the Irish Sea have shown that almost all the plutonium discharged is associated with the sea bed sediments, particularly the fraction less than 62.5 μm in size. However, measurements of the distributions of other radionuclides also known to be associated with the fine fraction have shown that the areas of highest activity are not those having the highest proportion of fine sediment. Indeed, the region having the highest activity of $^{95}Zr/^{95}Nb$ appears to be moving away from the region having the highest proportion of fine sediment. Detailed near field distributions of plutonium in the sediments are required before the full importance of these results can be assessed. However, it is clear the sea bed sediments play a major, if little understood, role in the transport and distribution of the transuranic elements.

CHAPTER 6

THE SEDIMENTOLOGICAL INTERPRETATION OF RADIONUCLIDE DISTRIBUTION IN SEDIMENTS

6.1 Introduction

The study of the distribution of radionuclides within the sea bed is a potentially powerful tool in the study of sedimentation processes and rates.

The possibility exists for using observations of the distribution of radionuclides in sea bed sediments to place isochrones or 'time lines' in the sediment so that the sedimentological history of a particular site can be evaluated. Data from a number of sites can then be used to establish the sedimentological regime of a particular area. In general, the technique is to correlate the depth distribution of a particular radionuclide (or the ratio of two isotopes of the same element) in the sediment with the known temporal variation of activity (or isotopic ratio) of that radionuclide at the sediment surface, including the known decay rate of the particular radionuclides under consideration. Ideally, a pronounced maximum (or minimum) will be present in the temporal variation of surface activity which can then be easily associated with an equivalent equally pronounced maximum (or minimum) in the depth profile of activity in the sediment.

For example, in the Great Lakes of the USA a major proportion of the plutonium input to the system is from atmospheric fallout due to weapons testing which has two major peaks in 1959 and 1963. The second of these peaks is apparently clearly seen in the vertical distribution of plutonium in Lake Michigan sediments (Edgington et al, 1976b). Thus, it appears reasonable to conclude that activity, which was known to be on the sediment surface at a particular time, has been located at a specfic depth in the sediment substrate after a known time interval. However, Bowen et al (1976) pointed out that subsurface peaks in the activity of a particular radionuclide may also represent material drawn to depth in the ventilation water of worm burrows and immobilised at a particular level in the sediment. Thus it is clear that the radionuclide distribution in a particular sediment core can be the result of many interacting processes. Consequently, if confident accurate sedimentological interpretations/deductions of radionuclide distributions in sediments are to be made, it is necessary to identify all the processes governing the incorporation of radionuclides into the sediments at a particular site. It is also necessary to know details of the activity arriving at a particular site and great care must be taken in the extrapolation of this information from details of radionuclide releases some distance away from the sampling site.

This chapter discusses the mechanisms of incorporation and transport of radionuclides in sea bed sediments and the sedimentological significance of resulting radionuclide distributions, with the aim of providing a set of guidelines for the sedimentological interpretation of radiochemical data.

Finally, the proposed techniques are applied to the radionuclide distributions in the Irish Sea and a number of previous inconsistencies are noted and explained.

6.2 Transport of Radionuclides within the Sea Bed

Radionuclides arriving at the sediment surface can be incorporated into the sediment by three physical processes:

(i) sedimentation, in which particulate or particle associated activity is added directly to the sediment framework or activity is trapped within the pore water included within the framework of the accumulating sediment;
(ii) diffusion from the overlying water column into the sediment pore water;
(iii) bioturbation, in which activity associated with the overlying water or suspended particulate matter is drawn down into the sediment by the action of the biota.

Radionuclides can be present at a particular level in the sea bed sediments as surface sorped species, active particulates or in solution in the pore water and it is important to distinguish between particle associated activity and pore water associated activity. Using the sediment surface as a reference level, the net transport of activity in both phases due to sedimentation is downward into the sediment whereas diffusion can transport pore water associated activity either upward or downward dpending on the direction of decreasing concentration. The effect of biotrubation on radionuclide transport is usually considered as a diffusive type process and as such will transport both particle associated and pore water associated activity in the direction of decreasing concentration. In addition, burrowing animals influence the physical character of the sediment and also the sediment chemistry, in particular the position of the redox potential discontinuity (RPD, sometimes called the redox potential boundary, RPB). This can lead to temporal and spatial variations of the partition coefficient of a particular radionuclide and hence the amount of activity available for diffusive transport. A fourth process, that of consolidation of the sediment can also be important in transporting radionuclides within the substrate. This can lead to direct transport of activity due to the upward movement of pore water relative to the sediment surface and also to apparent upward transport of particle associated activity due to the compression of the substrate.

Finally, activity can be removed from the sea bed by:

(i) erosion of the sediment surface;

(ii) diffusive transport from the sediment pore water into the overlying water column;

(iii) biological action in which activity is ejected from the substrate into the overlying water either as part of the feeding cycle or during burrowing when excavated material is deposited on the sediment surface and may subsequently be resuspended (Hill and Hunter, 1976);

(iv) consolidation, which can advect activity from the substrate into the overlying water column with the ejected pore water.

6.3 Interpretation of Radionuclide Distribution in Terms of Sedimentary Processes

Essential information for the rigorous application concentrations on surface sediments includes:

(i) The variation with time of radionuclide concentrations on surface sediments

(ii) the form and association of activity with the various sediment size fractions

(iii) the potential for redistribution of activity in the sediment either by remobilisation into the pore water or by the redistribution of contaminated particles within the sediment, for example by marine organisms.

In general, for subtidal sites, the temporal variation of activity in surface sediments is unknown and must be deduced from the discharge history of the radionuclides under consideration. This requires data on the travel times and the various transport pathways between the discharge point and the sample site which is frequently unavailable. For example, in the Irish Sea little information exists on the travel times of radionuclides except that for ^{106}Ru, ^{144}Ce and ^{95}Zr/^{95}Nb between the pipeline and the Ravenglass Estuary, discussed in Chapter 5 (para 5.3.2).

Information on the biological reworking of sediments,in terms of the depth of sediment disturbance and time scales over which the reworking takes place, is scarce although some studies have been made (Rhoads, 1974). Disturbance depths of 10 cm to 15 cm appear to be reasonable with time scales of approximately one year. Thus, as most artificial radionuclides occupy, at most, the top

50 cm of the seabed sediments and as radionuclide variability is generally measured on time scales of the order of one year, it is clear that a detailed investigation of the effects of bioturbation on sediment reqorking is requied.

It is interesting to note that the penetration of caesium-137 into an unbioturbated marine substrate due to the action of diffusion is of the order of 5 cm in fifteen years (Kirby and Parker, 1980) which is considerably less than the potential penetration due to bioturbation.

The above discussion has shown that, in general, the information required for the rigorous application of radionuclide dating of sediments is unavailable. Most applications of this technique are based on the known discharge history of various radionuclides and the vertical distribution of activity within the core. This information is then used to date the sediment and hence determine the sedimentation rate (Hetherington, 1976a). These data have even been used to estimate the magnitude of the effective dispersion coefficient, a parameter representative of the degree of bioturbation, at particular sites (Hetherington and Jefferies, 1974; Aston and Stanners, 1979). Many assumptions are required in these analyses. The major assumption is that contaminated sediment is transported directly to the sample site from the discharge point and does not interact with sediment contaminated at a different time travelling via another transport path. The second assumption is that the time lag between the discharge of activity and its arrival at the sample site is very much less than the time scale over which the variability of the discharge is measured (usually one year), ie that the measured surface activity at the sampling site is representative of the activity discharged in the preceding year. Finally, it is usually assumed that the radionuclide partition coefficient is both spatially and temporally constant, which assumes a steady, homogeneous chemical environment throughout the study area.

If the sample consists of sediment contaminated at two different times, the activity in the sample will be some weighted mean of the activity in the two sediment streams and will not represent any particular time, although it may appear to do so. This is also true of any isotopic ratios of the same radionuclide measured from the sample. Similarly, even if the sediment at the given level in the sample was contaminated at one time, any temporal variability in the transport time or transport path would distort the distribution of activity with depth in the sample core. Finally, if the area under consideration is depositional in the long term, any short term natural cycles of erosion and redeposition will tend to mix sediments contaminated at different times which further distorts the vertical distribution of radionuclides.

Consequently, before confident sedimentological deductions can be made on the basis of artificial radionuclide distributions in sea bed sediments, data are required on:

(i) the discharge history of the radionuclides under consideration;
(ii) the major sediment transport paths between the discharge point and the sample site;
(iii) the time lag between discharge of activity and its arrival at the sampling site;
(iv) the chemical conditions in the sediments at the sampling site and along the sediment transport paths;
(v) the magnitude and variability of bioturbation at the sample site.

If information on one or more of these five topics is unavailable then at least estimates of the effect of the unknown parameters should be included in the analysis.

6.4 Application to the Irish Sea

The distribution of artificial radionuclides in the Irish Sea sediments has been used to estimate the sedimentological regime of a number of subtidal and intertidal sites (Hetherington, 1976a). The measured temporal variation of the ratio of ^{239}Pu to ^{238}Pu in sediment samples taken from an intertidal mud flat at Newbiggin in the Ravenglass Estuary was used as a reference and fitted to the observed vertical distributions of ^{239}Pu:^{238}Pu in a number of sediment cores from various sites. The fitting procedure assumed that the sedimentation rate (s), was constant and that there was no bioturbation or remobilisation of activity within the sediments. Under these conditions the activity A(z) per unit weight of dry sediment of a particular isotope at a level, z, beneath the sediment surface should be given by

$$A\ (z) \quad = \quad A'\ (t' - \frac{z}{s}) \qquad (6.1)$$

where A' (t) is the activity per unit weight of dry sediment at the sediment surface as a function of time, t, and t = t' is the time at which the core was taken.

Similarly the variation of the ratio, R (z), of two isotopes of the same element should be given by

$$R\ (z) = R'\ (t' - \frac{z}{s}) \qquad (6.2)$$

where R' (t) is the isotopic ratio in the surface sediments. Hetherington (1976a) varied the sedimentation rate at a particular site by a trial and error method until a best fit, as given by equation (6.2), was obtained between the ^{239}Pu:^{239}Pu ratio in the surface sediments at Newbiggin and the depth distribution of isotopic ratio in a sediment core from the site under consideration.

Due to the lack of data on the temporal variation of isotopic ratio at each of the subtidal sites, this particular application was forced to assume that, at any particular time, the plutonium isotope ratio on the surface sediments at all intertidal subtidal sites up to 20 km from the Windscale outfall is proportional to that at Newbiggin. This implies that the travel time for sediment-borne activity over this distance is considerably less than the one year sampling period used in the data and that the ratio of contaminated to uncontaminated sediment deposited at a particular site is constant.

No data are available for the travel times to subtidal sites. However, a serial correlation between the discharge history of ^{106}Ru and the temporal variation of the concentration of this isotope in surface sediments in Newbiggin suggested a time lag of approximately one month between the discharge and the arrival of the activity at Newbiggin (Hetherington and Jefferies, 1974). Thus, for the site at Newbiggin at least, there was some justification for assuming that the travel time for plutonium is significantly less than one year. However, it should still be remembered that ruthenium and plutonium have completely different environmental chemistries and quite different sediment association as discussed in Chapter 5. Thus, what is true for ruthenium may not necessarily hold for plutonium or any of the other transuranic elements.

This particular application of sediment dating using artificial radionuclide profiles also produced a curious anomaly. The method adopted assumed that the sediments were undisturbed after being laid down which implied there was no transport of activity within the sea bed. However, subtidal sediment cores from the area within 20 km of the discharge show abundant evidence of bioturbation of the sediments (Pantin, 1978) while examination and X-radiography of sediment cores from intertidal mud flats at Newbiggin collected by the authors shows that the sediment is subtantially disturbed by bioturbation. At Newbiggin the main organism is Corophium volutator whose burrows are relatively shallow (approximately 1.5 cm) and probably only mix recent activity (R J Pentreath - personal communication) although other burrows or tubes extend much deeper (>5 cm) (Figure 5). In addition, faunal lists from the offshore area (Jones, 1952) include a number of burrowing organisms likely to create extensive annual bioturbation of the top 10 cm - 15 cm. Two explanations of these results are possible, either bioturbation has no effect on the radionuclide profiles or such radiochemical measurements as have been made have been unable to detect any effect of bioturbation. The second alternative is probably more likely as it can be easily shown that, if the effects of bioturbation on the distribution of activity can be described by a Fickian diffusion process with a constant diffusion coefficient, then for an area with constant sedimentation rate, the combined effects of sedimentation and bioturbation will yield a constant 'apparent' sedimentation rate provided the distribution of activity with depth is exponential. This was shown in chapter 4 to be the case for plutonium in both subtidal and intertidal sites in the Irish Sea. Consequently the good fit obtained between the temporal variation of surface activity and the depth distribution of activity obtained by Hetherington (1976a) was probably fortuitous with the resulting sedimentation rates being the combined action of sedimentation and bioturbation.

This explanation is also consistent with more recent measurements of ^{239}Pu:^{238}Pu ratio in subtidal cores, some of which show signs of apparent extensive mixing while other nearby are apparently undisturbed (Peatreath et al, 1980).

6.5 Concluding Remarks

The preceding discussion has centred on the mechanisms by which radioactivity can be incorporated and redistributed within a sediment core and the subsequent interpretation of the radioactivity distribution in sedimentological terms.

It has been shown that a number of processes control the incorporation and transport of activity in the sea bed. In general, this transport will be downwards relative to the sediment surface although some processes can lead to an upward movement of activity.

Current interpretations of radionuclide distributions in a sediment core in terms of sedimentological history of the core depend on a number of assumptions. These are:

(i) the activity is irreversibly bound to the sediment;
(ii) all sediment particles contaminated at the same time were contaminated with the same radionuclide concentrations and isotopic ratios;
(iii) all sediment particles at a particular depth in a sediment core were contaminated simultaneously;
(iv) all sediment particles at a particular depth in a sediment core arrived at the sample site at the same time and by the same route;
(v) the discharge characteristics are averaged over a time period very much greater than the travel time of particles between contamination and arrival at the sampling site.

Before any confidence can be placed on sedimentological interpretations of radionuclide distributions in sea bed sediments the validity of these assumptions must be examined for each case. Finally, it is particularly necessary to consider the role of the fauna and the subsequent effects of bioturbation on radionuclide distributions within each core.

CHAPTER 7

CONCLUSIONS

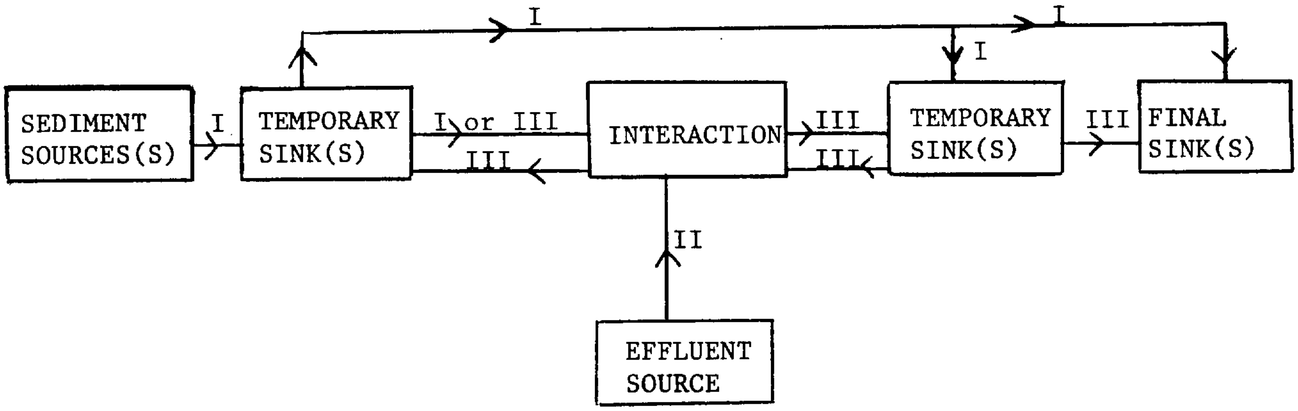
The radiation doses resulting from low-level liquid discharges from the nuclear fuel reprocessing plant at Windscale in Cumbrian have been consistently shown to be within internationally recognised limits (Hetherington, 1976b; Hunt, 1979; Mitchell, 1973, 1975, 1977a, 1977b, 1978). However, the low-level discharges are likely to continue, particularly since the construction of the new Thermal

Oxide Reprocessing Plant has been approved, although the quantity of radionuclides discharge is expected to decrease even with an additional reprocessing plant on the site as a result of the construction of new effluent treatment plants (F E Taylor, personal communication). It has been shown that the transuranic elements are predominantly associated with the sea bed sediments and, consequently, a knowledge of the sedimentology of the Irish Sea is vital if the fate of these elements is to be estimated.

The precise mechanism binding the radionuclides to the sediments in the Irish Sea and the sensitivity of the binding mechanism to variations in environmental parameters such as Eh, pH and salinity are not clearly understood. Laboratory studies have provided some information but generally fail to reproduce all the variables found in marine sediments. However, these studies are valuable in determining the specific influence of a particular parameter on radionuclide uptake by sediments. Field studies on the uptake mechanism of radionuclides by sediment have defined a number of different mechanisms which depend, upon other things, on a sediment type and the chemical nature of the discharge. It is concluded that no general statement on the uptake of activity can be made nor can its potential for remobilisation and migration be estimated without direct experimental evidence from each site considered. These data are not yet available for the Irish Sea.

The distribution of radionuclides in Irish Sea sediments tends to be concentrated in the vicinity of the outfall although activities of an order of magnitude greater than those due to atmospheric fallout have been detected over 100 km from the discharge point. The ultimate fate of these radionuclides is unknown but is intricately bound with the ultimate fate of the fine sediment population in the Irish Sea.

A simple model for the interaction of the sediment and effluent has been adopted. A schematic diagram of this model is shown below.



I - sediment
II - radioactivity
III - contaminated sediment

Transport Path for Fine Sediment - Radioactive Effluent Interaction

The indigeneous fine sediment population is assumed to have one or more uncontaminated sources within the Irish Sea basin. It is also assumed that the sediment is transported in suspension and is deposited at sites along its route to a final sink for varying lengths of time ranging from the period over tidal slack water to numbers of years.

During its passage from the source to the sink, some of the sediment becomes contaminated with activity. It is sensible to consider that this takes place within the normal cycles of erosion, transport and deposition which comprises the mechanism whereby the sediment is exchanged between temporary sinks. Within the Irish Sea, it is evident that the source of activity can interact with a series of temporary deposition sites with a timescale less than the normal travel time of sediment between those sites. Thus sediment particles contaminated at the same time may arrive at the same sink at different times or sediment particles contaminated at different times may arrive at the same sink simultaneously. Recognition of this fact is important in the sedimentological interpretation of the available radiochemical data.

Finally, it is evident that the fate of the sediment is significant in determining the fate of the radionuclides. However, until further information concerning the precise nature of the interaction between the radionuclides and the sediment is known, the degree of significance cannot be estimated.

A consideration of the simple model defines those areas which require investigation. These areas of study relate to an understanding of circumstances as they are now and how they have arisen. The work required can be summarised by the following questions:

(i) where is the fine sediment, what is its composition and what physical, chemical and biological conditions prevail within the sediment?

(ii) where are the present day sources, temporary and final sinks of sediment?

(iii) what are the routes taken by the sediment between its sources and sinks?

(iv) what are the mechanisms governing the movement of sediment along these routes?

(v) what is the role of bioturbation in the dispersion of particles within the substrate?

In order to assist with answering these questions and also to provide information on the interaction between the sediments and the radionuclides a further question needs to be answered:

(vi) what is the detailed horizontal and vertical distribution of the radionuclides in the sea bed sediments?

These questions were directed specificially at the Irish Sea but would be equally applicable to any low-level radioactive waste discharge.

The initialproblem is to provide an answer to these questions.

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Particle size		1970 (%)				1971 (%)				1972 (%)			
ø	µm	1st qtr	2nd qtr	3rd qtr	4th qtr	1st qtr	2nd qtr	3rd qtr	4th qtr	1st qtr	2nd qtr	3rd qtr	4th qtr
+9	1.95	6	13	3	6	5	3	6	6	3	6	3	5
+8	3.9	4	3	3	4	3	3	3	6	2	3	1	2
+7	7.8	5	5	3	6	3	4	4	7	4	4	1	4
+6	15.6	10	10	4	8	9	5	3	7	9	7	5	8
+5	31.2	23	26	19	21	19	17	16	17	17	18	13	17
+4.5	44.2	18	18	15	14	16	18	17	15	13	15	16	16
+4	62.5	13	9	18	16	15	19	14	14	19	15	18	16
+3.5	125	13	7	21	16	19	18	22	20	14	21	27	20
+3	250	5	5	10	6	9	9	10	8	8	8	12	9
+2	500	3	1	4	3	2	4	4	0	1	3	4	3

TABLE 1 Ravenglass Estuary sediments: percentage by dry weight as a function of particle size (from Hetherington and Jefferies, 1974)

Element	Isotope	Mode of decay	Half - life
Tritium	$^{3}_{1}H$	β^-	12.26 y
Sulphur	$^{35}_{16}S$	β^-	88 d
Manganese	$^{54}_{25}Mn$	E.C.	303 d
Iron	$^{55}_{26}Fe$	E.C.	2.6 y
Cobalt	$^{60}_{27}Co$		5.26 y
Nickel	$^{63}_{28}Ni$	β^-	92 y
Zinc	$^{65}_{30}Zn$	β^+, E.C.	243.6 d
Strontium	$^{89}_{38}Sr$	β^-	52 d
	$^{90}_{38}Sr$	β^-	28.1 y
Zirconium	$^{95}_{40}Zr$	β^-	65 d
Niobium	$^{95}_{41}Nb$	β^-	35.15 d
Technetium	$^{99}_{43}Tc$	β^-	2.12×10^{5} y
Ruthenium	$^{103}_{44}Ru$	β^-	39.6 d
	$^{106}_{44}Ru$	β^-	367 d
Silver	$^{110m}_{47}Ag$	β^-, I.T.	253 d
Antimony	$^{125}_{51}Sb$	β^-	2.7 y
Iodine	$^{129}_{53}I$	β^-	1.7×10^{7} y
Caesium	$^{134}_{55}Cs$	β^-	2.05 y
	$^{137}_{55}Cs$	β^-	30.23 y
Cerium	$^{144}_{58}Ce$	β^-	284.9 d
Europium	$^{152}_{63}Eu$	β^+, E.C., β^-	13 y
	$^{154}_{63}Eu$	β^-	16 y
	$^{155}_{63}Eu$	β^-	1.81 y
Uranium	Unspecified		
Neptunium	$^{237}_{93}Np$	α	2.14×10^{6} y
Plutonium	$^{238}_{94}Pu$	α , S.F.	86 y
	$^{239}_{94}Pu$	α , S.F.	2.44×10^{4} y
	$^{240}_{94}Pu$	α , S.F.	6580 y
	$^{241}_{94}Pu$	β^-	13.2 y
	$^{242}_{94}Pu$	α	3.79×10^{5} y
Americium	$^{241}_{95}Am$	α	458 y
Curium	$^{242}_{96}Cm$	α	163 d
	$^{243}_{96}Cm$	α	32 y
	$^{244}_{96}Cm$	α	17.6 y

TABLE 2 Radioactive isotopes in the low-level liquid effluent (compiled from British Nuclear Fuels Limited, 1979, 1980)

Year	Annual Discharge (Curies)												
	^{90}Sr	^{95}Zr	^{95}Nb	^{103}Ru	^{106}Ru	^{134}Cs	^{137}Cs	^{144}Ce	238 + 239 + 240 Pu	^{241}Pu	^{241}Am	Total α	Total β *
1957	1644	708	6420	3600	26616	NA	3720	2580	NA	NA	NA	57.6	64392
1958	2520	2520	6120	5904	42264	NA	6192	5964	NA	NA	NA	62.4	82152
1959	1548	4980	10140	8952	35472	NA	1980	6996	NA	NA	NA	67.2	91908
1960	516	2352	6276	11568	39624	NA	912	768	96	NA	NA	81.6	77532
1961	492	1680	7896	3180	25140	NA	1092	2160	144	NA	NA	133.2	47772
1962	1020	936	4272	1836	22992	NA	1104	2400	192	NA	NA	186.0	44904
1963	552	564	3264	9600	33372	NA	372	1392	240	NA	NA	228.0	48240
1964	972	21560	20880	1200	24504	NA	2800	3216	288	NA	NA	282.0	60660
1965	1512	17480	32200	1800	20148	NA	2960	3888	300	NA	NA	405.6	54720
1966	912	14080	23360	NA	24924	NA	4890	6852	300	NA	NA	NA	NA
1967	1392	18800	25720	NA	17232	NA	4050	13704	492	NA	NA	NA	NA
1968	1356	28080	37160	NA	24204	NA	10040	9960	828	NA	576	1416	NA
1969	2940	31560	30120	NA	22896	NA	12060	13536	816	NA	396	1356	NA
1970	6276	9080	9920	NA	27660	6775	31170	12480	936	NA	540	1656	NA
1971	12332	17380	18120	NA	36468	6372	35820	17252	1128	NA	1020	2688	NA
1972	15160	25624	23520	NA	30500	5815	34840	13564	1548	NA	2172	4380	NA
1973	7444	14900	28100	NA	37800	4481	20770	14548	1776	NA	2952	4380	NA
1974	10648	2560	6996	NA	29160	26993	109770	6532	1248	NA	3192	4560	NA
1975	12636	2629	5924	NA	20556	29211	141377	5608	NA	NA	NA	NA	NA
1976	10344	3099	5980	NA	20698	19953	115926	3996	1266	35048	323	1613	183482
1977	11534	2482	5480	NA	22053	16066	121032	4114	981	26517	99	1241	192768
1978	16160	2210	3995	231	21897	10909	110483	2819	1567	47928	214	1837	192550

* Does not include low energy β emitters such as tritium and plutonium - 241

NA - not available

TABLE 3 Annual discharges of fission products from the Windscale outfall (compiled from a number of published sources from BNFL and MAFF (FRL) all of which appear in the bibliography)

Size fraction μm	Activity pCi/g dry weight			^{239}Pu/^{238}Pu [2]
	Total [1]		^{239}Pu [2]	
	Jan 1972	Feb 1972		
< 2			322	4.1
2 - 5.5	340	75	339	4.5
5.5 - 8	110	55	300	3.9
8 - 15	65	37		
15 - 22	38	21	106	4.2
22 - 31	18.5	9.5		
31 - 44	15.5	8.5	44	4.4
44 - 63	11.5	6.5	28	4.1
63 - 125	12	9	16	5.2
> 125	10.5	6		

1. from Hetherington et al, 1975

2. from Hetherington, 1978

TABLE 4 Distribution of total alpha activity and plutonium nuclides with particle size in surface sediment from the Ravenglass Estuary

Station No.	30 (subtidal)			40 (subtidal)				42 (subtidal)			43 (subtidal)			Newbiggin (intertidal)		
Distance from Windscale (km)	110			18.5				9			9					
Profile(cm)	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$	^{241}Am	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$
0-2	-	1.2	-	.630	3.4	5.4	5.2	2.0	12	6.0	5.58	29	5.2	20.2	101	5
2-4	-	0.6	-	1.65	3.8	2.3	4.9	1.55	11	7.1	10.0	44	4.4	14.29	100	7
4-6	.035	0.6	17	.608	3.1	5.1	3.2	1.05	8.6	8.2	6.73	33	4.9	6.50	65	10
6-10	-	0.3	-	.354	2.8	7.9	2.4	.629	8.8	14	4.26	26	6.1	2.46	32	13
10-15	.006	0.18	29	.211	1.9	9.0	1.5	.191	4.2	22	1.33	16	12	.71	22	31
15-20	-	0.04	-	.081	1.3	16	0.8	.105	2.2	21	1.15	15	13	.43	15	25
20-25	.0007	0.02	27	.100	1.3	13	0.4	.057	1.7	30	.335	5.7	17	.29	14	49

TABLE 5 Concentrations of plutonium and americium in selected subtidal and intertidal core samples (Pu and Am concentrations are pCi/g dry weight) (compiled from Hetherington et al, 1976 and Hetherington, 1976a)

Profile (cm)	pCi/g dry weight		
	^{238}Pu	^{239}Pu	$^{239}Pu/^{238}Pu$
0-2	3.93	27.5	7
2-4	4.11	22.6	5.5
4-6	3.67	22.0	6
6-10	1.96	15.7	8
10-15	1.14	6.3	5.5
15-20	0.162	1.7	10.5
20-25	0.256	2.3	9
25-30	0.140	1.4	10
30-35	0.078	0.47	6
35-40	0.052	0.26	5
40-45	0.028	0.17	6
45-50	0.028	0.11	4
50-55	0.018	0.11	6

TABLE 6 Concentrations of ^{238}Pu and ^{239}Pu in a long gravity core from Station 43

(from Hetherington, 1976a)

Profile cm	Solid Phase pCi/g		Liquid Phase pCi/ml		Activity of solid / Activity of liquid
	^{239}Pu	$^{239}Pu/^{238}Pu$	$^{239}Pu \times 10^4$	$^{239}Pu/^{238}Pu$	
0- 4.5	91	4.3	5.9*	1.0	1.6×10^5
4.5- 9.5	72	5.0	7.6	3.0	9.5×10^4
9.5-14.5	16	21	9.2	4.8	1.7×10^4
14.5-19.5	19	54	4.8	1.7	4.0×10^4
19.5-24.5	6.3	53	5.1	5.5	1.2×10^4
24.5-29.5	4.1	162	3.6	3.5	1.1×10^4

Profile cm	Solid Phase pCi/g		Liquid Phase pCi/ml		Activity of solid / Activity of liquid
	^{239}Pu	$^{239}Pu/^{238}Pu$	$^{239}Pu \times 10^4$	$^{239}Pu/^{238}Pu$	
0- 3.5	153	4.1	8.5	4.1	1.8×19^5
3.5- 8.5	148	3.7	2.3	6.9	6.4×10^5
8.5-13.5	107	8.5	3.2	1.3	3.3×10^5
13.5-18.5	43	13	2.0	11.0	2.1×10^5
18.5-23.5	27	19	3.6	1.2	7.5×10^4
23.5-28.5	18	50	3.2	4.6	5.6×10^4

* NB This activity is 5.9×10^{-4} pCi/ml

TABLE 7 Distribution of plutonium nuclides with depth in the solid and interstitial water phases of two intertidal cores from Newbiggin
(from Hetherington, 1978)

Location	Distance from Windscale km	Activity pCi/g dry weight		
		^{241}Am	^{239}Pu	^{241}Am/^{239}Pu
	6	17	19	0.89
		57	93	0.61
Mouth of R Irt	7.5	-	0.4	-
Mouth of Ravenglass(N)	10	170	213	0.80
Mouth of Ravenglass(S)	11	231	228	1.01
Mouth of R Esk (S)	12	232	267	1.21
Mouth of R Esk (N)	12	44	67	0.66
		232	211	1.10
Head of Duddon Esk	25.5	17	17	1.00
Mouth of R Leven	38	2	3	0.67
Mouth of R Kent	52.5	1	1	1.00
N shore of Lune Est	64	5	10	0.50

N = north shore   S = south shore

TABLE 8 Comparison of the concentrations of americium-241 and plutonium-239 from the Cumbrian coast.

(from James, 1978; NRPB)

Fraction	% Mass	% Activity	Concentration factor*
Organic residue	2 ± 1.5	1.5 ± 2.2	0.6 ± 0.6
Sand	57 ± 9	7.4 ± 1.1	0.13 ± 0.03
Silt > 1 µm	35 ± 10	67 ± 15	1.9 ± 0.2
Silt < 1 µm	6 ± 1.4	25 ± 15	3.8 ± 1.3

* Concentration factor is the ratio of the concentration per unit dry weight in a given fraction to the concentration per unit dry weight in the bulk sample

TABLE 9 Fractionation of americium - 241 in a range of Ravenglass sediments

(from James, 1978; NRPB)

Year	Radionuclide							
	^{95}Zr + ^{95}Nb		^{106}Ru		^{137}Cs		^{144}Ce	
	A pCi/g	B pCi/g	A pCi/g	B pCi/g	A pCi/g	B pCi/g	A pCi/g	B pCi/g
1967	610	5	614	13	-	-	563	15
1968	1430	8	995	15	-	-	737	27
1969	2028	12	1317	21	-	-	668	18
1970	677	13	1212	16	85	1	752	22
1971	778	8	1499	15	98	1	1040	22
1972	808	6	1337	16	95	1	780	21
Mean	1055	9	1162	16	93	1	757	21

A - Mean annual activity in surface sediments

B - Mean annual activity per Ci/day discharged

TABLE 10 Radioactivity in surface fine sediment from the Ravenglass Estuary

(from Hetherington and Jefferies, 1974)

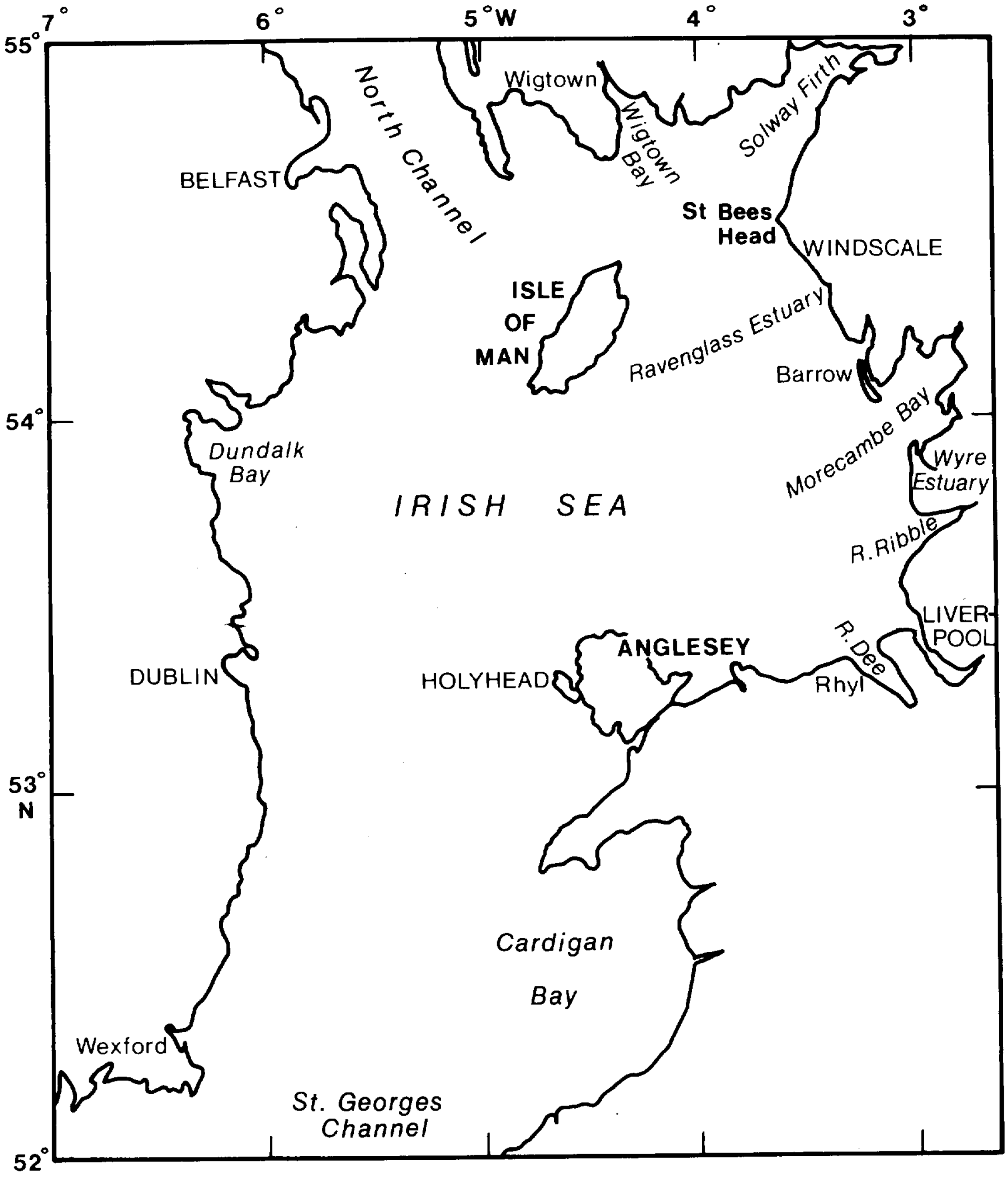


Figure 1 Locality map of the Irish Sea

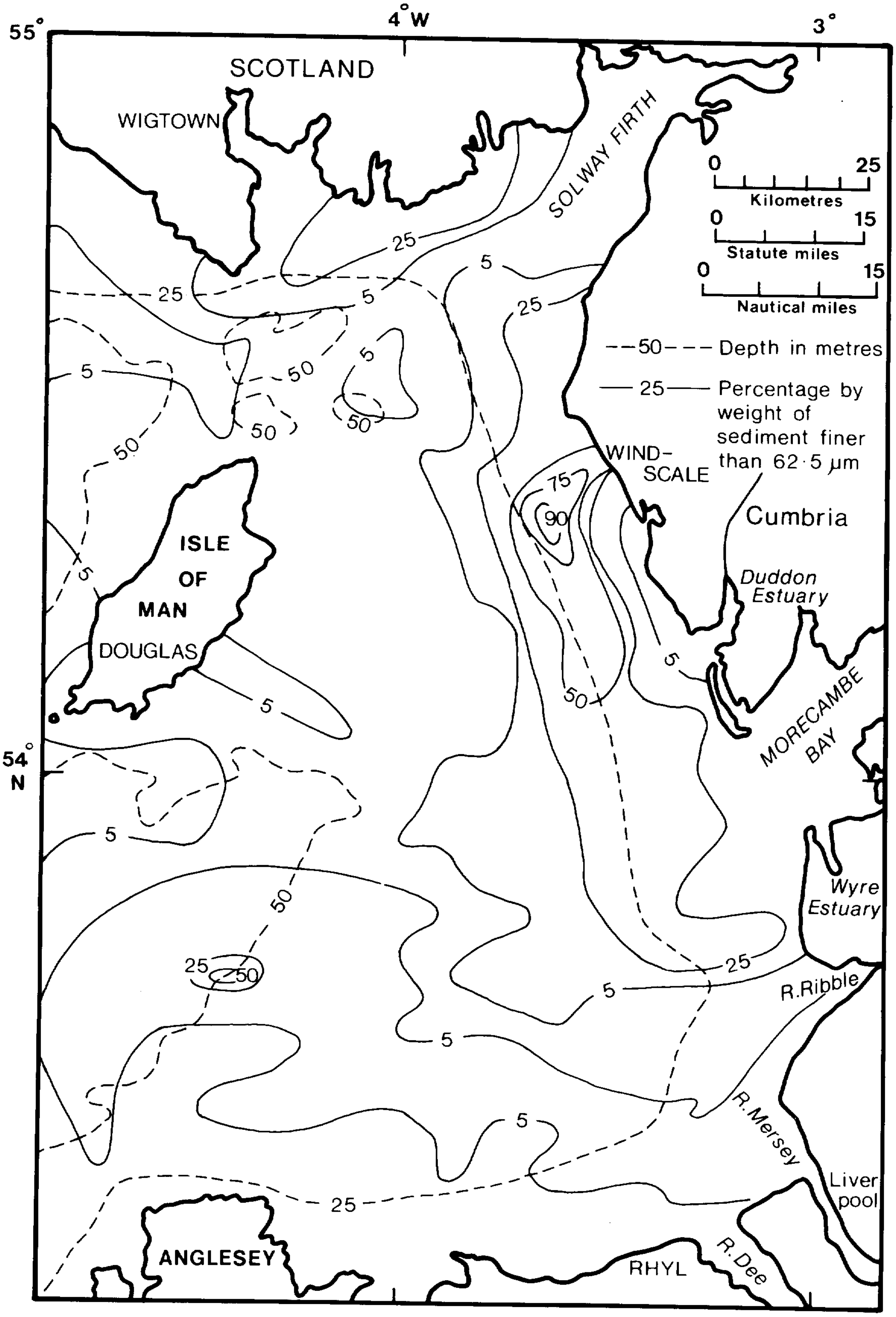


Figure 2 Surface sediment distribution in the north-eastern Irish Sea (from Nunny 1978 based on data by Pantin 1978)

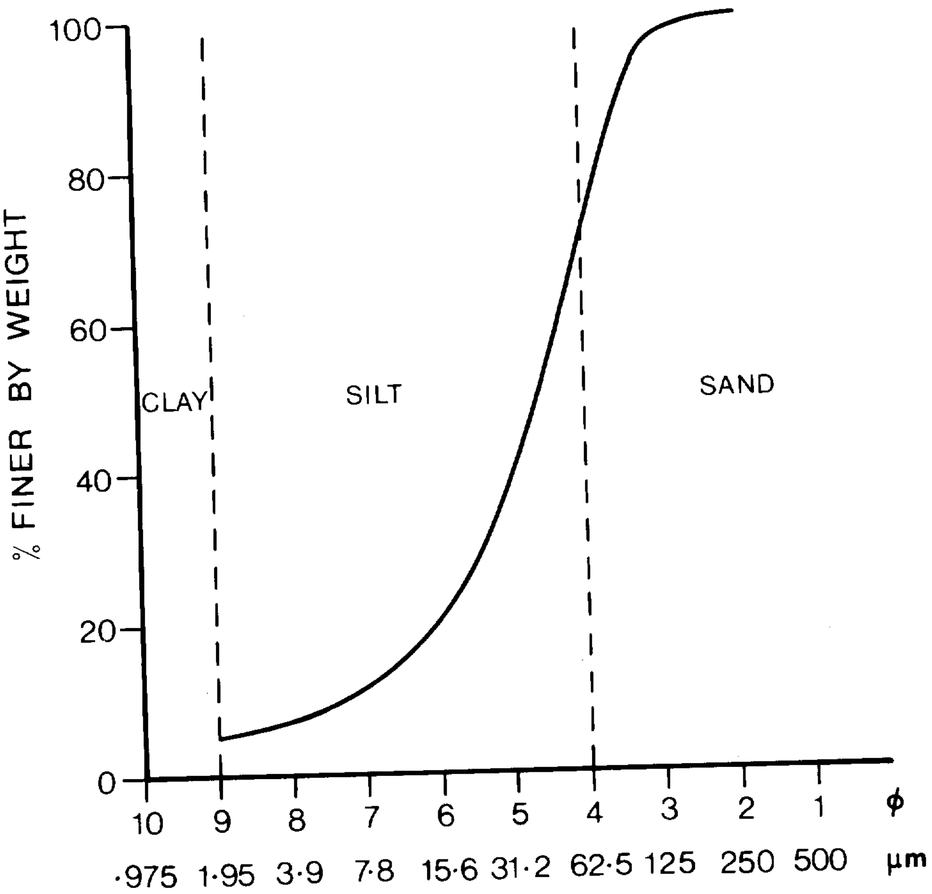


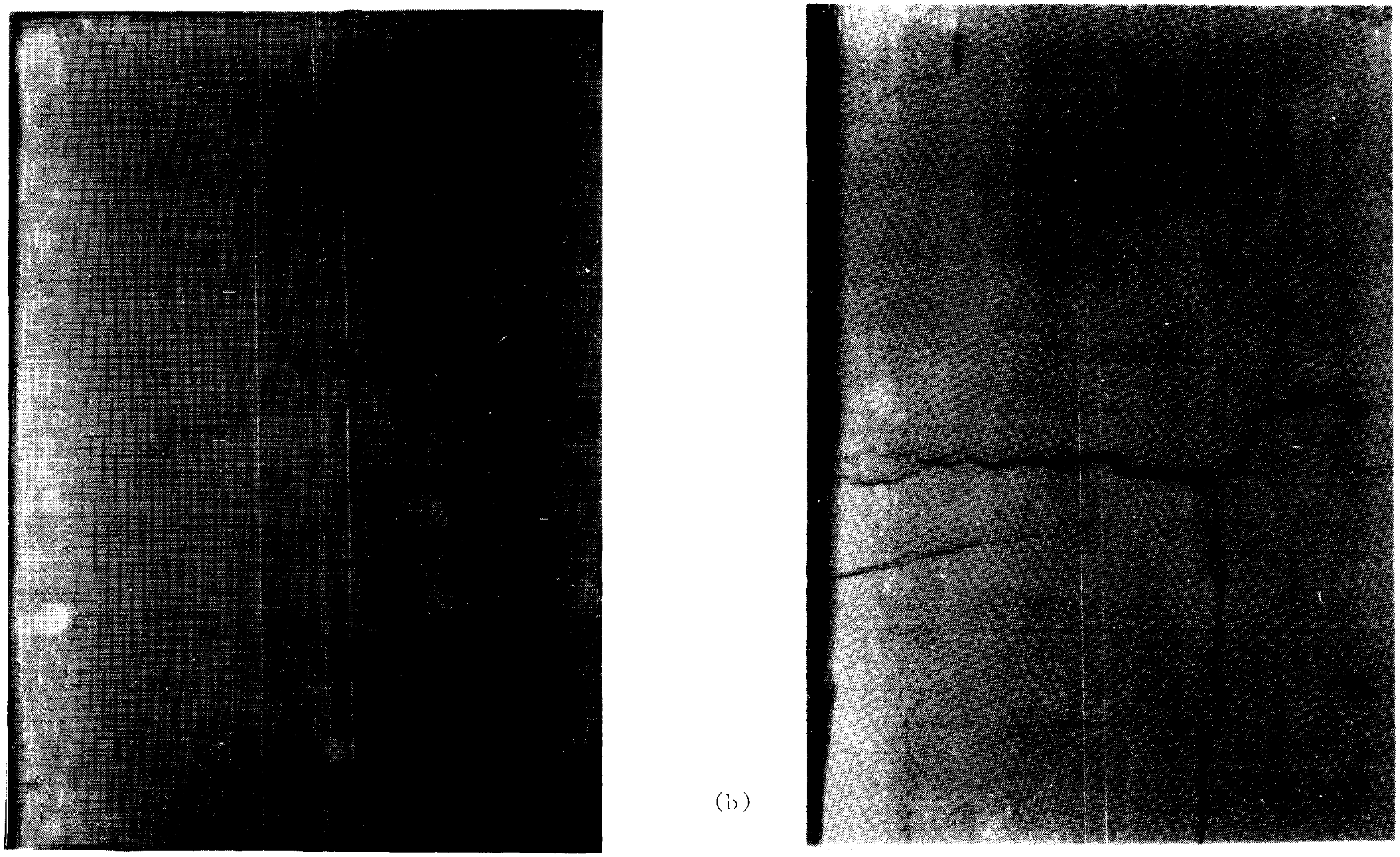
Figure 3 Cumulative particle size distribution of an intertidal sediment sample from the Ravenglass Estuary, January-March 1971 (from Hetherington and Jefferies, 1974)

(a)

(b)

Figure 4 Locations of the sample sites at Newbiggin in the Ravenglass Estuary

a) box core WRP 20 b) box core WRP 23



(a) (b)

Figure 5 X-radiographs of box cores from intertidal mud flats at Newbiggin in the Ravenglass Estuary

a) box core WRP 20 b) box core WRP 23

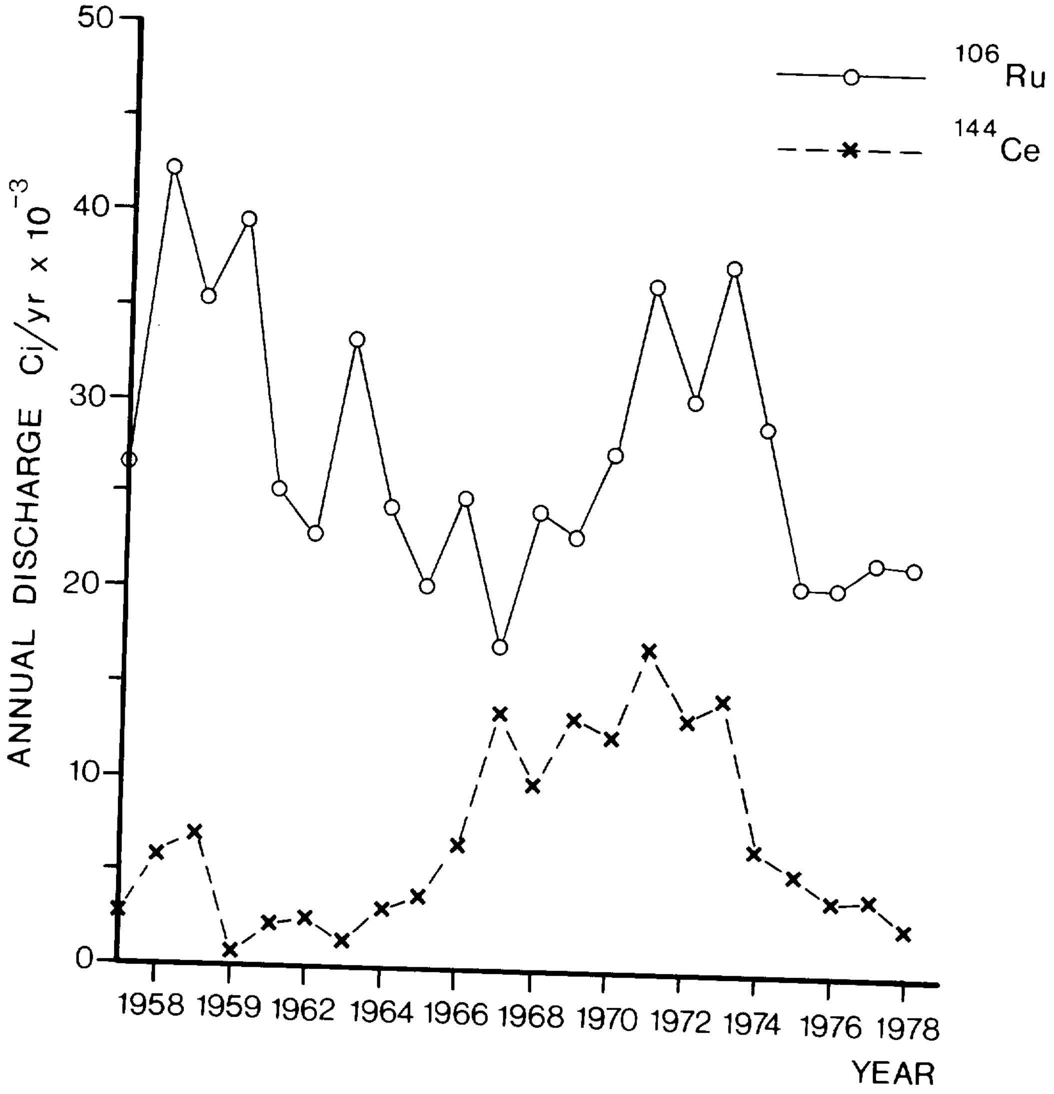


Figure 6 Annual discharges of ruthenium-106 and cerium-144 in the low level liquid effluent

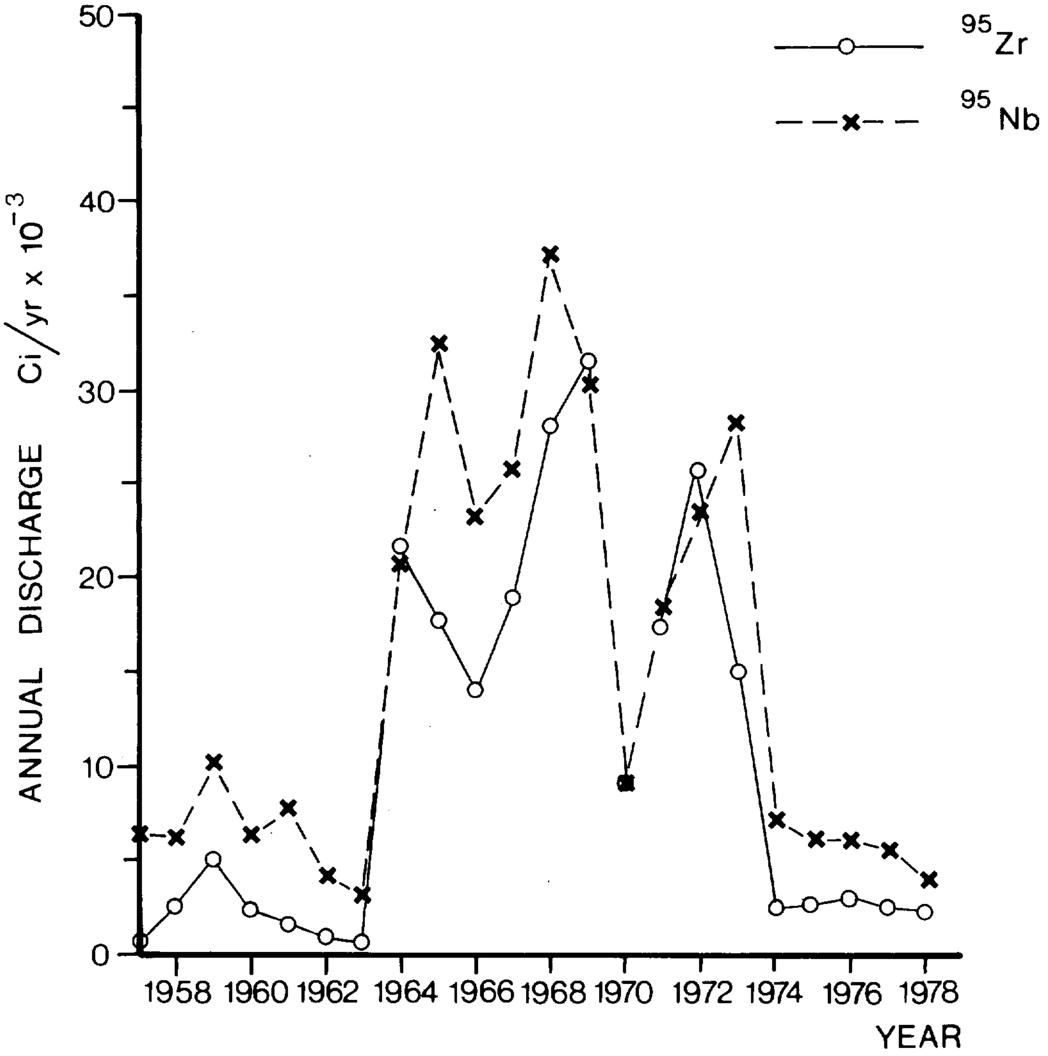


Figure 7 Annual discharges of zirconium-95 and nobium-95 in the low level liquid effluent

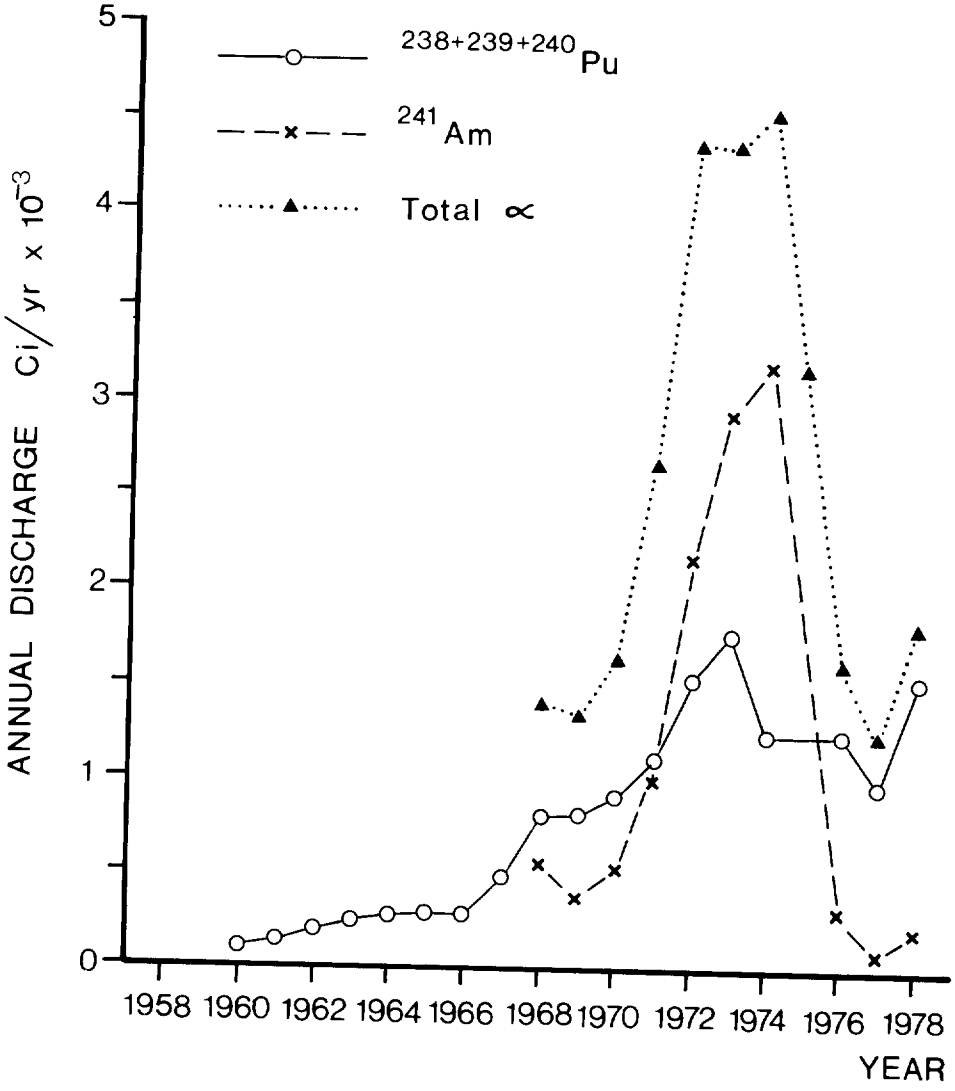


Figure 8 Annual discharges of caesium-134 and caesium-137 in the low level liquid effluent

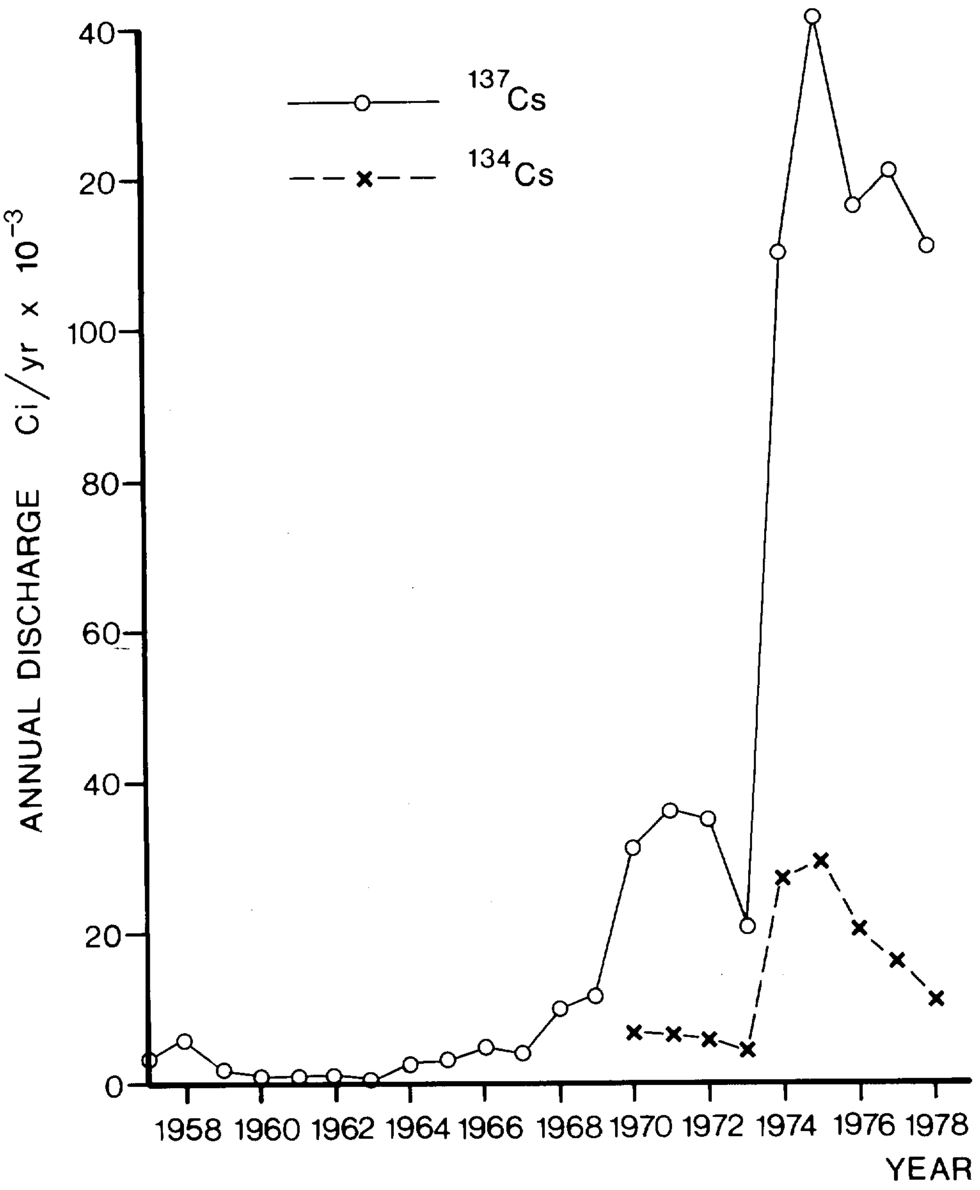


Figure 9 Annual discharge of total alpha activity, plutonium-238 + 239 + 240 and americium-241 in the low level liquid effluent

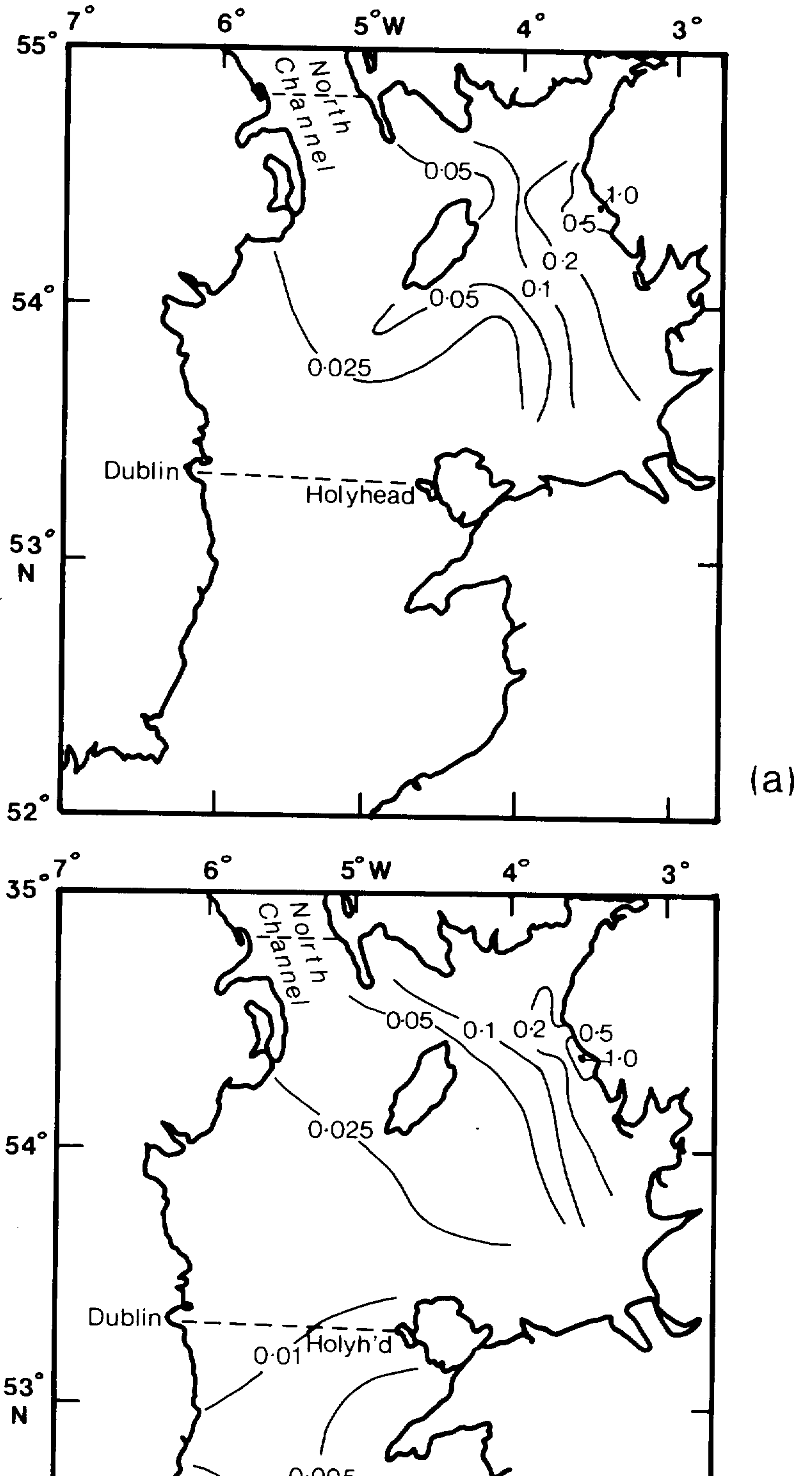


Figure 10 Distribution of ^{239}Pu in filtered surface water of the Irish Sea. a) July 1973; b) July 1974. Contours are in pCi/l. (Hetherington, 1976a).

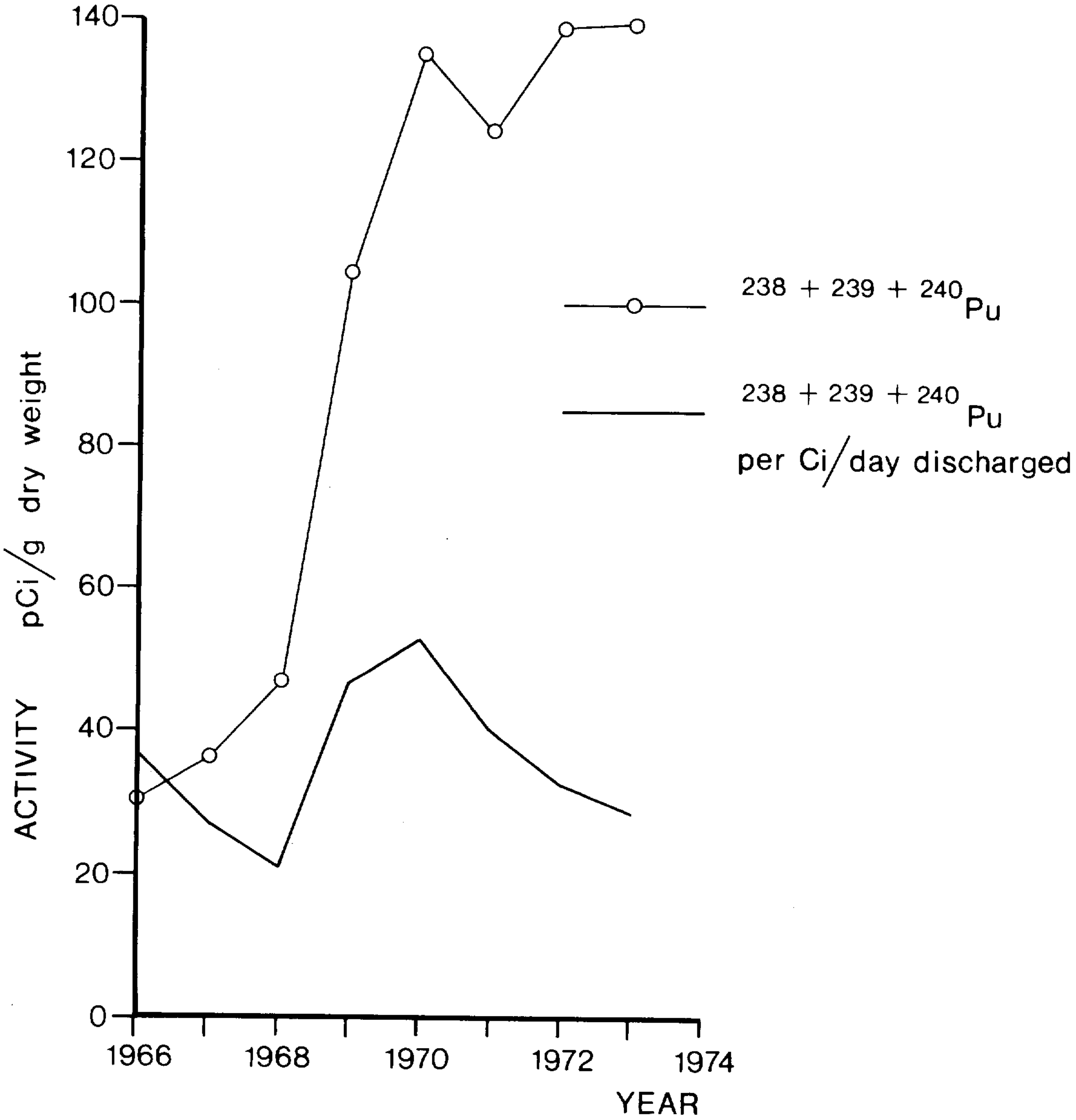


Figure 11 Plutonium activity in intertidal surface sediment from the Ravenglass Estuary
(from Hetherington, 1976a)

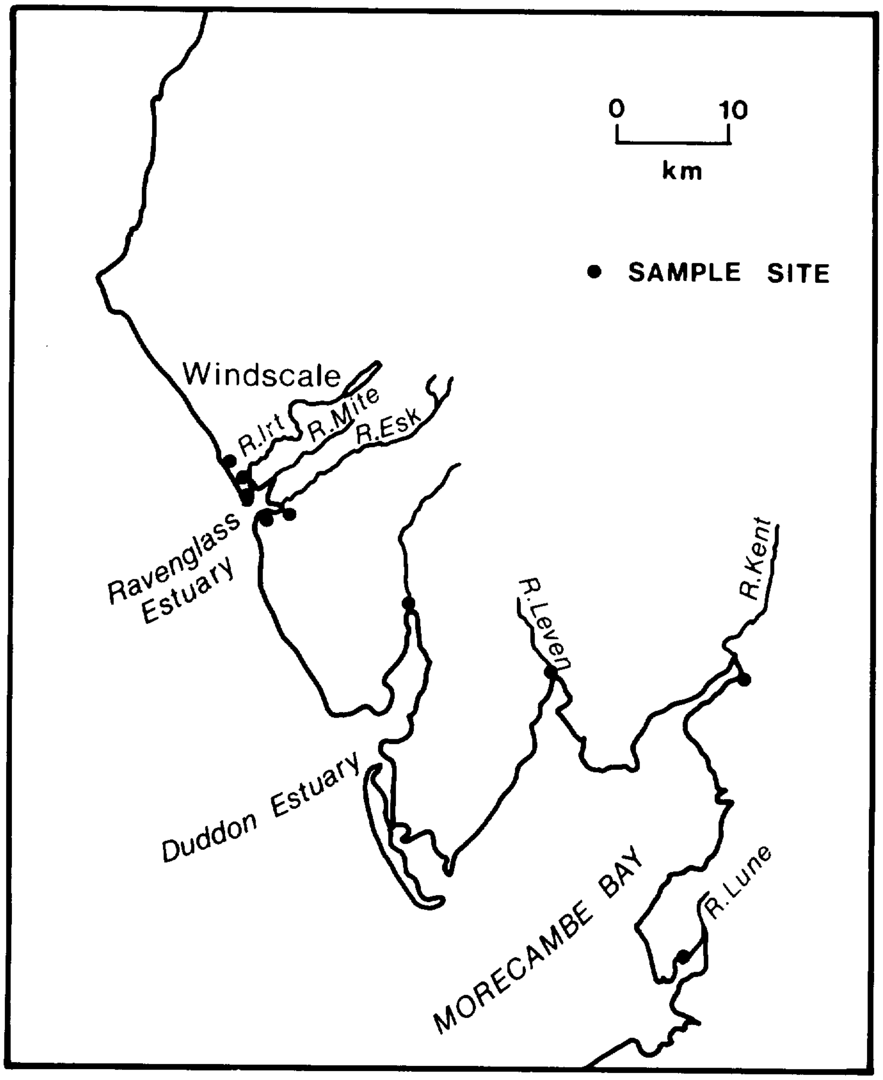


Figure 12 N.R.P.B. surface sediment sampling sites (from James et al, 1978)

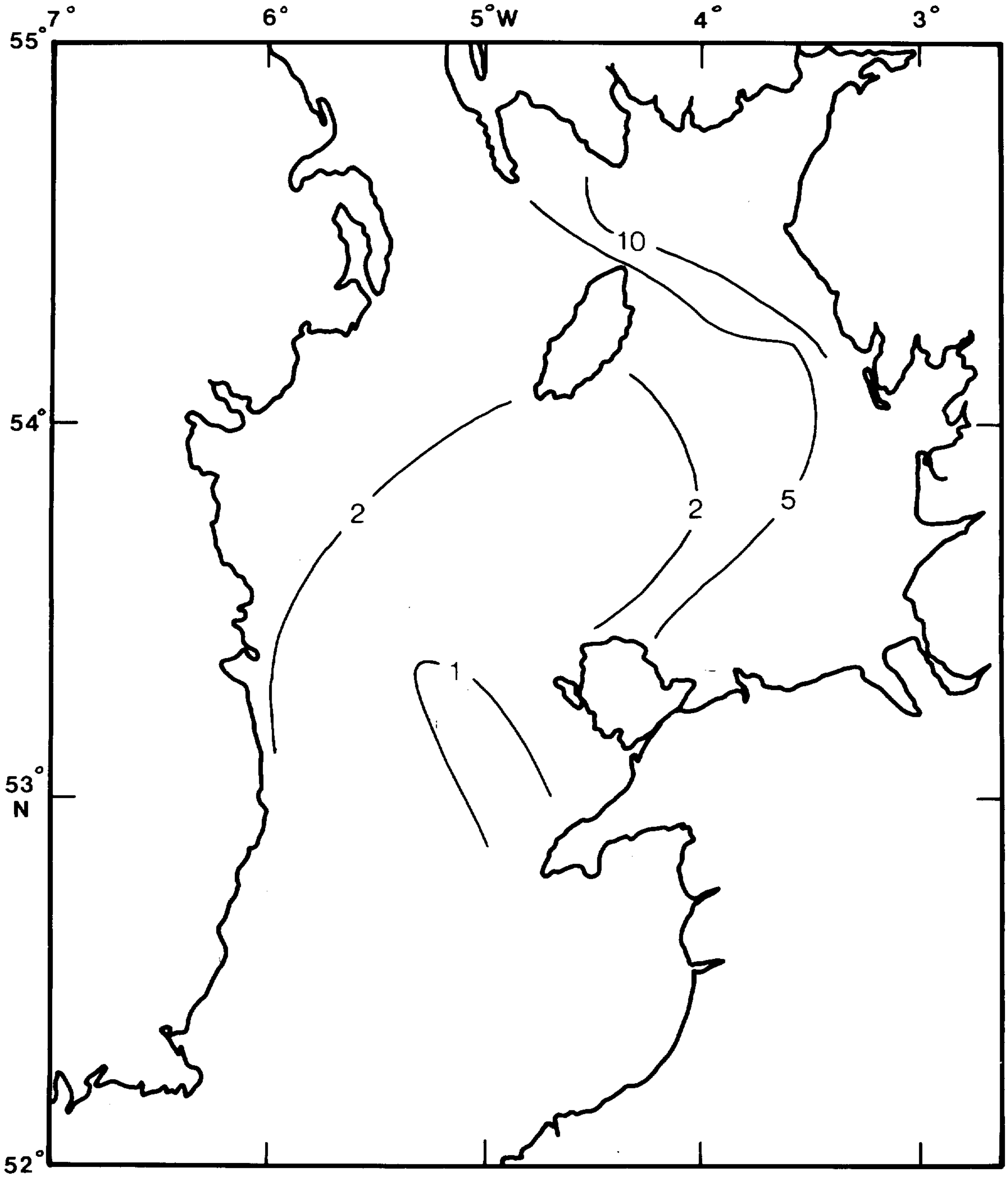


Figure 13 Concentration of caesium-137 in filtered sea water of the Irish Sea, September 1968. Contours are in pCi/l.

(from Preston et al, 1971)

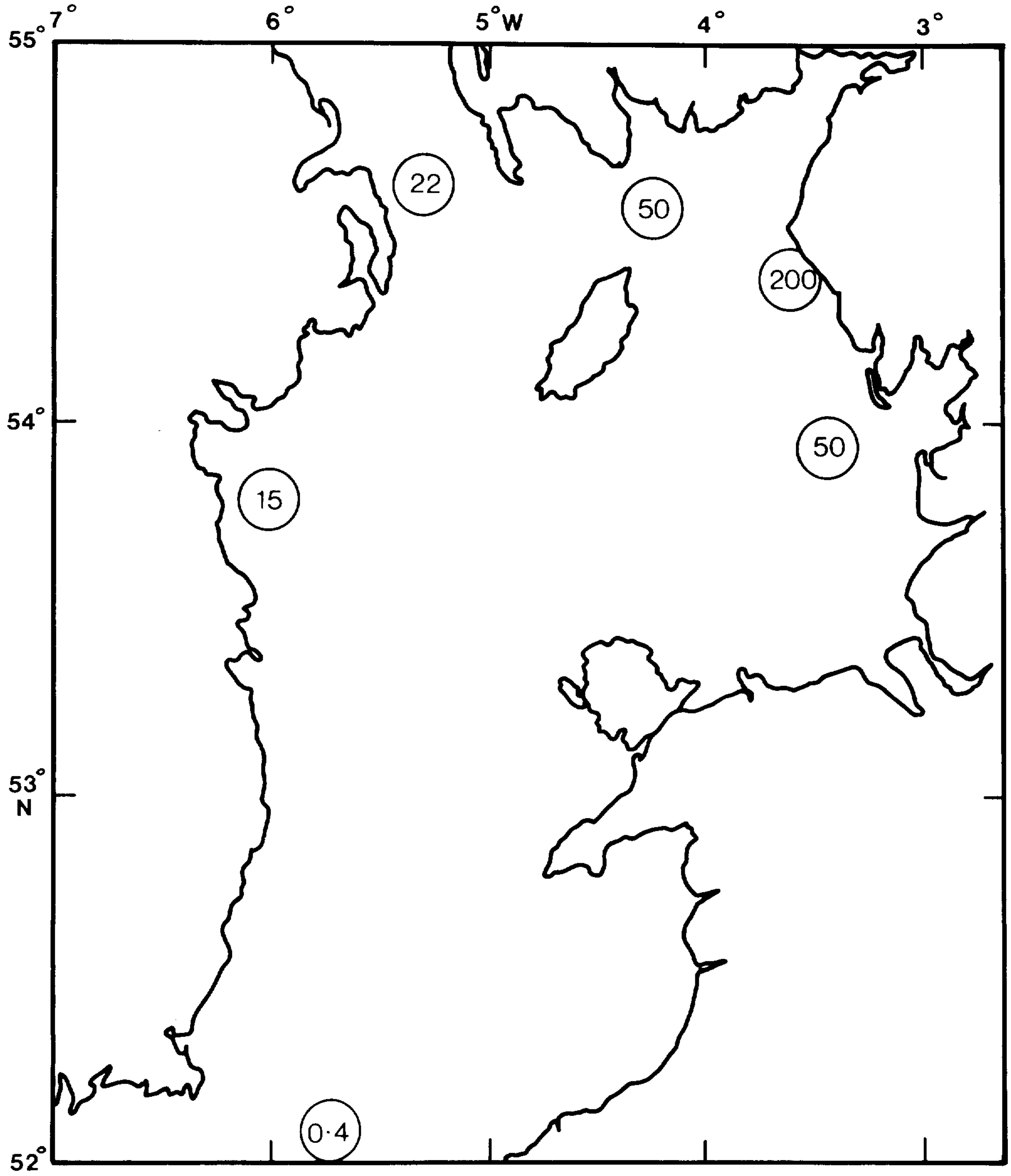


Figure 14 Concentration of caesium-137 in filtered sea water of the Irish Sea, May/June 1972. Values are in pCi/l

(from Mitchell, 1975)

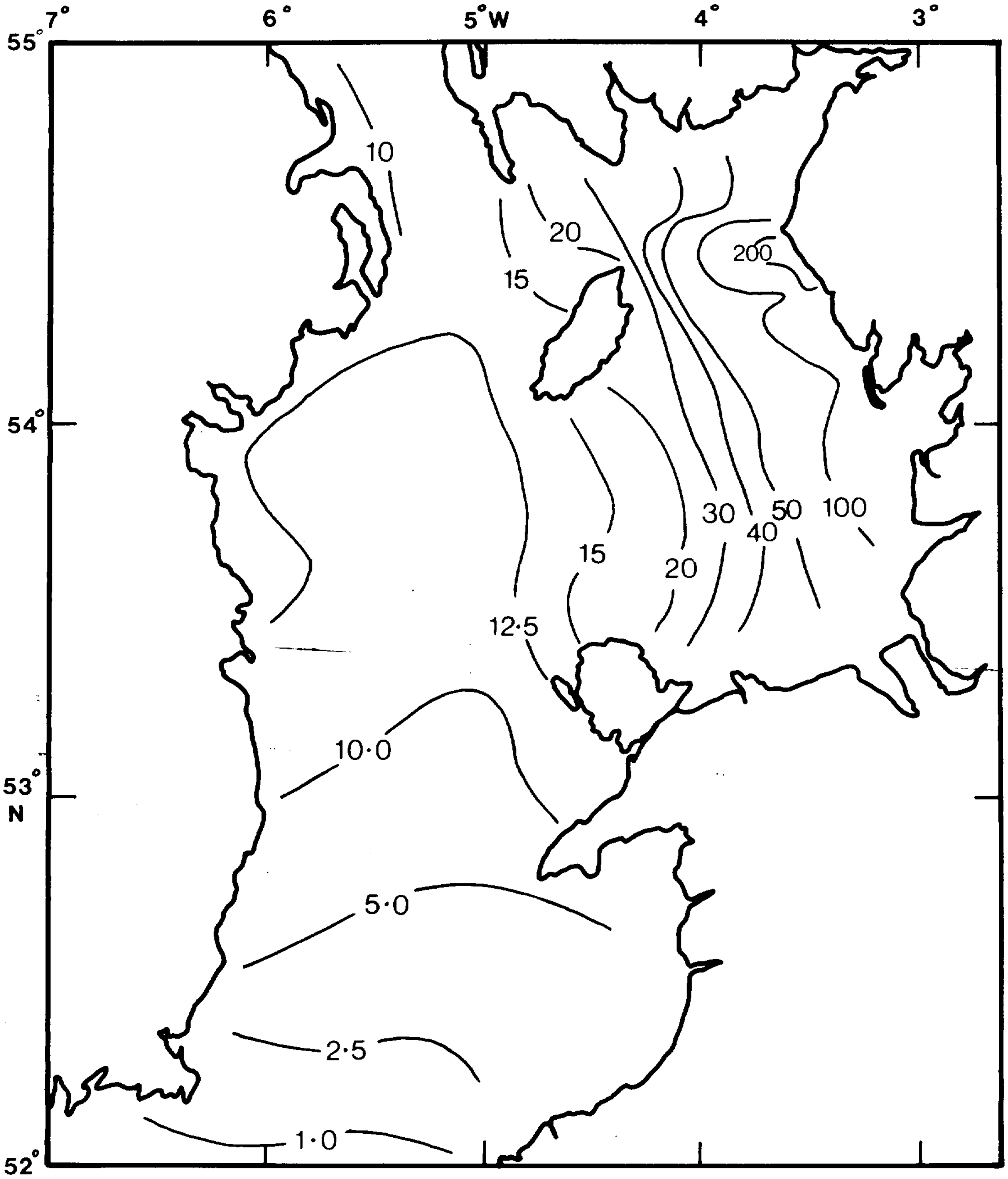


Figure 15 Concentration of caesium-137 in filtered sea water of the Irish Sea, July 1973. Contours are in pCi/l

(from Hetherington, 1976a)

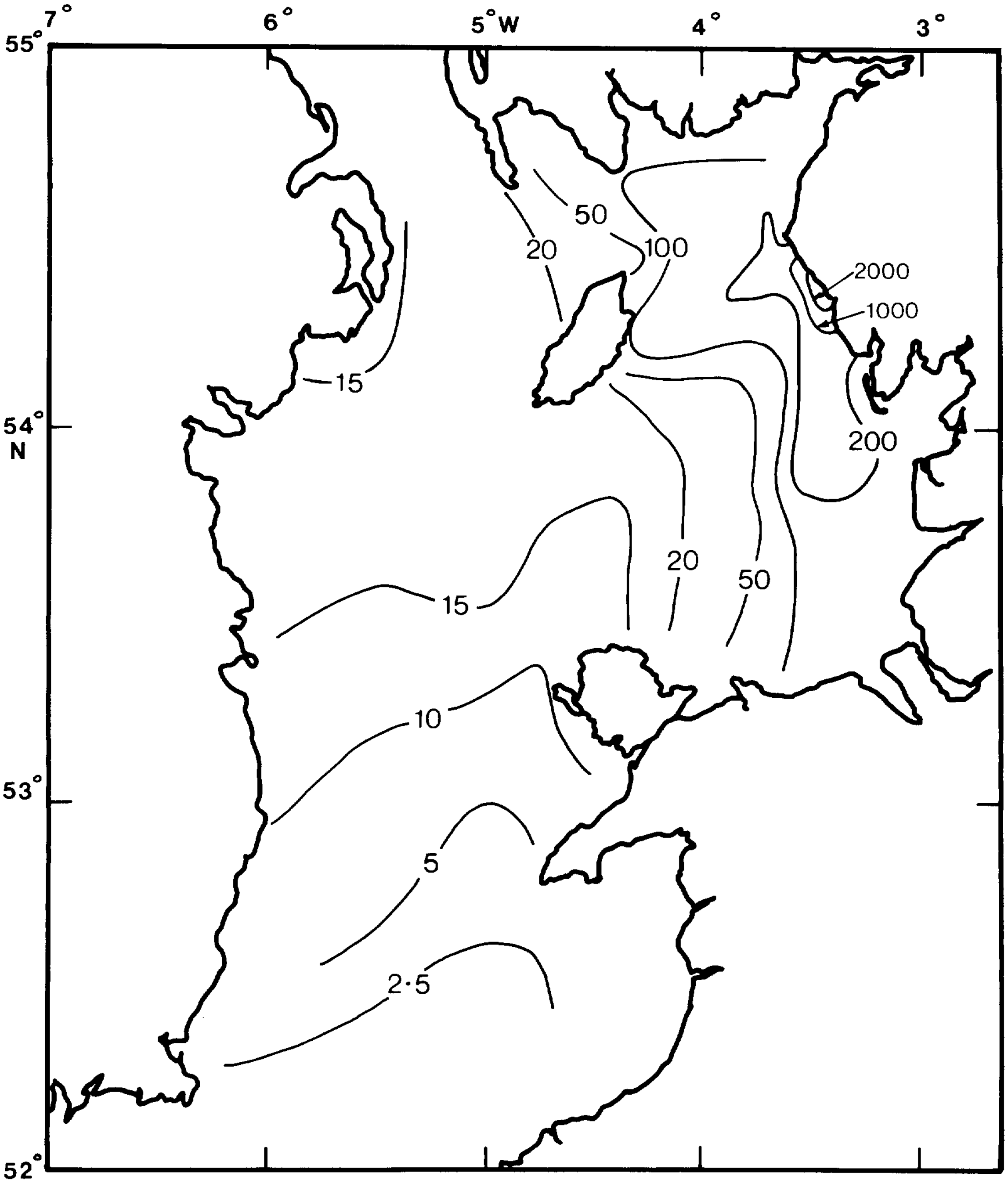


Figure 16 Concentration of caesium-137 in filtered sea water of the Irish Sea, July 1974.
Contours are in pCi/l

(from Hetherington, 1976b)

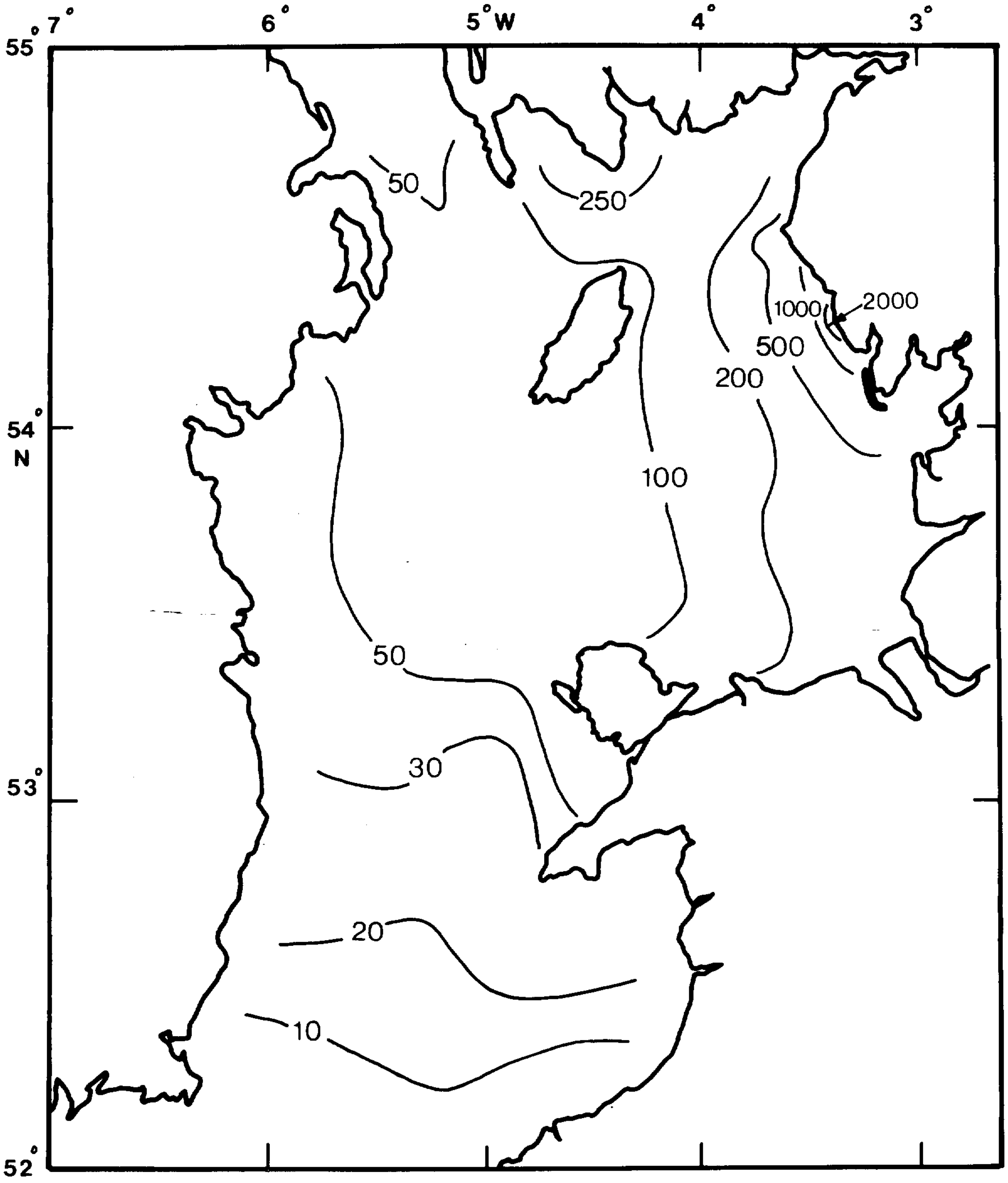


Figure 17 Concentration of caesium-137 in filtered sea water of the Irish Sea, January 1976.
Contours are in pCi/l

(from Mitchell, 1977b)

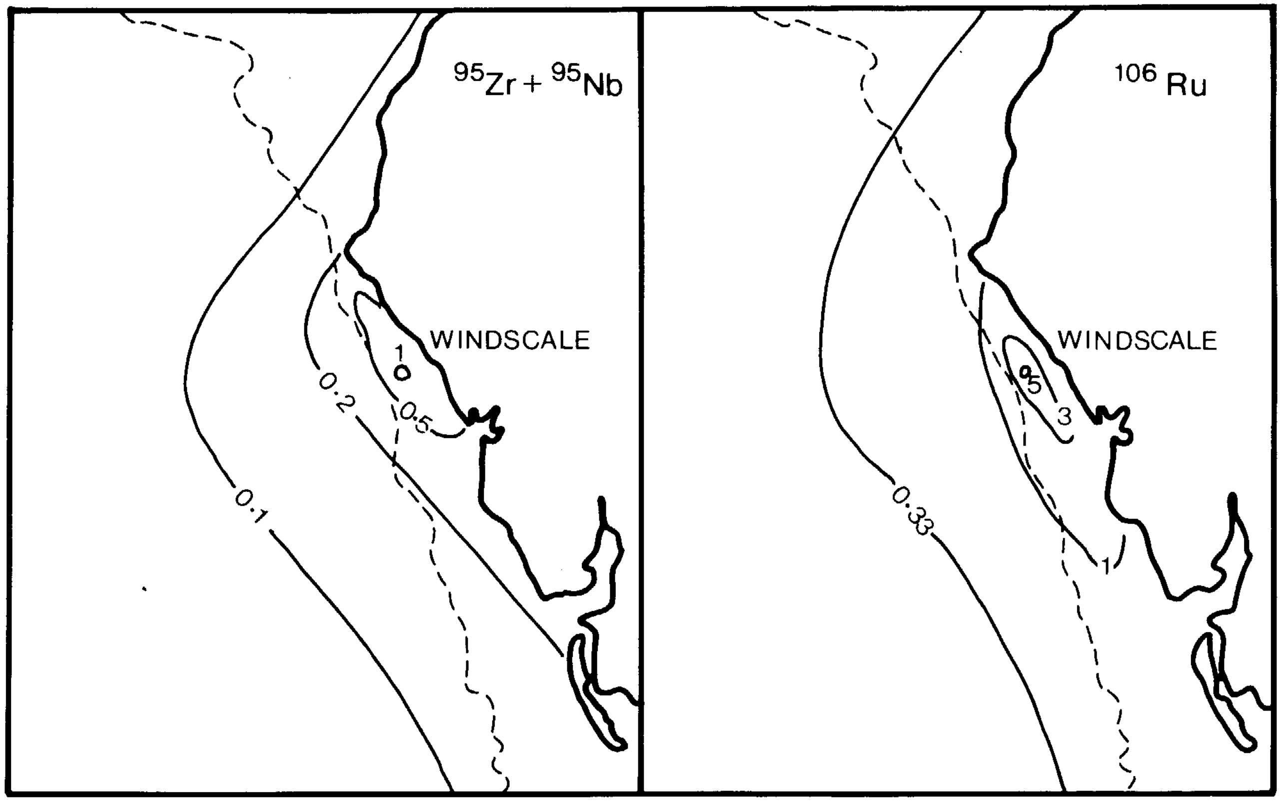


Figure 18 Radionuclide concentrations in surface sea water near the Windscale outfall (1963-1966). Contours are pCi/l per Ci/day discharged (from Hetherington and Jefferies, 1974)

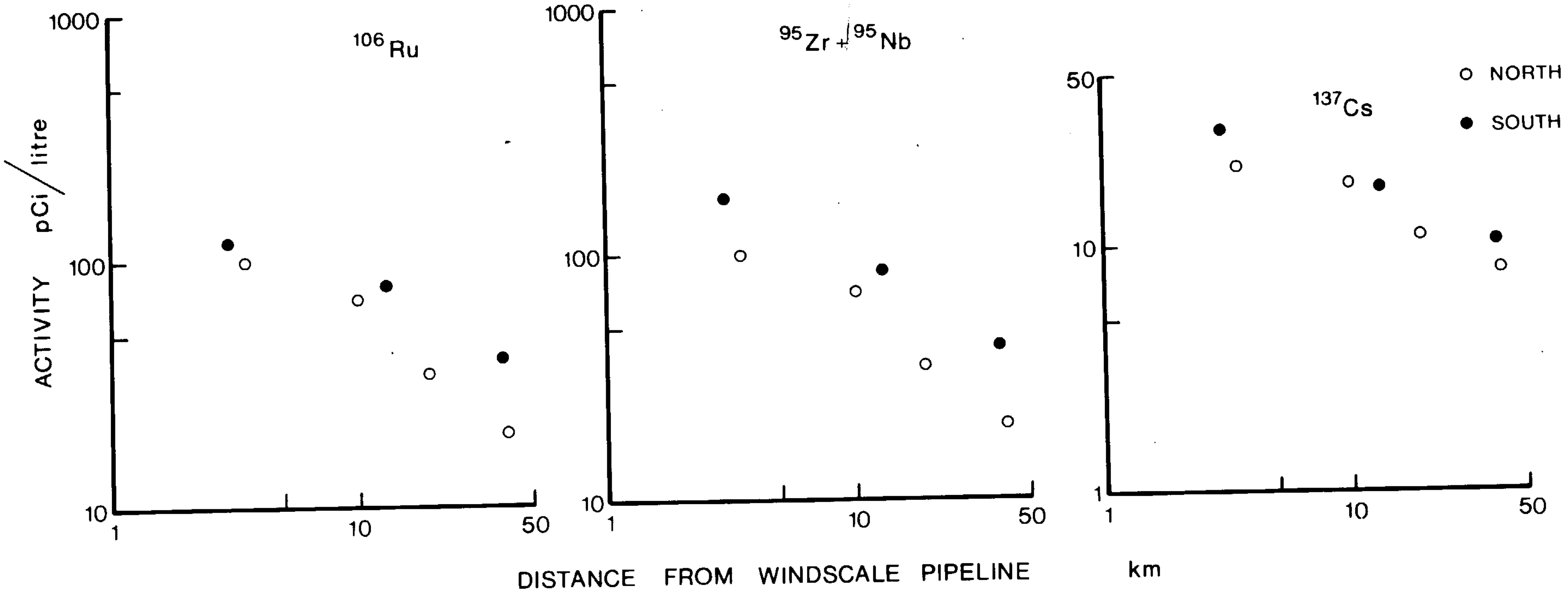


Figure 19 Radionuclide concentrations in coastal filtered sea water as a function of distance from Windscale, 1964-1966 (from Preston et al, 1981)

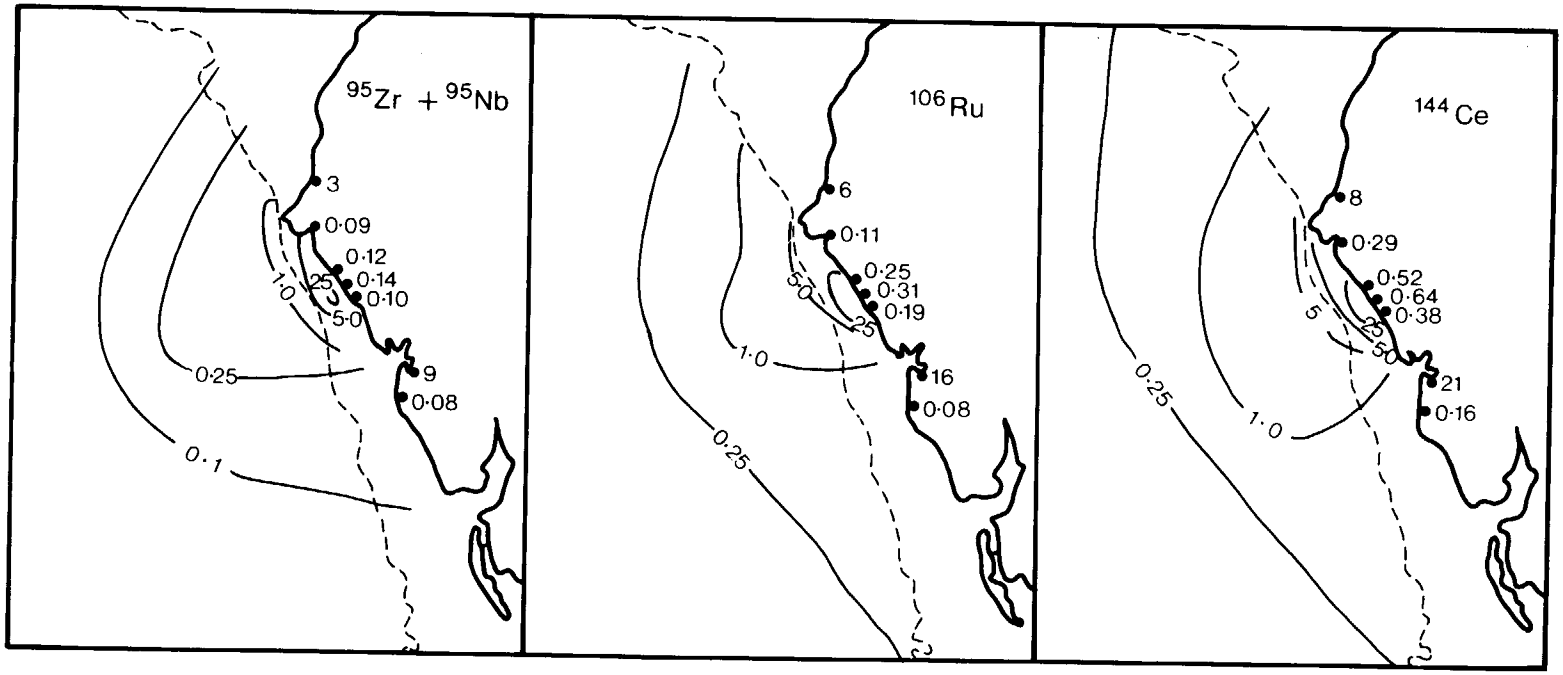


Figure 20 Radionuclide concentrations in surface sea bed sediments near the Windscale outfall. Contours are the mean values over the period 1968 to 1971 in pCi/l dry weight per Ci/day discharged (from Hetherington and Jefferies, 1974)

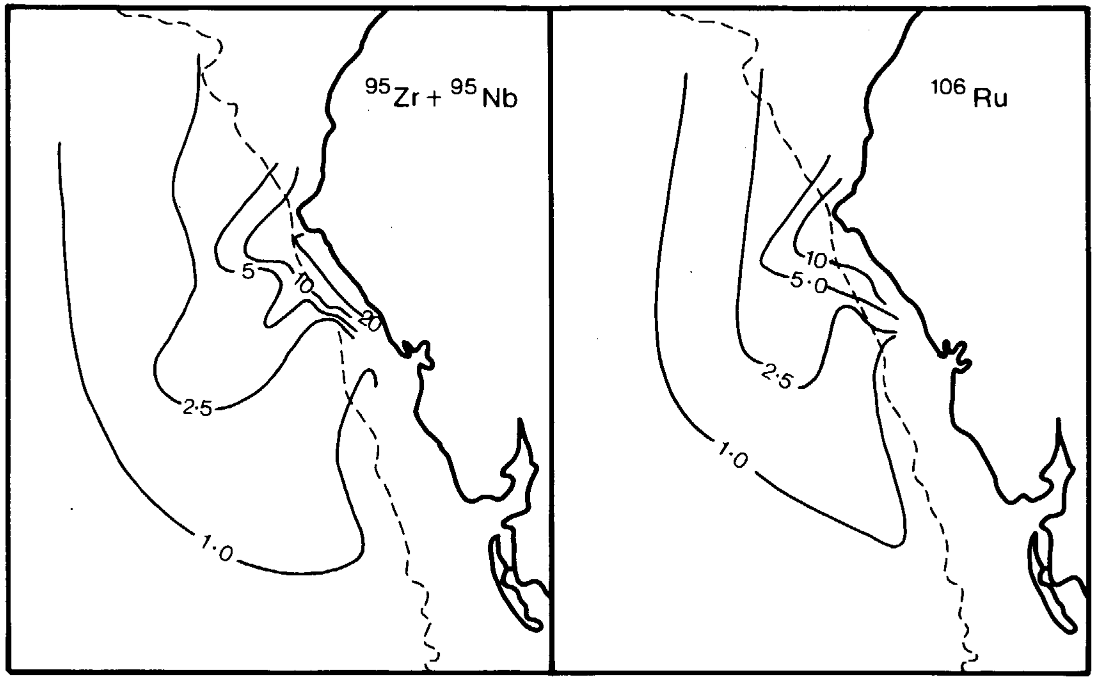


Figure 21 Radionuclide partition coefficients (x 10^{-3}) near the Windscale outfall (from Hetherington and Jefferies, 1974).

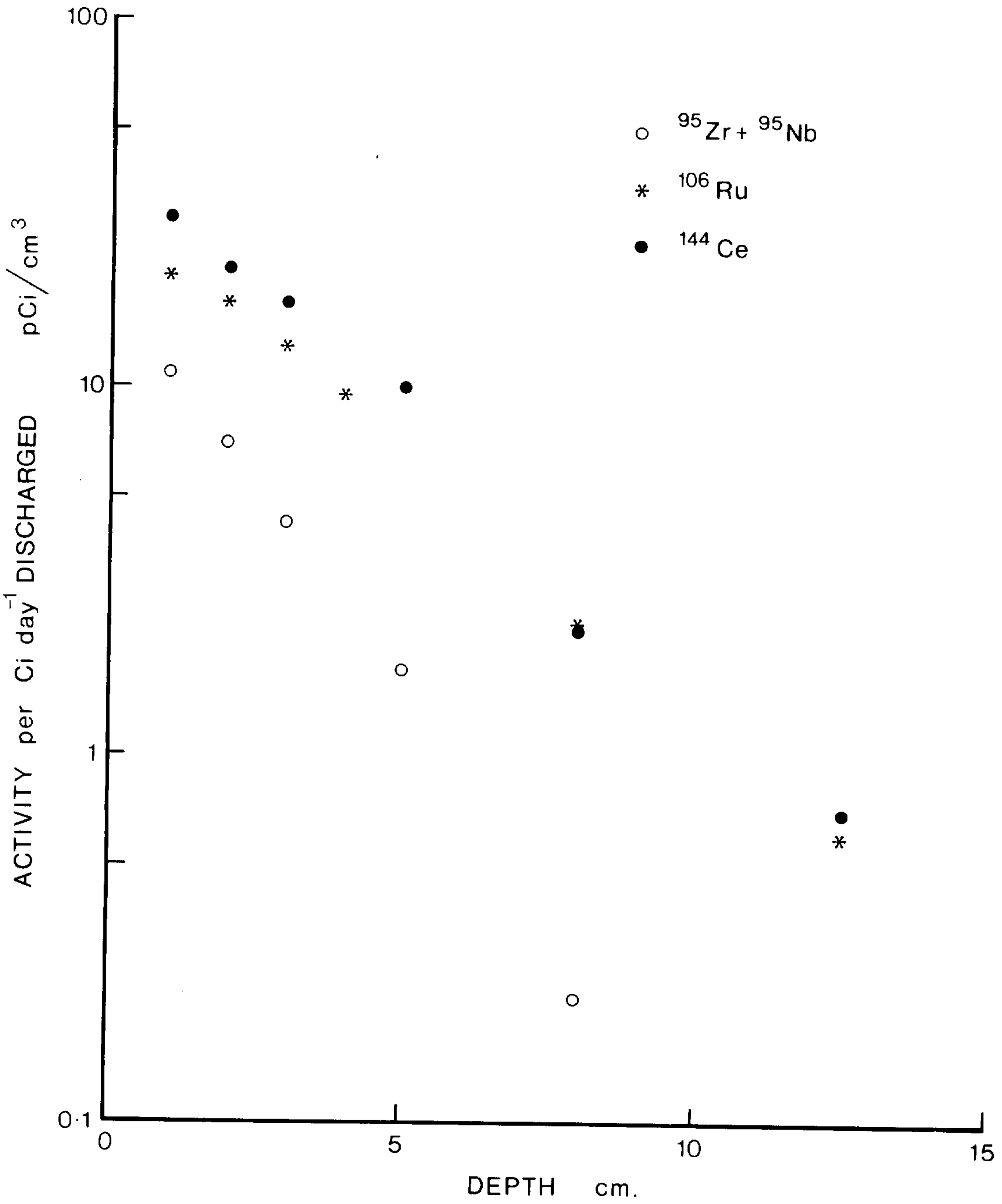


Figure 22a Depth distribution of radionuclide activity in sediments from the Ravenglass Estuary (from Hetherington and Jefferies, 1974)

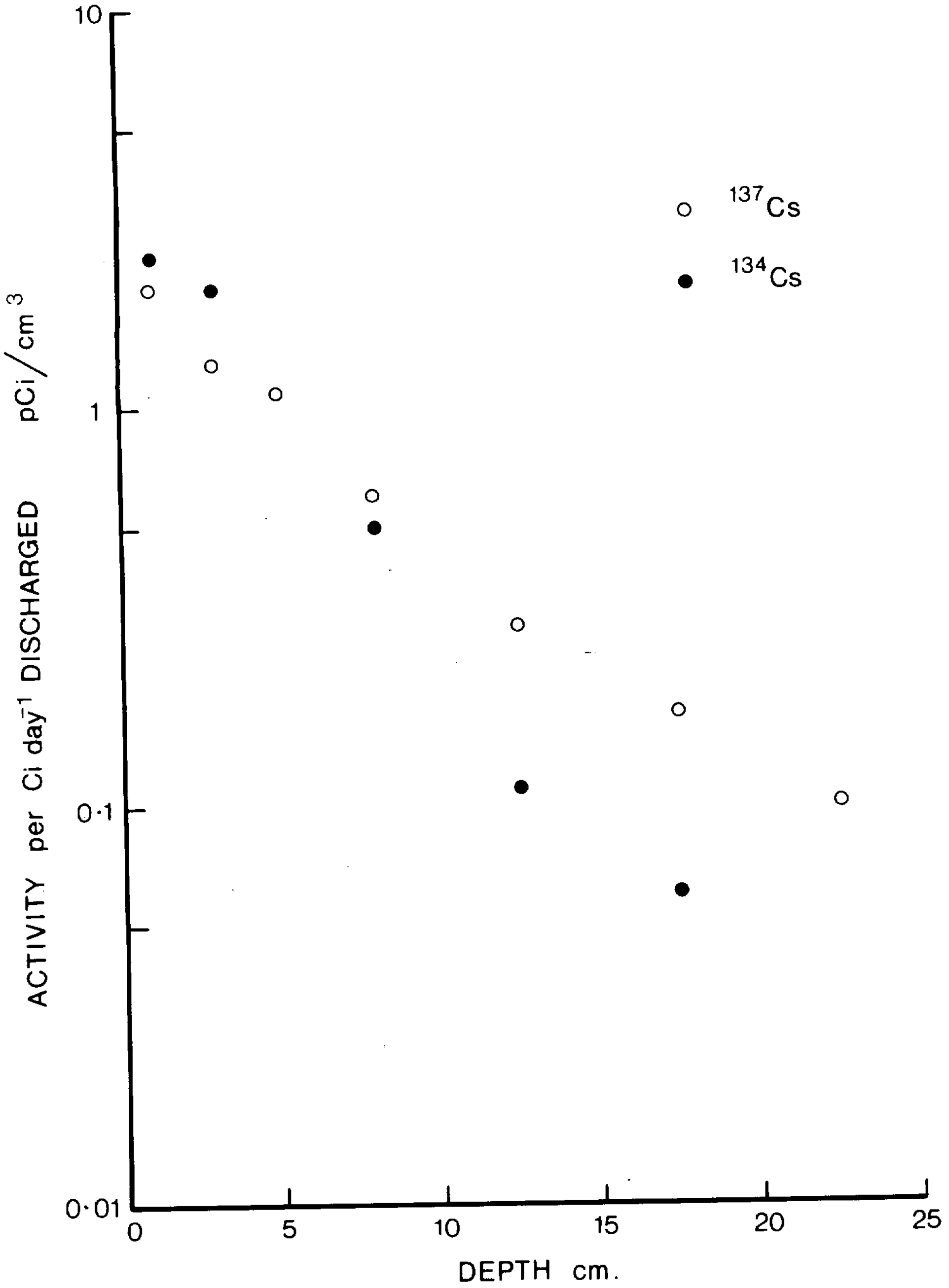


Figure 22b Depth distribution of radionuclide activity in sediments from the Ravenglass Estuary (from Hetherington and Jefferies, 1974)

APPENDIX A

THE INTERACTION BETWEEN RADIONUCLIDES AND SOILS AND SEDIMENTS

A.1 General

The precise mechanism by which radionuclides are retained by soils and sediments under the variety of possible environmental conditions is not fully understood. In Irish Sea sediments activity associated with various grain sizes has been found to be proportional to the specific surface area of the sediment (Jones, 1960, Jefferies, 1968). This has been interpreted as evidence of a surface adsorption phenomenon (Hetherington, 1976a). However, many radionuclides appear to be retained by certain clay minerals either within the crystal lattice interlayers or at exchange sites on the edges of the interlayers (Fredriksson et al, 1966). The ion exchange can be with other elements or a stable isotope of the same element (Jeene and Wahlberg, 1968; Duursma and Bosch,1970). This was supported by evidence that radionuclides are more strongly sorbed* to minerals with a high cation exchange capacity (Duursma and Eisma, 1973). For example, radiocaesium is retained very strongly by illite (Tamura and Jacobs, 1960) and chlorite (Garder and Skulberg, 1964) but less strongly by kaolinite and montmorillonite (Graham and Killion, 1962; Tamura, 1964). An increased carbonate content has also been found to be slightly correlated with a reduction in radionuclide uptake which could be due to the lower cation exchange capacity of carbonate minerals (Duursma and Gross, 1971).

The ability of soils and sediments to retain radionuclides and the degree to which they are able to migrate has been found to depend on many factors. Nishita et al (1956) demonstrated that the retention of caesium on clay minerals varied slightly with pH over the range pH 3.5 to pH 10.0. Rhodes (1957) also found that pH affected the uptake by soils of radioactive isotopes of various elements, including caesium and plutonium, from solution. Rhodes (1957) also showed that

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* The term sorption is used to denote any reaction between the sediments and a radioactive solution whereby activity is transferred to the sediment, and thus includes both absorption and adsorption reactions.

the retention of caesium was reduced in the presence of sodium chloride, a result confirmed by Aston and Duursma (1973). Graham and Killion (1962) demonstrated that the uptake of cobalt, caesium and strontium depended not only on the characteristics of the nuclide and the soil mineral type but also on the concentration of organic matter in the soil. The uptake of caesium has also been found to depend on the concentration of the radionuclide, the concentration of ions which compete with the radionuclide ions for retention sites and the time available for sorption (Tamura, 1964; Garder and Skulberg, 1964). Duursma and Bosch (1970) argued that the weak sorption of strontium-90 (^{90}Sr) and calcium-45 (^{45}Ca) suggested an exchange reaction with their stable isotopes. However, the sorption of cobalt-60 (^{60}Co) and zinc-65 (^{65}Zn) was found to be independent of the stable carrier concentration at low concentrations of the carrier, which implied that exchange reactions with other ions dominated over ion exchange with the stable isotope of the same element.

The concentrations of chelating agents and other chemicals which could form complexes with the radionuclides also influence the uptake of radionuclides by soils (Essington and Nishita, 1966). Finally, Duursma and Gross (1971) concluded that sorption was affected by the chemical properties of the radionuclide and the physiochemical and biological condition of the sediment, for example the pH, Eh, zeta potential, bacterial activity etc, rather than the bulk sediment composition.

Radionuclides can also be retained on soils and sediments by other mechanisms. These include retention of the thin films of water and hydrated oxide or humus on particle surfaces (Edgington et al, 1976a) and direct prcipitation or nucleation onto existing sediments (Aston and Duursma, 1973). The formation of particulate radioisotopes has also been shown for a number of radionuclides in the absence of sediment particles (Aston and Duursma, 1973). Murray and Fukai (1975) demonstrated that the formation of plutonium particles depended on the valence state of the plutonium, pH and salinity. The formation of particulate americium-241 (^{241}Am) was also found to be sensitive to pH and salinity although the pH dependence may have been influenced by colloidal substances occurring in the experimental media.

Radionuclides have been found to occur in solution, as ions retained on mineral and organic particles, as colloids, particulate matter and as complexes with minerals and particularly with organic matter. Sediments with higher iron content are found to have higher associated activities (Duursma and Gross, 1971). The iron may occur as particle coatings (Carroll, 1958) enhancing the formation of sorption complexes, particularly for ruthenium-106 (^{106}Ru) (Jones, 1960). Organic matter appears to be far less important in the retention of caesium than clay minerals although organic material can trap caesium before it reaches the mineral soil layer (Waller and Olson, 1965).

Laboratory studies have indicated that many radionuclides attain an equilibrium distribution between the sediment and the overlying water column, although the times taken for different radionuclides to attain equilibrium do vary (Garder and Skulberg, 1964). It is interesting to note that, for many radionuclides, the equilibrium distribution is the same with distilled water as it is in river water although the times to attain equilibrium are altered (Garder and Skulberg, 1964; Aston and Duursma, 1973). It is not known whether this similarity extends to marine waters.

A.2 Plutonium

The behaviour and chemistry of the transuranic elements in soils and sediments is particularly complex (Wilding and Drucker, 1976) with considerably more data available for plutonium than the other transuranics. The adsorption of plutonium is sensitive to pH, reaching a maximum at approximately pH 7 and decreasing markedly above pH 9-12 and below 2-4, the precise value depending on test conditions (Rhodes, 1957; Prout, 1959), Bulman (1976) found that plutonium compounds form pseudo-colloids above pH 2.8 and genuine aggregates above pH 7.5. Plutonium (Pu) has four oxidation states, Pu (III) to Pu (VI) which can coexist in the environment and it has been shown that the oxidation state can influence the behaviour of the element (Prout, 1959), although plutonium is more strongly adsorbed than the other transuranic elements (Dahlman et al, 1976). In the marine environment plutonium has been found to distribute itself between the soluble and particulate phases in a manner dependent on the mixture of the oxidation states (Nelson and Lovett, 1978).

The adsorption of the transuranics is strongly associated with hydrous oxide films on the soil particles, particularly with manganese oxides, rather than organic matter (Means et al, 1978; Muller, 1978) although plutonium can form complexes with the soil components (Bulman, 1976; Wilding and Drucker, 1976). Plutonium forms very strong complexes with a variety of organic and inorganic ligands, although at environmental activities it is expected that hydrolysis and sorption of Pu (IV) as well as complexation with naturally occurring organic substances will be important (Bondietti et al, 1976). Carbonate complexes of plutonium have also been proposed as being environmentally important (Murray and Fukai, 1975). Bondietti et al (1976) studied that reactions of plutonium with selected organic substances found in the environment, in order to evaluate the valence and metacomplex behaviour of the element. Substantial differences were found to exist between the sorption behaviour of Pu (IV) and Pu (VI). The low sorption of Pu (VI) previously reported for montmorillonite (Jacabson et al, 1948) was confirmed and it was shown that the sorption of Pu (IV) by montmorillonite was substantially greater than that of Pu (VI). It was concluded that plutonium was at least partially associated with humic materials and forms solid phase organic complexes. However, the more inert soil-plutonium reactions effectively immobilise the element in soil with the result that plutonium should show limited chemical mobility in the terrestrial environment. Edgington et al (1976a) also found little diagenetic mobility of plutonium in consolidated freshwater sediments.

A.3 Concluding Remarks

This review of radionuclide-sediment interaction is incomplete due to the large number of recent publications in this area during the preparation of this report. Recent work on radionuclide sediment interactions was presented at the recent IAEA Symposium on Impacts of Radionuclide Releases in the Marine Environmental held in Vienna, October 1980. Consequently, it is recommended that the proceedings of this conference, which are currently in press, are consulted in conjunction with this appendix. However, these recent results do not invalidate the conclusions of this review concerning those parameters which influence radionuclide uptake and retention. An updated review of the interaction between radionuclides and sediments will be included in a subsequent report in this series.

APPENDIX B

THE QUATERNARY SEDIMENTS OF THE IRISH SEA

Following Pantin (1977), it is convenient to consider the northern Irish Sea in terms of three areas.

(i) The North-Eastern Section

In the north-eastern sector, which comprises the area to the north-east and east of the Isle of Man, the rockhead consists mainly of Permo-Triassic red sandstones which are overlain, for the most part, by a rather uniform mantle of boulder clay a few metres thick. There is no widespread evidence of internal stratification within the boulder clay but acoustic profiles do show some faint, diffuse, local banding. Sediment cores show the boulder clay to be unbedded muddy sediment, sometimes with pebbles, in which some intermittent and often highly distorted lamination occurs locally. Over most of the area the boulder clay is overlain by well-bedded proglacial water-laid sediments up to several tens of metres of thick. In some parts of the area these are missing and the boulder clay comes to within one metre of the sea bed being overlain only by thin marine* sediments. Seismic records indicate that the proglacial, water-laid sediments are typically well-bedded with quasi-parallel reflectors on scales of one metre of more. This was confirmed by long sediment cores taken in the area which showed that these beds are characteristically muddy with frequently numerous sand or coarse silt laminae. The sediment cores also revealed very little evidence of bioturbation in these beds.

Overlying the proglacial beds is a series of marine sediments which extends up to the present sea bed. These are muddy, sandy or gravelly depending on the locality. However, over most of the sector muddy sands or sandy muds form the major sediment types in roughly equal proportions. The proportions of sand and gravel in the sediment rise in a westerly direction towards the east and

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* Pantin (1977) uses the term "marine" in its broadest sense encompassing subtidal, intertidal and estuarine sediments. However, the term is not applicable to the proglacial water-laid beds as these are characterised by evidence of low salinity as well as a proglacial environment.

north of the Isle of Man until the order of bulk dominance is gravel > sand > mud. Large scale bedding occurs in these marine sediments but is much less well defined than in the proglacial water-laid sediments. Cores from the east of this sector show a well marked disconfirmity in the marine sediments separating interbedded units containing sand and mud in various proportions from underlying coarser sediments. The latter comprise interbedded sand and gravel grading to mainly sand in the extreme east of the sector.

The bathymetry and stratigraphy of this sector are shown in Figure B.1 compiled from Pantin (1977, 1978) which shows the thickness of the marine sediments above the disconformity, as well as the total thickness of marine sediments, and in some cases the thickness of the underlying proglacial water-laid beds.

Finally, Pantin (1978) notes that in the marine sediments lamination is rare even though colour banding is quite common and there is extensive evidence of bioturbation.

(ii) The South-Eastern Sector

In the south-eastern sector, to the south-east and south of the Isle of Man, the same stratigraphy applies as in the north-eastern sector. The underlying hard rocks are replaced by large areas of Carboniferous and north of Anglesey by Pre-Cambrian or Lower Palaezoic rocks. In at least two small areas the bed rocks comes to within 0.5 m of the sea bed with the overlying layer of boulder clay being locally absent. Proglacial water-laid beds are widespread in the western part of the sector. The overlying marine sediments possess a considerably higher sand/mud ratio than in most of the sector further north such that in Liverpool Bay dominantly sandy sediments form the bulk of the assemblage with gravelly sediments in minor amounts.

(iii) The Western Sector

The western sector comprises the area to the north-west, west and south-west of the Isle of Man and is significantly different from the other two areas. The rockhead is overlain by a more or less continuous cover of boulder clay which itself is directly overlain by marine sediments over most of the area. Between the Isle of Man and Northern Ireland there is a very large area consisting almost entirely of mud (Belderson, 1964). This is separated from the underlying boulder clay by a layer of coarser sediments only a few tens of centimetres thick. Outside the mud area the surface sediments of the sector consist predominantly of sand and gravel in various proportions.

On the basis of these sediment distributions and other evidence it is possible to deduce the depositional history of the area (Pantin, 1977, 1978). The layer of boulder clay overlying the bed rock in most of the area resulted from the melting and ablation of the Irish Sea portion of the Devensian ice-sheet. The proglacial water-laid sediments were probably late Devensian when de-glaciation was partly completed; the bodies of water in which these beds were laid down may have included arms of the sea, lagoons with access to the sea restricted by ice or topography, or lakes. However the almost total lack of macrofauna in these beds probably indicates a low salinity in comparisons with the present day Irish Sea. Also the foraminifera and organic walled microplankton found in cores from the south-east of the Isle of Man indicate that the proglacial water-laid beds were deposited in a body of water colder and less saline than the present Irish Sea but still connected to the open sea. The marine sediments were probably laid down in the late Devensian and the Flandrian, with the belt of muddy sediments running parallel to the Cumbrian coast between St Bees Head and Morecambe Bay representing the latest stages of infilling of a valley. Most of the marine sediments were evidentally deposited under temperature and salinity conditions converging to those of the present day and are chiefly sub-tidal. However, at certain levels, deposits characteristic of beaches and tidal flats occur. This and other evidence suggest one or more lowerings of relative sea level since the melting of the Devensian ice-sheet.

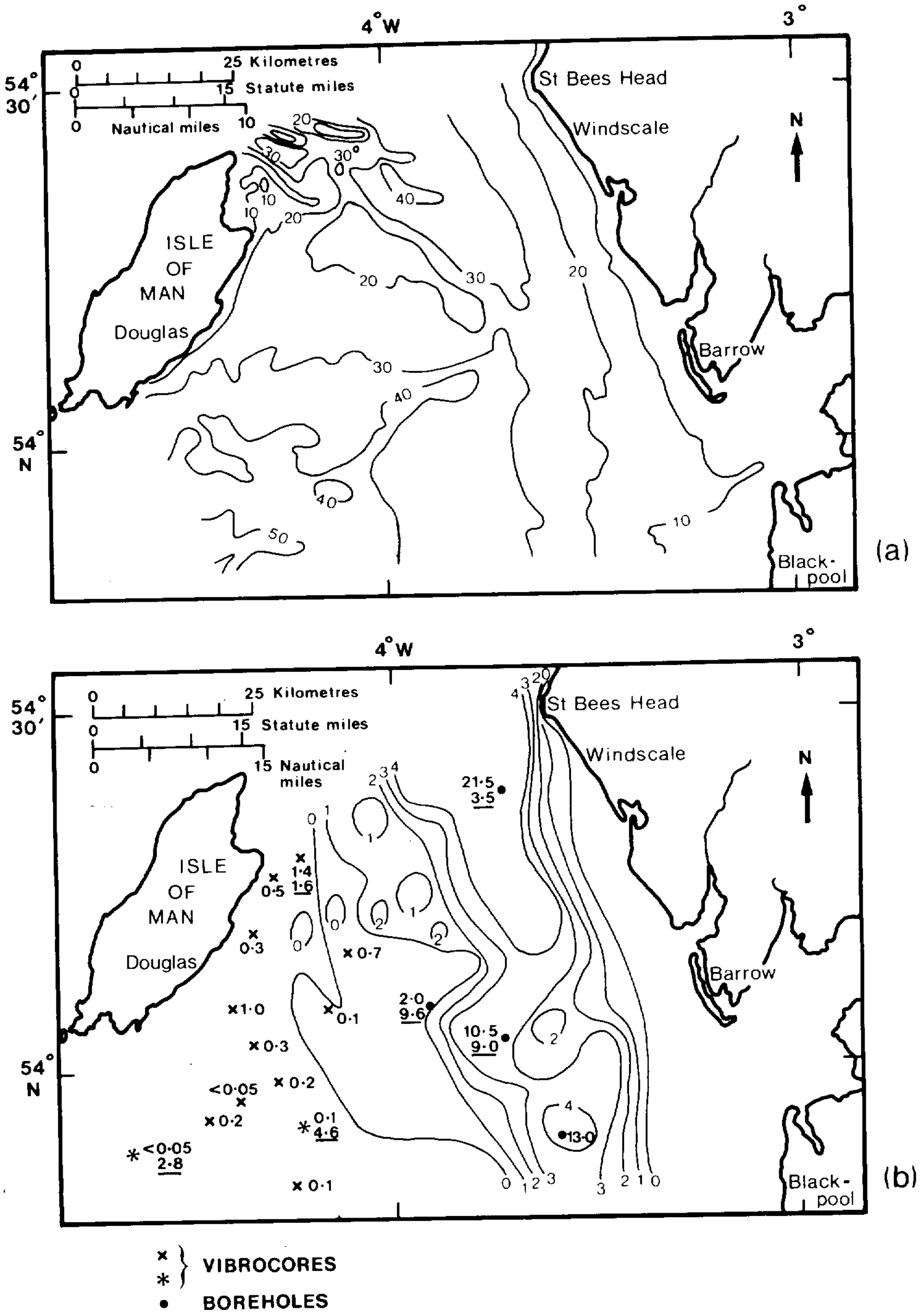

Figure B1 Stratigraphy of the north-eastern Irish Sea

a) Bathymetry showing depth contours in metres.

b) Distribution of marine and proglacial lagoon sediments. Contours are isopachs in metres for fine marine sediments above disconformity. Plain figures alongside symbols represent observed thickness of marine sediment overburden. Underlined figures represent thickness of water-laid sediment. (Thicknesses are in metres and are not corrected for core shortening.) Compiled from Pantin (1977, 1978).

APPENDIX C

UNITS OF RADIATION MEASUREMENTS

The unit of radioactivity used in this report is the curie (Ci) which is the quantity of any radioactive material that undergoes 3.7×10^{10} atomic disintegrations per second. This is the disintegration rate of one gram of radium. The curie is divided into a number of smaller units as follows:

1 millicurie	(1 m Ci) = 10^{-3} Ci
1 microcurie	(1 μ Ci) = 10^{-6} Ci
1 nanocurie	(1 n Ci) = 10^{-9} Ci
1 picocurie	(1 p Ci) = 10^{-12} Ci
1 femtocurie	(1 f Ci) = 10^{-15} Ci

Following the recommendations of the British Committee on Radiation Units and Measurements[1] the curie is being replaced by an S.I. unit, the becquerel (Bq), which is defined as the quantity of any radioactive material that undergoes one disintegration per second. This unit is not used in this report. However, some relevant conversion factors are presented below:

1 Ci = 3.7×10^{10} Bq

1 p Ci/g = 37 Bq/kg

1 p Ci/l = 37 Bq/m^3

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[1] BRITISH COMMITTEE ON RADIATION UNITS AND MEASUREMENTS, 1978. Draft recommendations on the introduction of new S.I. Units for use with radioactivity and ionising radiations. Teddington: National Physical Laboratory, 8 pp.