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Trends in plutonium, americium and radiocaesium accumulation and long-term bioavailability in the western Irish Sea mud basin

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Abstract

Time-series data on plutonium, americium and ^{137}Cs concentrations in surficial sediments and seawater, gathered at selected locations in the western Irish Sea mud basin in the period 1988–97, are examined and modelled in an attempt to reconstruct the deposition history of Sellafield-sourced radionuclides in the basin and estimate representative mean availability times for these nuclides in this zone. Predictions using a semi-empirical modelling approach have been confirmed by the analysis of ^{210}Pb -dated sediment cores retrieved from the basin, and interpreted in terms of the processes likely to control the transport of particle-reactive radionuclides from the northeastern Irish Sea to the western Irish Sea. The proposed interpretation has been supported by the analysis of transuranium concentrations and radionuclide ratios along two east–west transects from Sellafield, which has highlighted the importance of sediment remobilisation processes in the dispersion of particle-reactive radionuclides post-input. These processes have been incorporated in a low-resolution compartmental model of the Irish Sea and used to predict future $^{239,240}\text{Pu}$ concentration trends in the western Irish Sea mud basin. Model predictions for $^{239,240}\text{Pu}$ in the surface sediment and seawater compartments in this zone, validated by comparison with independent data sets, indicate that concentrations have already peaked and are beginning to decline slowly with mean availability times of ca. 100 years in both compartments. In the case of ^{137}Cs , the decline is much more rapid, the corresponding availability times being at least an order of magnitude shorter. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The initial dispersion of radionuclides discharged to the marine environment from Sellafield is influenced by a number of factors including the chemical form of the radionuclides in the effluent, local hydrographic conditions, the composition of bottom sediments and variations in the discharge rate. Data collected over a number of decades have shown that those radionuclides which are relatively soluble in seawater (e.g., ^{90}Sr , ^{99}Tc and ^{137}Cs) are advected principally to the north and west, leaving the Irish Sea via the North Channel with a mean transit time of approximately one year (Jefferies et al., 1982; McKay et al., 1986; Leonard et al., 1997). In contrast, non-conservative nuclides such as plutonium and americium, released in particulate or hydrolysed form, are quickly removed from the water column by direct precipitation or scavenging by suspended particulate matter (Hetherington, 1976).

The tendency of actinide radionuclides to adsorb onto particles and become associated with deposited sediments strongly influences their present distribution and is probably the most relevant feature controlling their long-term fate. Indeed, seabed sediments and, in particular, muddy sediments, are known to be a sink (at least temporarily) for non-conservative, long-lived radionuclides. In the Irish Sea, muddy sediments are mainly confined to two areas: an extensive belt of muds and muddy sands parallel to the Cumbrian coast, and a large and relatively deep mud basin lying between the Isle of Man and the coast of Ireland (Fig. 1).

In this paper, extensive new data, gathered annually since 1988 for radiological assessment purposes and with a view to predicting the likely long-term behaviour of Sellafield-sourced radionuclides in the western Irish Sea, are reviewed in detail. Specifically, transuranic concentrations in seawater, surficial sediment and sediment cores collected by our laboratory at selected locations in the western Irish Sea mud basin throughout a ten-year period are examined and modelled. To assist interpretation, data on the temporal evolution of the levels of the considerably more soluble nuclide, ^{137}Cs , at the same stations are also included.

Two distinct modelling approaches have been adopted. Firstly, a semi-empirical model, originally proposed by Nicholson and Hunt (1995), has been applied to these data sets in an attempt to (a) estimate concentrations arising from past discharges before our sampling commenced, (b) predict future concentrations, and (c) establish the likely time-span over which the various radionuclides are likely to remain biologically available in the western Irish Sea. Model predictions for the period 1952–97 have been confirmed by the analysis of ^{210}Pb -dated sediment cores retrieved from the mud basin, which has enabled us to reconstruct the deposition history of these nuclides with some confidence. Secondly, a simple (low-resolution) compartmental model, previously used by Jefferies and Steele (1989) to predict the concentrations of Sellafield-discharged ^{137}Cs throughout the Irish Sea, and modified here to take account of the remobilisation of radionuclides from the seabed back into the water column after the manner of MacKenzie and Nicholson (1987), has been used to predict the concentrations of plutonium in seawater and sediment in the western Irish Sea. These predictions have been validated by comparison with our measured

time-series data for plutonium in seawater and sediment in the same zone, and compared with the predictions of the semi-empirical model.

Finally, data on plutonium and americium levels and activity ratios in seawater along two transects from Sellafield, one to the north of the Isle of Man and the other to the south (Fig. 1), are presented and interpreted in terms of the processes thought to be responsible for the transfer of these nuclides from the northeastern Irish Sea to the western Irish Sea mud basin.

2. Materials and methods

2.1. Sampling and sample pre-treatment

Surficial sediment and matching seawater samples (50–150 l) were collected annually in the period 1988–97 at selected monitoring stations (Stations #7, #8 and #9) in the western Irish Sea mud basin (Fig. 1). A *Van Veen* grab was employed to retrieve the sediment and a 2 cm thick surface scrape (taken as representative of surficial sediments at the site in question) removed for subsequent analysis. A small

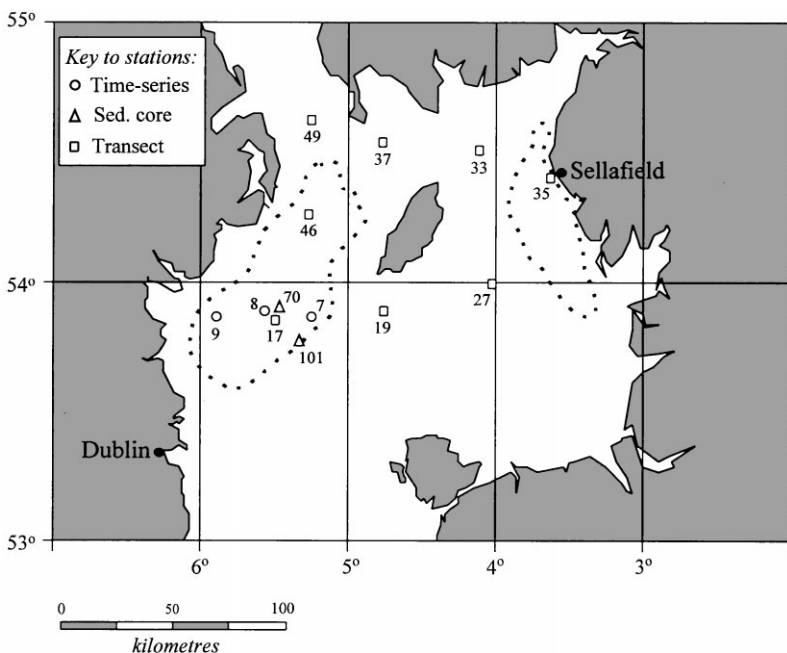


Fig. 1. Sampling stations in the Irish Sea. The dashed lines enclose regions of muddy sediments where >25% of the material is finer than 63 μm .

number of sediment cores were also retrieved from the mud basin at Stations #8, #70 and #101 using a box corer and, in one case, a gravity corer. Sectioning of these cores into 2 cm slices was carried out immediately after sampling. The samples were sealed in plastic bags and returned to the laboratory, where they were dried, ground and homogenised. In addition, samples of near-surface seawater (50–150 l) were collected at eight stations along two east-west transects in the Irish Sea (Fig. 1) in December 1995. The samples were immediately filtered ($<0.45\ \mu\text{m}$) and acidified prior to pre-concentration onboard ship.

2.2. Sample analysis

Cs-137 concentrations in sediment were determined by high-resolution gamma spectrometry using an n-type germanium detector with a relative efficiency of 30% and resolution of 1.70 keV (FWHM) at 1.33 MeV. Transuranic nuclides (^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Pu and ^{241}Am) were extracted and purified from sub-samples ($\approx 10\ \text{g}$) of the same sediment using standard radiochemical techniques based on ion exchange and solvent extraction (Condren, 1998). Following electrodeposition onto polished stainless-steel discs and a storage period of at least two weeks, alpha-emitting nuclide levels were determined by high-resolution alpha spectrometry using passivated, ion-implanted silicon detectors, while beta-emitting ^{241}Pu was measured by supported-disc liquid scintillation counting in a Wallac Quantulus LSC (Condren et al., 1996a). Radiochemical recoveries were determined using NIST-certified ^{242}Pu and ^{243}Am as yield monitors.

2.3. Modelling

2.3.1. Semi-empirical modelling

The semi-empirical (or inverse compartment analysis) approach of Nicholson and Hunt (1995) considers the environmental material in question (e.g., sediment) to be in equilibrium with its environs. This means that even though concentrations are controlled by a number of complex processes, the period of time in which a certain nuclide will be available to the material will only depend on the rates of physical decay and loss of the nuclide from the environment. Two parameters, optimised by a maximum likelihood process, are derived from the experimental time-series data: the mean availability time (i.e., the time for which the nuclide will effectively be available to the material, defined as the time in which the original concentration will decrease by the exponential factor, e) and a constant incorporating the concentration factor and any scaling effects such as distance from the discharge point. The values obtained are then used to calculate the nuclide concentration in the material for a particular year, taking into account the contributions of contemporary and historic discharges.

We have used the above approach here primarily to estimate concentrations of plutonium, americium and ^{137}Cs in sediment and seawater in the western Irish Sea in the period prior to 1988 (when our measurements commenced), and to determine representative mean availability times for these radionuclides in the same zone.

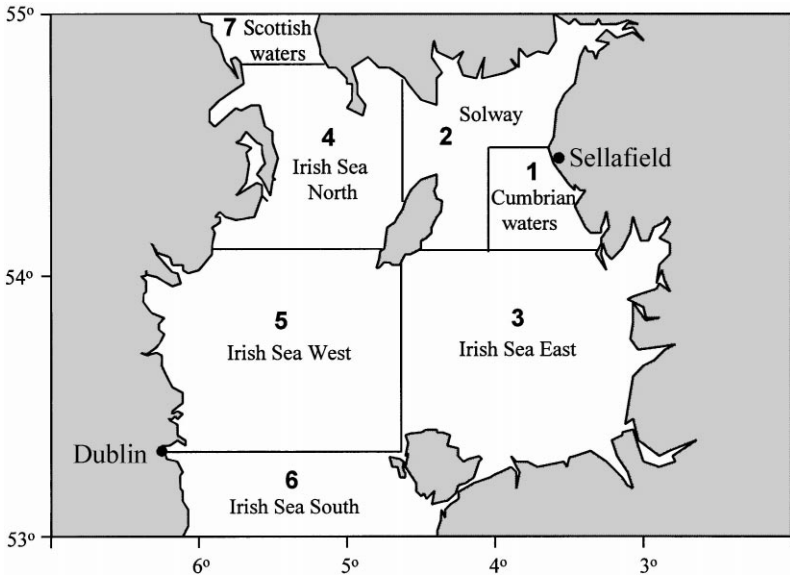


Fig. 2. Regional structure of a low-resolution compartmental model for the Irish Sea (from: Jefferies & Steele, 1989).

2.3.2. Compartmental modelling

The compartmental model used by Jefferies and Steele (1989) to predict the concentrations of ^{137}Cs in seawater throughout the Irish Sea is based on the simple regional structure proposed by Camplin et al. (1982). It consists of a small number of interconnected compartments representing various sea areas within the Irish Sea (Fig. 2). Radionuclide transport by water movement due to advection and dispersion processes is simulated by exchanges between compartments which are described by a set of transfer (rate) coefficients. These were determined by Jefferies and Steele (1989) using geographically and temporally characterised data on measured, Sellafield-sourced, ^{137}Cs concentrations throughout the Irish Sea, constrained by hydrological data on residual circulation in the Irish Sea. Although the adsorption of radionuclides on suspended particulate and subsequent transfer to the sediment compartment by particle scavenging are taken into account in this model, other sedimentary processes such as bioturbation/mixing and resuspension (grouped together here as re-working), pore-water diffusion, and transfer to deep sediments are not. We have modified the original model to include these processes by assigning to each compartment the more complex vertical structure depicted in Fig. 3, following the approach of other workers (MacKenzie & Nicholson, 1987; Nielsen et al., 1995). A list of model compartments/regions including the volume, mean depth, sedimentation rate and suspended load assumed for each are given in Table 1, while the parameter values used to define transfer of radionuclides between seawater and sediment are given in Table 2. Many of these parameter values are identical to those used by Jefferies and Steele (1989), and

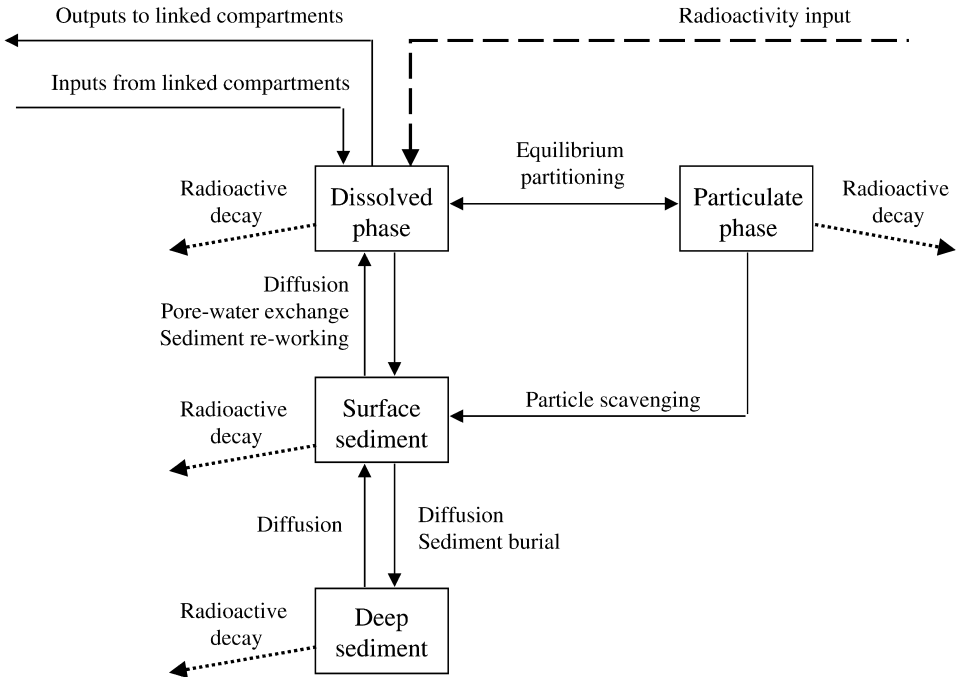


Fig. 3. Vertical structure of each regional compartment in the model.

Table 1

Model compartments and basic model parameters (from: Jefferies & Steele, 1989)

Compartment	Region	Volume (m ³)	Mean depth (m)	Sed. rate (t m ⁻² yr ⁻¹)	Susp. load (t m ⁻³)
1	Cumbrian waters	2.7×10^{10}	26	6×10^{-3}	10×10^{-6}
2	Solway	1.2×10^{11}	26	1×10^{-4}	3×10^{-6}
3	Irish Sea East	3.3×10^{11}	33	1×10^{-4}	2×10^{-6}
4	Irish Sea North	2.7×10^{11}	61	1×10^{-4}	2×10^{-6}
5	Irish Sea West	5.8×10^{11}	65	1×10^{-3}	3×10^{-6}
6	Irish Sea South	1.1×10^{12}	57	1×10^{-4}	1×10^{-6}
7	Scottish waters	1.5×10^{13}	110	1×10^{-4}	1×10^{-6}
8	Celtic Sea	4.0×10^{12}	150	1×10^{-4}	1×10^{-6}

Note: Values in *italics* modified from the original reference.

Nicholson and Hunt (1987), though small modifications were made to some, including the sedimentation rates and representative suspended loads in a few of the regions, and the sediment re-working and pore-water turn-over rates. These changes were necessitated following optimisation of the parameter values using measured ¹³⁷Cs data for surface sediments in both the eastern and the western Irish Sea.

Table 2

Model parameters describing the transfer of radionuclides between seawater and sediment (from: MacKenzie & Nicholson, 1987)

Parameter	Value
Sediment porosity	0.8
Depth of surface sediment layer	0.1 m
Diffusion coefficient	$1 \times 10^{-2} \text{ m}^2 \text{ yr}^{-1}$
Sediment re-working rate	0.005 m yr^{-1}
Pore-water turn-over rate	1 yr^{-1}

Note: Values in *italics* modified from the original reference.

The model was implemented with the aid of commercially available modelling software (STELLA[®] II), in which linear first order differential equations are used to describe the transfer between compartments. Numerical solution of the system of equations driving the model was carried out using a fourth-order Runge-Kutta integration and time-dependent concentrations in each of the compartments were generated using reported and estimated annual Sellafield activity discharges for the period 1952–96 (Gray et al., 1995; MAFF, 1994–97). These predictions have been validated by comparison with our time-series data for plutonium in the western Irish Sea, as well as with time-series data for plutonium in Cumbrian waters published elsewhere. None of these data, of course, had been used to calibrate the model.

3. Results and discussion

3.1. Time-trend analyses of ¹³⁷Cs, ²³⁸Pu, ^{239,240}Pu, ²⁴¹Pu and ²⁴¹Am levels in the western Irish Sea mud basin

3.1.1. Surficial sediment

The concentrations of ²³⁸Pu, ^{239,240}Pu, ²⁴¹Pu, ²⁴¹Am and ¹³⁷Cs, together with the corresponding radionuclide ratios, in surficial sediment collected at Stations #7, #8 and #9 in the western Irish Sea over the period 1988–97 are given in Table 3.

The most striking feature of these time series is the fact that while ¹³⁷Cs concentrations have been falling continuously over the period of our sampling, comparatively little change appears to have occurred in plutonium concentrations. This is in sharp contrast to the pattern observed in the northeastern Irish Sea, where ¹³⁷Cs, plutonium and americium concentrations have all been falling steadily since the mid-1970s as a result of successive reductions in annual discharges, leading to falling concentrations in the water column and consequent remobilisation from the sediments (Hunt & Kershaw, 1990).

Comparison of our 1997 data with those of 1988 reveals a decrease in ¹³⁷Cs concentrations over this period of 30–70%, i.e., an annual decrease of 3–8%. This is in good agreement with the value of $\approx 6.5\%$ obtained from estimated total inventories

Table 3
 Concentrations ($\pm 1\sigma$) of ^{238}Pu , $^{239,240}\text{Pu}$, ^{241}Pu , ^{241}Am and ^{137}Cs in surficial sediments sampled in the western Irish Sea, 1988–97

Location	Year	Concentration (Bq kg^{-1} , dry wt.)							
		^{238}Pu	$^{239,240}\text{Pu}$	^{241}Pu	^{241}Am	^{137}Cs			
Stn. #7 53°52'N 05°14'W	1988	1.34 ± 0.15	9.6 ± 0.6	156 ± 12	12.1 ± 0.5	115 ± 4	0.140 ± 0.018	16.2 ± 1.6	1.26 ± 0.09
	1989	2.13 ± 0.15	11.6 ± 0.5	157 ± 11	11.8 ± 0.4	104 ± 4	0.183 ± 0.015	13.5 ± 1.1	1.02 ± 0.06
	1990	1.79 ± 0.11	9.4 ± 0.5	123 ± 10	13.4 ± 0.6	93 ± 4	0.189 ± 0.007	13.0 ± 1.2	1.42 ± 0.10
	1991	1.87 ± 0.07	10.5 ± 0.2	151 ± 8	12.2 ± 0.5	109 ± 4	0.177 ± 0.007	14.4 ± 0.8	1.16 ± 0.05
	1992	2.10 ± 0.14	10.7 ± 0.6	131 ± 10	13.5 ± 0.5	99 ± 4	0.196 ± 0.017	12.3 ± 1.2	1.26 ± 0.08
	1993	1.85 ± 0.10	9.2 ± 0.2	124 ± 7	15.8 ± 0.6	70 ± 3	0.203 ± 0.010	13.5 ± 0.8	1.72 ± 0.08
	1994	2.44 ± 0.12	12.9 ± 0.4	150 ± 9	9.7 ± 0.4	88 ± 3	0.189 ± 0.009	11.6 ± 0.8	0.75 ± 0.04
	1995	2.40 ± 0.08	12.9 ± 0.3	143 ± 8	14.6 ± 0.4	70 ± 3	0.186 ± 0.006	11.1 ± 0.7	1.13 ± 0.04
	1996	1.74 ± 0.06	10.9 ± 0.2	89 ± 5	15.4 ± 0.4	75 ± 3	0.159 ± 0.006	8.2 ± 0.5	1.41 ± 0.04
	1997	1.87 ± 0.09	10.8 ± 0.3	101 ± 6	13.4 ± 0.3	79 ± 3	0.173 ± 0.008	9.4 ± 0.6	1.24 ± 0.04
	1988	2.3 ± 0.15	14.8 ± 0.5	190 ± 12	14.9 ± 0.8	276 ± 8	0.155 ± 0.009	12.8 ± 0.9	1.00 ± 0.07
	1989	2.49 ± 0.15	14.0 ± 0.5	194 ± 12	8.4 ± 0.7	258 ± 8	0.177 ± 0.010	13.8 ± 1.0	0.60 ± 0.06
	1990	2.72 ± 0.17	14.1 ± 0.5	167 ± 13	13.3 ± 0.7	259 ± 8	0.193 ± 0.012	11.9 ± 1.0	0.95 ± 0.06
	1991	2.49 ± 0.14	15.5 ± 0.8	185 ± 13	19.2 ± 0.8	268 ± 4	0.161 ± 0.005	11.9 ± 1.1	1.24 ± 0.08
	1992	2.17 ± 0.08	13.9 ± 0.3	164 ± 10	17.8 ± 0.6	198 ± 6	0.156 ± 0.005	11.8 ± 0.7	1.28 ± 0.05
	1993	2.79 ± 0.15	18.7 ± 0.6	227 ± 12	26.0 ± 0.9	153 ± 5	0.149 ± 0.008	12.1 ± 0.8	1.39 ± 0.06
	1994	5.58 ± 0.12	33.3 ± 0.9	377 ± 21	35 ± 5	148 ± 5	0.167 ± 0.006	11.3 ± 0.7	1.05 ± 0.15
1995	3.52 ± 0.09	19.8 ± 0.4	195 ± 9	16.2 ± 0.6	118 ± 3	0.177 ± 0.004	9.8 ± 0.5	0.82 ± 0.03	
1996	2.44 ± 0.13	14.1 ± 0.4	117 ± 7	22.4 ± 0.6	106 ± 3	0.173 ± 0.009	8.3 ± 0.5	1.59 ± 0.06	
1997	3.36 ± 0.12	19.8 ± 0.5	165 ± 10	28.5 ± 0.6	150 ± 4	0.169 ± 0.005	8.3 ± 0.5	1.44 ± 0.03	
1988	1.59 ± 0.09	9.1 ± 0.3	147 ± 12	2.1 ± 0.1	230 ± 6	0.175 ± 0.011	16.1 ± 1.4	0.23 ± 0.02	
1989	1.49 ± 0.05	8.0 ± 0.2	109 ± 9	5.1 ± 0.3	138 ± 4	0.185 ± 0.008	13.6 ± 1.2	0.64 ± 0.04	
1990	1.66 ± 0.06	9.2 ± 0.2	125 ± 8	7.0 ± 0.3	144 ± 4	0.180 ± 0.007	13.6 ± 0.9	0.77 ± 0.03	
1991	1.67 ± 0.08	9.8 ± 0.3	83 ± 7	10.0 ± 0.3	102 ± 3	0.170 ± 0.012	8.5 ± 0.8	1.02 ± 0.04	
1992	1.57 ± 0.10	8.5 ± 0.3	93 ± 8	6.4 ± 0.4	104 ± 3	0.185 ± 0.014	11.0 ± 1.1	0.75 ± 0.05	
1993	1.46 ± 0.10	9.4 ± 0.4	104 ± 7	7.9 ± 0.4	126 ± 3	0.155 ± 0.011	11.0 ± 0.8	0.84 ± 0.05	
1994	1.56 ± 0.06	8.6 ± 0.2	43 ± 3	6.5 ± 0.5	95 ± 3	0.181 ± 0.007	5.0 ± 0.4	0.75 ± 0.06	
1995	1.68 ± 0.06	9.3 ± 0.2	91 ± 6	6.5 ± 0.3	75 ± 3	0.180 ± 0.006	9.8 ± 0.7	0.70 ± 0.04	
1996	1.64 ± 0.07	9.2 ± 0.2	92 ± 6	7.5 ± 0.2	63 ± 4	0.179 ± 0.007	10.0 ± 0.7	0.82 ± 0.03	
1997	1.40 ± 0.07	8.5 ± 0.2	65 ± 4	8.4 ± 0.2	80 ± 3	0.164 ± 0.008	7.6 ± 0.5	0.99 ± 0.06	

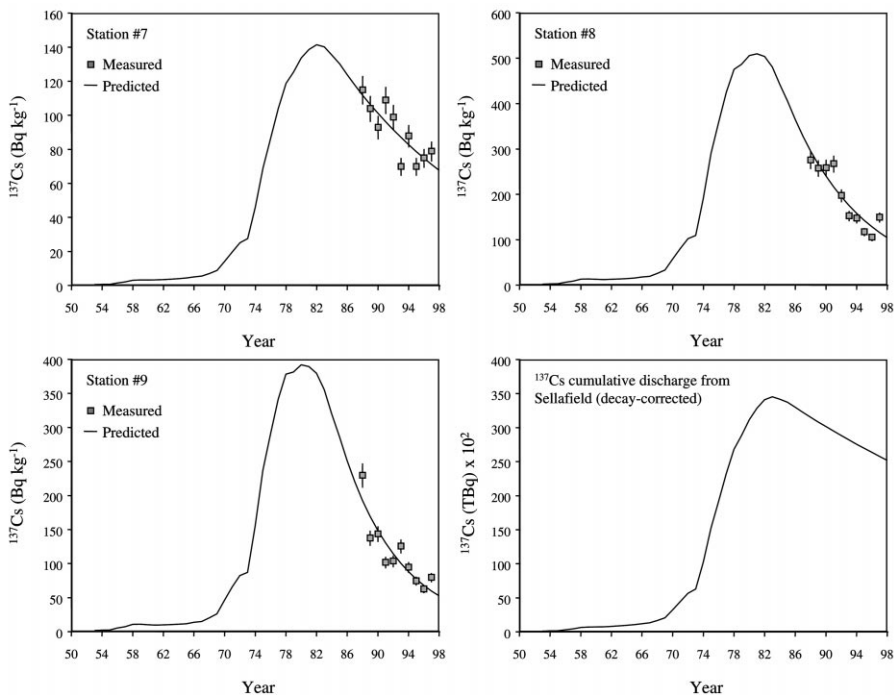


Fig. 4. Temporal evolution of measured ($\pm 2\sigma$) and model-predicted concentrations of ^{137}Cs (Bq kg^{-1} , dry wt.) in surficial sediments at Stations #7, #8 and #9 in the western Irish Sea. The cumulative ^{137}Cs release from Sellafield in the period 1952–97 is also shown.

in Irish Sea sediments over the same period (Poole et al., 1997), and with calculations by Hunt and Kershaw (1990) based on increased ^{137}Cs concentrations in seawater relative to the discharge rate over the period 1983–88. Predicted ^{137}Cs concentrations for each of the three stations using the semi-empirical modelling approach of Nicholson and Hunt (1995) show a similar pattern (Fig. 4), with concentrations increasing sharply in the early to mid-1970s, peaking in the late 1970s to early 1980s and declining thereafter. Although the broad shape of the concentration versus time trend at these stations is similar to that of the decay-corrected cumulative ^{137}Cs release from Sellafield (Fig. 4), the fall-off since the early 1980s (factor of 2–5) is more pronounced and lends weight to the view that ^{137}Cs is also desorbing from western Irish Sea sediments as a consequence of the general reduction in seawater concentrations.

Model-estimated ^{137}Cs mean availability times for Stations #7, #8 and #9 were found to be 16, 9 and 7 years, respectively. Variations between the three stations most likely reflect differences in physical dispersion and dilution processes which, in turn, are dependent on local hydrological conditions such as currents and depth. These availability times are considerably longer than the estimate of 3 years reported by Nicholson and Hunt (1995) for sediments close to the Sellafield outfall and the value of

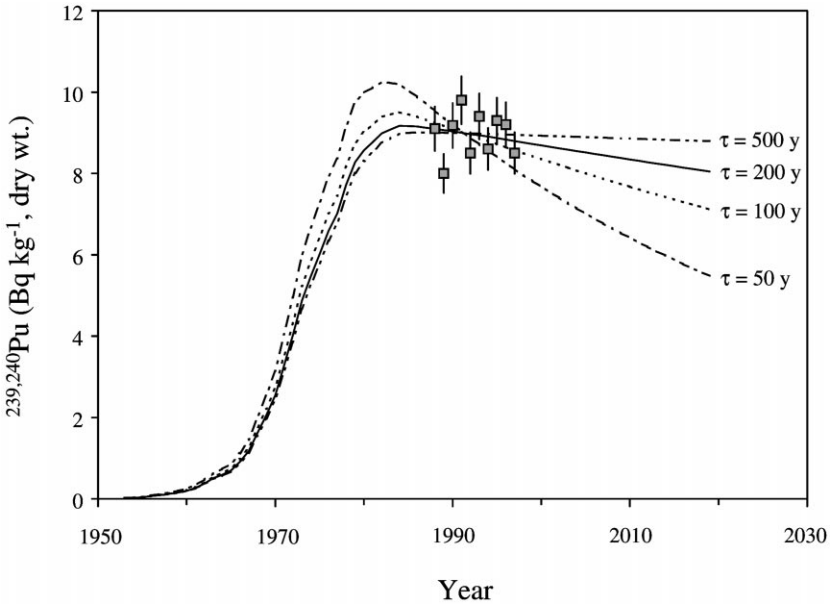


Fig. 5. Estimation of the mean availability time for $^{239,240}\text{Pu}$ at Station #9 in the western Irish Sea to the year 2020. Note the sensitivity of the plots to the choice of availability time, particularly the shorter times.

5 years reported by MacKenzie et al. (1994) for sediments in the Solway Firth. This is not surprising, as the likelihood of sediment resuspension is considerably higher in the shallower eastern Irish Sea (Kershaw et al., 1988a).

In the case of plutonium and americium, time-series analyses of surficial sediment concentrations in the northeastern Irish Sea show mean availability times of 5–8 years and 5–20 years, respectively (Hunt, 1985; MacKenzie et al., 1994; Nicholson & Hunt, 1995). Accurate estimation of actinide mean availability times in the western Irish Sea using our time-series data is hampered by the near constancy of the measured concentrations over the period of sampling. This constancy implies an availability time which, at the very least, is considerably longer than that for ^{137}Cs . Predicted $^{239,240}\text{Pu}$ concentrations, using a range of availability times, τ , are shown in Fig. 5 (for the purpose of the calculation it has been assumed that annual discharges from Sellafield will remain at their present low level).

It is clear from these plots that a further decade of monitoring will be required before the availability time for $^{239,240}\text{Pu}$ can be pinned down with accuracy using the semi-empirical approach. Nevertheless, it would seem, on the basis of the existing dataset, that the actual value is likely to lie between one hundred and several hundred years. If an availability time of 200 years is assumed, model-predicted $^{239,240}\text{Pu}$ concentrations for each of the three stations show concentrations increasing rapidly from the late 1960s until the early 1980s, at which point they level off and then begin to decline slowly. An example of the time dependence of $^{239,240}\text{Pu}$ concentrations at one of the stations (#9) is shown in Fig. 6. Note the satisfactory agreement with the measured

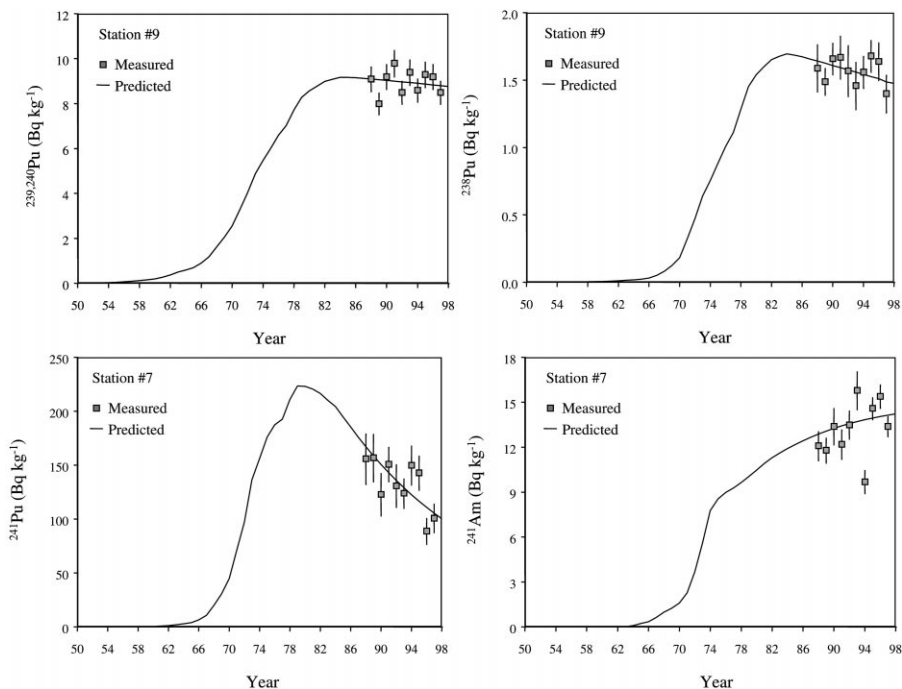


Fig. 6. Temporal evolution of measured ($\pm 2\sigma$) and model-predicted concentrations (Bq kg^{-1} , dry wt.) of $^{239,240}\text{Pu}$, ^{238}Pu , ^{241}Pu and ^{241}Am in surficial sediments at selected stations in the western Irish Sea.

time-series data. Clearly, there is little doubt but that $^{239,240}\text{Pu}$ will remain biologically available within western Irish Sea sediments for many hundreds of years to come.

Environmental processes are unlikely to differentiate between plutonium isotopes, at least to first order; thus, one might expect ^{238}Pu and ^{241}Pu to undergo the same physical dispersion and mixing processes as $^{239,240}\text{Pu}$. However, as the half-lives of ^{238}Pu and ^{241}Pu (at 87.7 and 14.4 years, respectively) are considerably shorter than the estimated mean availability time for $^{239,240}\text{Pu}$, i.e., 200 years, it is obvious that the mean availability time for each of these nuclides will be even shorter than their respective half-lives. Examples of model predictions for ^{238}Pu and ^{241}Pu , based on an effective decay constant given by $\lambda_{\text{eff}} = \ln(2)/T_{1/2} + 1/200$, are also shown in Fig. 6.

In the case of ^{241}Am , predictions of the concentrations of this nuclide are complicated by the fact that ^{241}Pu decays to ^{241}Am , making its availability dependent on the relative discharges of both parent and daughter, and their respective mean availability times. Given that americium is more particle-reactive than plutonium, one might expect its availability time to be comparable to (or greater than) that of $^{239,240}\text{Pu}$. Doubtless, this would be the case were the half-life of ^{241}Am long compared to the availability time and were ingrowth from ^{241}Pu not a factor. However, ingrowth is clearly important, as evidenced by the appreciably longer availability times for ^{241}Am compared with $^{239,240}\text{Pu}$ in the eastern Irish Sea (Hunt, 1985; Nicholson & Hunt,

1995). Indeed, studies have shown that while the cumulative environmental inventory of ^{241}Am in seabed sediments was 860 TBq by 1988, the total activity of ^{241}Am released from Sellafield up to this time was only 540 TBq (McCartney et al., 1994). The additional 320 TBq had been introduced into the environment by the decay of ^{241}Pu , also discharged from Sellafield. In the western Irish Sea, although the half-life of ^{241}Am is comparable to the mean availability time for $^{239,240}\text{Pu}$, the (semi-empirical) model predicts that ingrowth from ^{241}Pu will give rise to a continuing slow increase in ^{241}Am concentrations in surficial sediments (Fig. 6), which should peak in or about the year 2010 when levels are expected to be approximately 5% higher than at present. After this, the model predicts that ^{241}Am concentrations will diminish slowly with an estimated mean availability time of approximately 150 years.

3.1.2. Seawater

Surveys of the concentrations of radiocaesium in filtered seawater from throughout the Irish Sea have been conducted on a regular basis for many years (MAFF, 1967–97; Cunningham & O'Grady, 1986; Cunningham et al., 1988; O'Grady & Currivan, 1990; McGarry et al., 1994; Pollard et al., 1996; Long et al., 1996). The extensive data available show that general ^{137}Cs levels peaked between 1975 and 1979 and have been declining more or less steadily ever since in line with the reduction in annual discharges. At their peak, ^{137}Cs concentrations in the northeastern Irish Sea, close to the Sellafield outlet, were more than three orders of magnitude higher than representative fallout levels at similar latitudes in the northern hemisphere. In general, concentrations prevailing in the western Irish Sea zone in any given year were found to be about a factor of 20 lower than those in the north-eastern Irish Sea. Predicted and measured ^{137}Cs concentrations in western Irish Sea surface waters for this period are shown in Fig. 7. The predicted concentration maximum ca. 1977–79 is in good agreement with experimental observation and the estimated mean availability time of 17 months is entirely consistent with the accepted clearance half-time for the Irish Sea of ca. 12 months.

Data on the temporal evolution of transuranic levels in western Irish Sea surface waters are sparse, with few data available prior to 1988, when the surveys discussed in this paper commenced (Mitchell et al., 1991; Vives i Batlle, 1993; Mitchell et al., 1995). In Table 4, the concentrations of ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am in the dissolved and suspended particulate phases at Stations #7, #8 and #9 in the years 1988–90 and 1993–95 inclusive are given, together with the corresponding radionuclide ratios.

Again, in contrast to the general decrease in measured ^{137}Cs seawater concentrations in the western Irish Sea over the same period, comparatively little change appears to have occurred in transuranic concentrations. This trend also contrasts with the pattern in the eastern Irish Sea, where transuranic seawater concentrations have fallen more or less steadily since the mid-1970s (Fig. 8). Taken in conjunction with the relatively constant surficial sediment concentrations observed, it would seem that, in the case of the transuranics, near-equilibrium conditions currently prevail in the western Irish Sea.

The data given in Table 4 were gathered during surveys carried out in early summer and autumn when sea conditions were relatively calm, as evidenced by the suspended load values, which were typically $1\text{--}3\text{ mg l}^{-1}$. Under such conditions, some $10 \pm 8\%$ (range 2–21%, $n = 11$) of the plutonium and $50 \pm 15\%$ (range 30–71%, $n = 8$) of the

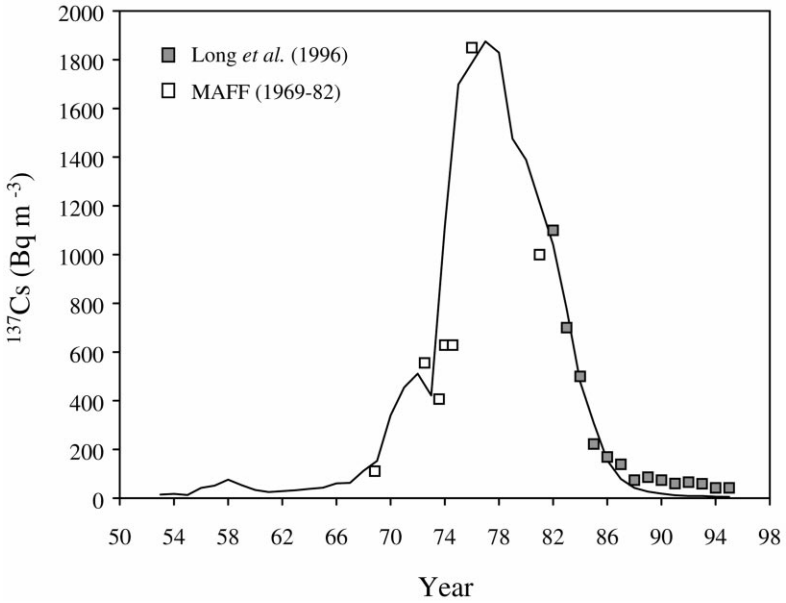


Fig. 7. Temporal evolution of measured and model-predicted ^{137}Cs concentrations (Bq m^{-3}) in surface seawater in the western Irish Sea (field data for the period 1982–1995 from Long et al., 1996; field data prior to 1982 from MAFF, 1969–82).

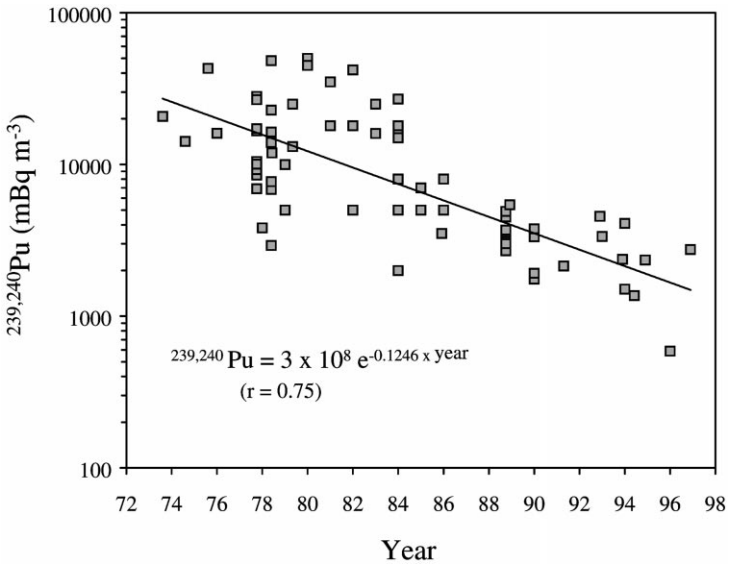


Fig. 8. Measured $^{239,240}\text{Pu}$ concentrations (mBq m^{-3}) in filtered surface seawater in the eastern Irish Sea, 1973–1996 (data from: Hunt, 1985; Walker & McKay, 1991; McKay & Pattenden, 1993; Leonard et al., 1999; this study).

Table 4

Partitioning of ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am between filtered seawater and suspended particulate in the western Irish Sea, 1988–95. Uncertainties given to $\pm 1\sigma$

Year	Fraction	Concentration (mBq m^{-3})			$^{238}\text{Pu}/$ $^{239,240}\text{Pu}$	$^{241}\text{Am}/$ $^{239,240}\text{Pu}$
		^{238}Pu	$^{239,240}\text{Pu}$	^{241}Am		
Stn. # 7:						
1988	Filtrate	65 ± 3	317 ± 12	—	0.205 ± 0.007	—
	Particulate	1.2 ± 0.3	8.0 ± 0.7	—	0.15 ± 0.04	—
	Total	66 ± 3	325 ± 12	—	0.204 ± 0.012	—
1989	Filtrate	69 ± 3	368 ± 11	21 ± 1	0.188 ± 0.005	0.056 ± 0.004
	Particulate	1.2 ± 0.3	8.9 ± 0.6	14 ± 1	0.14 ± 0.03	1.6 ± 0.2
	Total	70 ± 3	377 ± 11	35.0 ± 1.4	0.186 ± 0.009	0.093 ± 0.005
1990	Filtrate	34.3 ± 2.1	180 ± 8	36 ± 3	0.191 ± 0.009	0.199 ± 0.018
	Particulate	9.3 ± 0.8	49 ± 3	61 ± 3	0.188 ± 0.014	1.24 ± 0.09
	Total	44 ± 2	229 ± 9	97 ± 4	0.190 ± 0.012	0.423 ± 0.023
1993	Total	32 ± 7	200 ± 15	75 ± 6	0.16 ± 0.03	0.38 ± 0.04
1994	Total	14.5 ± 1.3	95 ± 5	43 ± 6	0.153 ± 0.013	0.45 ± 0.07
1995	Filtrate	68 ± 3	349 ± 8	61 ± 2	0.209 ± 0.015	0.175 ± 0.007
	Particulate	11.1 ± 0.8	53 ± 2	105 ± 4	0.197 ± 0.007	1.97 ± 0.10
	Total	80 ± 3	402 ± 8	166 ± 4	0.198 ± 0.008	0.413 ± 0.014
Stn. # 8:						
1988	Filtrate	100 ± 4	445 ± 16	—	0.225 ± 0.005	—
	Particulate	2.4 ± 0.3	12.7 ± 0.9	—	0.19 ± 0.03	—
	Total	102 ± 4	458 ± 16	—	0.224 ± 0.012	—
1989	Filtrate	82 ± 3	422 ± 13	38 ± 2	0.195 ± 0.005	0.090 ± 0.005
	Particulate	1.7 ± 0.3	12.8 ± 0.8	16 ± 1	0.13 ± 0.02	1.2 ± 0.1
	Total	84 ± 3	435 ± 13	54 ± 2	0.193 ± 0.009	0.124 ± 0.006
1990	Filtrate	39 ± 2	186 ± 9	20 ± 1	0.21 ± 0.08	0.109 ± 0.001
	Particulate	8.5 ± 0.7	50 ± 3	30 ± 2	0.170 ± 0.014	0.60 ± 0.05
	Total	47 ± 2	236 ± 9	50 ± 2	0.200 ± 0.013	0.213 ± 0.012
1993	Total	20 ± 4	134 ± 10	62 ± 5	0.15 ± 0.03	0.46 ± 0.05
1994	Total	44 ± 3	228 ± 11	18 ± 5	0.191 ± 0.011	0.08 ± 0.04
1995	Filtrate	71 ± 3	367 ± 10	60 ± 2	0.193 ± 0.008	0.163 ± 0.007
	Particulate	18.7 ± 1.2	82 ± 3	150 ± 3	0.229 ± 0.016	1.84 ± 0.08
	Total	90 ± 3	449 ± 10	210 ± 10	0.200 ± 0.009	0.47 ± 0.03
Stn. # 9:						
1988	Filtrate	54 ± 3	257 ± 10	—	0.211 ± 0.007	—
	Particulate	3.2 ± 0.4	16 ± 1	—	0.20 ± 0.03	—
	Total	57 ± 3	273 ± 10	—	0.209 ± 0.014	—
1989	Filtrate	65 ± 3	338 ± 11	18.0 ± 1.2	0.191 ± 0.008	0.053 ± 0.003
	Particulate	1.0 ± 0.2	5.6 ± 0.4	9.0 ± 0.7	0.17 ± 0.04	1.6 ± 0.2
	Total	66 ± 3	344 ± 11	27.0 ± 1.2	0.192 ± 0.011	0.079 ± 0.004
1990	Filtrate	47 ± 5	231 ± 14	14 ± 1	0.204 ± 0.019	0.062 ± 0.007
	Particulate	13.0 ± 0.9	62 ± 3	23 ± 2	0.210 ± 0.019	0.37 ± 0.04
	Total	60 ± 5	293 ± 14	37 ± 3	0.204 ± 0.019	0.126 ± 0.012
1993	Total	44 ± 7	380 ± 24	131 ± 9	0.115 ± 0.018	0.34 ± 0.03
1994	Total	55 ± 4	255 ± 14	57 ± 12	0.217 ± 0.013	0.22 ± 0.05
1995	Filtrate	23 ± 2	134 ± 5	10.2 ± 0.6	0.167 ± 0.013	0.076 ± 0.005
	Particulate	5.4 ± 0.6	27 ± 1	16 ± 1	0.198 ± 0.024	0.61 ± 0.06
	Total	28 ± 2	161 ± 5	27.0 ± 1.3	0.173 ± 0.012	0.165 ± 0.009

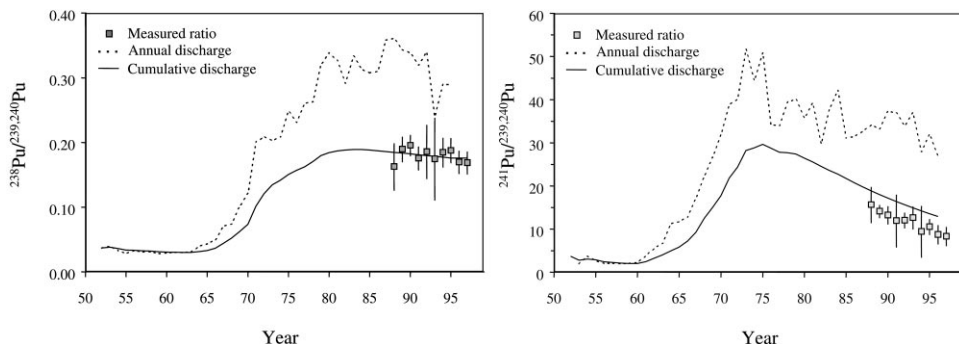


Fig. 9. Measured $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Pu}/^{239,240}\text{Pu}$ activity ratios ($\pm 2\sigma$) in surficial sediments in the western Irish Sea (averaged over Stations #7, #8 and #9) compared with ratios in annual and cumulative discharges. Discharge ratios taken from Gray et al. (1995).

americium in surface waters of the western Irish Sea were found to be associated with the particulate phase ($>0.45\ \mu\text{m}$).

3.1.3. Isotopic ratios in surficial sediment and seawater

Annually recorded $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Pu}/^{239,240}\text{Pu}$ activity ratios in surficial sediments (corrected for the contribution from global fallout and averaged over Stations #7, #8 and #9) are shown in Fig. 9, together with activity ratios derived from annual and cumulative discharges (decay-corrected to the year in question). Clearly, measured ratios in western Irish Sea sediment are consistently lower than those reported for recent discharges and closely reflect those of the time-integrated or cumulative Sellafield discharge. This observation is not new and has been attributed to ‘pre-depositional’ mixing of contemporary and past discharges, rather than ‘post-depositional’ mixing in situ (Hunt, 1985; Kershaw et al., 1990; MacKenzie et al., 1994). The first mentioned is believed to take place mainly in the muddy sediments close to the Sellafield outfall, where a combination of bioturbation, resuspension and settling, and very low net sedimentation rates ($<0.1\ \text{mm yr}^{-1}$, Kershaw et al., 1988b) leads to extensive vertical mixing (Kershaw, 1986; Kershaw et al., 1990).

Our mean $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio, at 0.174 ± 0.015 ($n = 30$), is identical to previously reported values for marine materials (*Fucus*, sediment and water) in the western Irish Sea (Mitchell et al., 1987, 1995), but somewhat lower than that observed along the Cumbrian and south-western Scottish coasts over the same period, namely 0.212 ± 0.009 ($n = 186$; MAFF, 1989–96). Although small, this difference appears to be real and has been attributed by various workers (e.g., McCartney et al., 1994) to the slow rate at which plutonium is dispersed following discharge, largely as a result of active sediment mixing and re-working in the vicinity of the release point. Moreover, surficial sediments near Sellafield are labelled with a relatively high proportion of plutonium from recent discharges, characterised by a higher $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratio. Further afield, the proportion from earlier discharges increases, resulting in lower $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratios.

The $^{238}\text{Pu}/^{239,240}\text{Pu}$ activity ratios in filtered seawater and suspended particulate in the western Irish Sea (Table 4) were found to be 0.199 ± 0.015 ($n = 12$) and 0.18 ± 0.03 ($n = 12$), respectively. These ratios clearly indicate that the plutonium in the water column at the present time is mainly sourced from sediments rather than from contemporary discharges. As suggested above, dispersion of plutonium reworked from a mixed pool of contaminated sediment, either by resolubilisation or resuspension, appears to be the most likely mechanism controlling plutonium concentrations in western Irish Sea waters. Within the limits of analytical uncertainty and natural variability between samples, it is possible on the basis of the measured ratios to make a rough estimate of the contribution of eastern and western Irish Sea sediments to present seawater concentrations. Taking the western and eastern Irish Sea sediment pools (top 10 cm approximately) to have $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratios of 0.174 and 0.212, respectively, the measured mean ratios for the dissolved and suspended particulate fractions given above suggest that most of the dissolved plutonium and comparatively little of the particulate plutonium is sourced directly from eastern Irish Sea sediments. In other words, most of the particulate plutonium in western Irish Sea waters has its origins in the resuspension of local seabed sediment. That most of the plutonium sourced from the eastern Irish Sea is transferred to the western Irish Sea in a soluble form after resolubilisation from seabed sediments is in accord with the observations of other workers (MacKenzie et al., 1987; Cook et al., 1997), who have suggested that particle transport dominates in the northeastern Irish Sea but not further afield. Additional data in support of this hypothesis is discussed in Section 3.2 below.

3.1.4. Reconstruction of ^{137}Cs , plutonium and americium deposition history in the western Irish Sea mud basin using dated sediment cores

Confirmation that the predicted concentration time-trends for ^{137}Cs , plutonium and americium in surficial sediments in the western Irish Sea are reliable has been obtained from the analysis of ^{210}Pb -dated sediment cores retrieved from the same zone. Excess ^{210}Pb deposition profiles for three such cores are shown in Fig. 10. In all three, a general decrease in the excess (or unsupported) ^{210}Pb with depth is observed, with some excess ^{210}Pb detectable at depths of over 50 cm. Measured inventories were found to be about $1 \times 10^4 \text{ Bq m}^{-2}$ and are consistent with the values reported previously by other workers for muddy sediments in the Irish Sea (McCartney et al., 1990). Elsewhere in the Irish Sea the inventories are considerably lower, being typically $\approx 1\text{--}3 \times 10^3 \text{ Bq m}^{-2}$ (McCartney et al., 1990). The higher inventories in muddy areas are readily explained by the higher absorption capacity of finer-grained sediments.

From the best exponential fit to the excess ^{210}Pb deposition profiles, a mean sedimentation rate of $3 \times 10^{-3} \text{ t m}^{-2} \text{ yr}^{-1}$ was determined for these core sites. This value is consistent with the range of values quoted in the literature for the north-western Irish Sea, i.e., $1\text{--}5 \times 10^{-3} \text{ t m}^{-2} \text{ yr}^{-1}$ (EC, 1995). The individual sedimentation rates for each core, as determined using the constant rate of supply (CRS) model (Goldberg, 1963; Appleby & Oldfield, 1978; Tobin & Schell, 1989), are given in Table 5. It should be appreciated that these are apparent sedimentation rates only; the

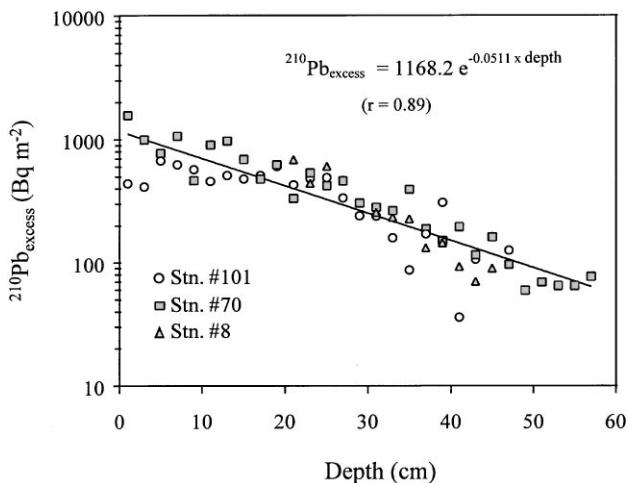


Fig. 10. Excess ^{210}Pb depth profiles in cores from three separate stations in the western Irish Sea mud basin.

Table 5

Apparent sedimentation rates in the western Irish Sea mud basin as derived from sediment cores using the CRS model

Core	Location	Sedimentation rate	
		($\text{t m}^{-2} \text{yr}^{-1}$)	(cm yr^{-1})
Stn. #101	53°46'N 05°27'W	3.3×10^{-3}	0.73
Stn. #70	53°53'N 05°33'W	3.0×10^{-3}	0.52
Stn. #8	53°53'N 05°33'W	2.7×10^{-3}	0.40

actual rates may be lower, as it is recognised that biological and physical mixing in the upper layers of the sediment column can disturb the stratigraphic record and lead to an overestimate of the sedimentation rate (Officer, 1982). Gas (methane) venting through fine-grained sediment to seafloor may also contribute to sediment disturbance in the western Irish Sea (Croker, 1995). In fact, when optimising our compartmental model for the Irish Sea (see Section 2.3.2 above), the best fit was obtained when a somewhat lower (generalised) sedimentation rate of $1 \times 10^{-3} \text{ t m}^{-2} \text{ yr}^{-1}$ (Table 1) was assumed for the western Irish Sea compartment.

Each of the ^{137}Cs profiles examined showed a clear sub-surface maximum at a depth of approximately 20 cm. If it is assumed that these maxima correspond to the year 1981 (as predicted by the semi-empirical model), apparent sedimentation rates of about 1.9 cm yr^{-1} are implied. The seeming discrepancy between these rates and those

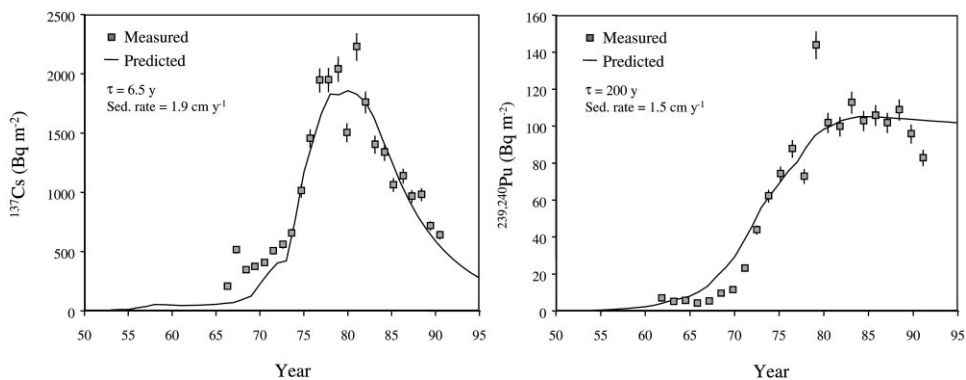


Fig. 11. Measured ($\pm 2\sigma$) and predicted (semi-empirical model) ^{137}Cs and $^{239,240}\text{Pu}$ deposition (vertical) profiles in seabed sediment at Station #101 in the western Irish Sea mud basin. The ^{137}Cs and $^{239,240}\text{Pu}$ inventories (to a depth of 50 cm) at this station are estimated to be 20 and 1.5 kBq m^{-2} , respectively, at the present time.

calculated on the basis of the ^{210}Pb profiles is almost certainly related to the vertical mobility of ^{137}Cs within the sediment column. This is not unexpected, since monovalent Cs^+ is less strongly adsorbed on sediment than bivalent cations such as Pb^{2+} .

The semi-empirical modelling approach has also been used here to predict ^{137}Cs concentration profiles in the sediments using as input both maximal and surficial ^{137}Cs concentrations and assuming that the former corresponds to the year 1981 as suggested above. Mean availability times for ^{137}Cs of 7–14 yr are predicted, in good agreement with the availability times estimated by modelling our time-series data (see Section 3.1.1). A typical example, highlighting the agreement between prediction and measurement for ^{137}Cs , is shown in Fig. 11. Confirmation that ^{137}Cs levels in surficial sediments had peaked by the early 1980s is provided by the shape of the ^{137}Cs profile in a sediment core sampled to the west of the Isle of Man in May 1982 (Mitchell et al., 1984), in which the sub-surface maximum appears to be just beneath the surface (Fig. 12).

The presence of a sub-surface maximum in these ^{137}Cs profiles lends weight to the view that appreciable sedimentation is taking place in the western Irish Sea mud basin. Indeed, numerical modelling of ^{137}Cs deposition under different mixing and accretion conditions has demonstrated that sub-surface maxima in sediment profiles will only be preserved when there is significant ongoing accumulation (MacKenzie & Scott, 1982).

The shape of the measured plutonium profiles closely resembles those predicted for Stations #7, #8 and #9 on the basis of the time-series data, with little variation in the top 20 cm of each profile. In fact, excellent agreement between measured deposition and that predicted by application of the Nicholson and Hunt semi-empirical model is obtained when apparent sedimentation rates of between 1.5 and 1.7 cm yr^{-1} are assumed. An example of the correspondence between measurement and prediction for $^{239,240}\text{Pu}$ is also shown in Fig. 11. Comparison of measured $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Pu}/^{239,240}\text{Pu}$ activity ratios with those predicted for Stations #7, #8 and #9

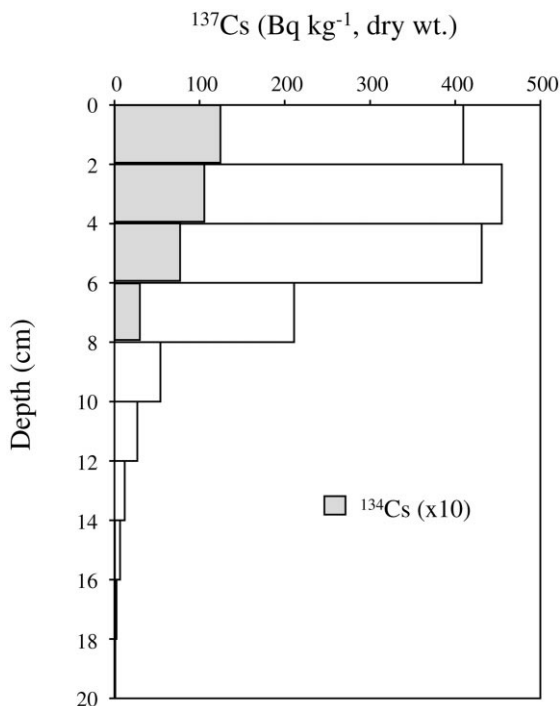


Fig. 12. Measured ^{137}Cs and ^{134}Cs depth profiles in a sediment core taken at a station ($54^{\circ}15'\text{N}$, $04^{\circ}55'\text{W}$) to the west of the Isle of Man in May 1982 (from: Mitchell et al., 1984).

confirms this chronology, with $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Pu}/^{239,240}\text{Pu}$ ratios increasing from ~ 0.04 and ~ 6 , respectively, in sediment layers corresponding to the late-1960s, to ~ 0.17 and ~ 13 , respectively, in more recently deposited layers close to the surface. The relevant plots for Station # 101 are shown in Fig. 13. Note that predicted concentrations and activity ratios are again based on an assumed $^{239,240}\text{Pu}$ availability time of 200 years.

The apparent sedimentation rates derived from the plutonium data are greater than those predicted by ^{210}Pb dating, but smaller than those predicted using the ^{137}Cs data. This places plutonium mobility in the muddy sediments of the western Irish Sea between those of lead and caesium. Similar observations have been made in respect of transuranic and caesium mobilities in other aquatic environments (Appleby et al., 1991).

In the case of ^{241}Am , the shape of the concentration profiles again closely resembles those predicted from the time-series data for Stations # 7, # 8 and # 9, with concentrations increasing towards the upper sections of the cores. The application of the semi-empirical model to the ^{241}Am concentration profile for the # 101 core, taking into account the ingrowth from ^{241}Pu , is shown in Fig. 14. Here, the apparent sedimentation rate was found to be 1.5 cm yr^{-1} , virtually identical to that determined on the basis of the plutonium data.

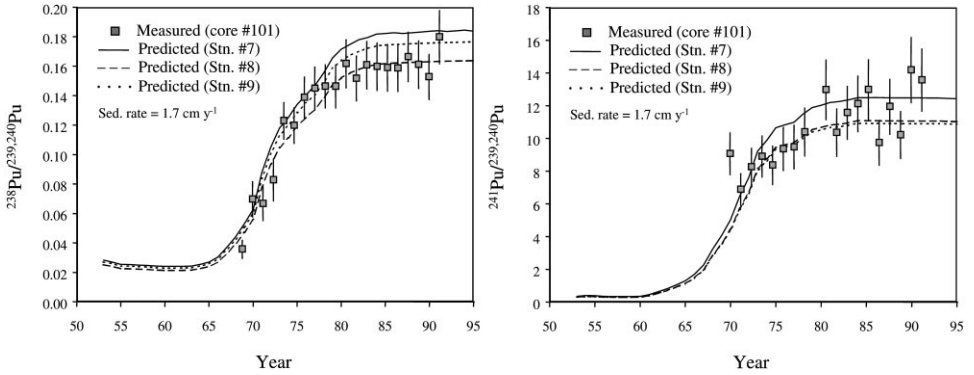


Fig. 13. Variation in measured $^{238}\text{Pu}/^{239,240}\text{Pu}$ and $^{241}\text{Pu}/^{239,240}\text{Pu}$ activity ratios ($\pm 2\sigma$) with estimated year of deposition at sediment station #101. For comparison purposes, the ratios predicted for surficial sediments at Stations #7, #8 and #9 using the semi-empirical model are also shown.

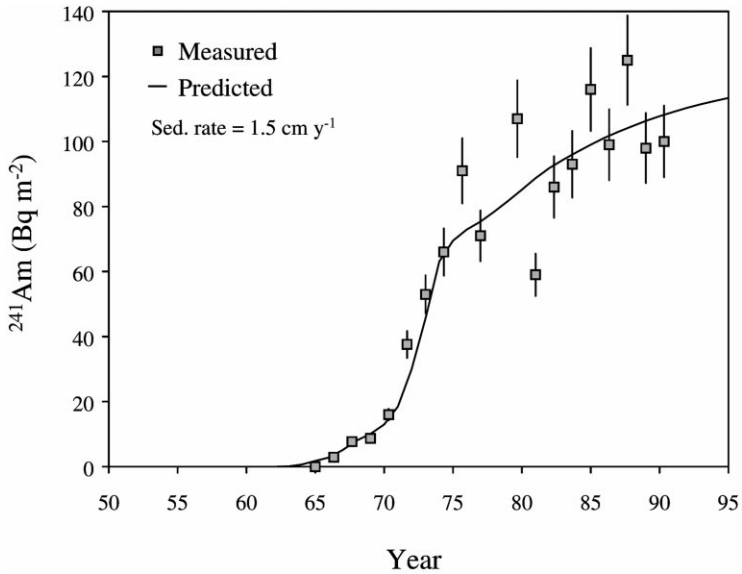


Fig. 14. Measured ($\pm 2\sigma$) and predicted (semi-empirical model) ^{241}Am deposition (vertical) profiles in seabed sediment at Station #101. The ^{241}Am inventory (to a depth of 50 cm) at this station is estimated to be 1.4 kBq m^{-2} at the present time.

The preservation of the integrated Sellafield signal and the agreement between measured concentration profiles and those predicted by modelling our time-series data, are further indications of recent sedimentation in the western Irish Sea mud basin.

3.2. Transect analysis and transport of actinides to the western Irish Sea

Concentrations of ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am in near-surface seawater sampled in December 1995 at eight stations along two separate transects from Sellafield, one to the north of the Isle of Man and the other to the south, are given in Table 6. The corresponding radionuclide ratios are also given.

Not unexpectedly, the concentrations of all three nuclides in filtered seawater were found to diminish as power functions with increasing distance from Sellafield (Fig. 15). In each case, the fall-off was less pronounced along the north-westerly transect, an observation consistent with the well-established pattern of water movement in the north eastern Irish Sea. Moreover, along both transects ^{241}Am concentrations declined more rapidly than those of ^{238}Pu and $^{239,240}\text{Pu}$. The preferential removal of americium from the dissolved phase with respect to plutonium is reflected in a decrease in the $^{241}\text{Am}/^{239,240}\text{Pu}$ activity ratio in this phase with increasing distance from Sellafield (Fig. 16). Other researchers have previously reported a similar decrease (Murray et al., 1978). In contrast, no diminution in the $^{241}\text{Am}/^{239,240}\text{Pu}$ ratio in suspended particulate is evident in our data.

Table 6
 ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am concentrations in seawater along transects running NW and SW from Sellafield, December 1995. Uncertainties given to $\pm 1\sigma$

Location	Fraction	Concentration (mBq m^{-3})			$^{238}\text{Pu}/$ $^{239,240}\text{Pu}$	$^{241}\text{Am}/$ $^{239,240}\text{Pu}$
		^{238}Pu	$^{239,240}\text{Pu}$	^{241}Am		
Stn. #17 53°52.74'N 05°33.42'W	Filtrate	8.8 ± 1.1	28.0 ± 2.0	5.6 ± 0.8	0.31 ± 0.04	0.20 ± 0.03
	Particulate	7.4 ± 0.7	41.3 ± 1.8	60 ± 3	0.179 ± 0.018	1.45 ± 0.09
Stn. #19 53°53.40'N 04°45.65'W	Filtrate	10.4 ± 0.7	58.3 ± 1.7	10.9 ± 0.6	0.179 ± 0.012	0.187 ± 0.012
	Particulate	11.2 ± 0.5	67.0 ± 1.3	106 ± 4	0.168 ± 0.007	1.58 ± 0.07
Stn. #27 54°00.20'N 04°01.04'W	Filtrate	8.6 ± 0.6	45.1 ± 1.5	16.0 ± 0.6	0.191 ± 0.015	0.355 ± 0.018
	Particulate	14.8 ± 1.8	69 ± 4	128 ± 6	0.22 ± 0.03	1.87 ± 0.13
Stn. #33 54°30.09'N 04°05.40'W	Filtrate	25.2 ± 1.4	133 ± 3	55.9 ± 2.4	0.190 ± 0.011	0.420 ± 0.020
	Particulate	66.9 ± 1.8	366 ± 6	684 ± 21	0.183 ± 0.005	1.87 ± 0.07
Stn. #35 54°24.71'N 03°35.14'W	Filtrate	124 ± 5	588 ± 13	429 ± 9	0.211 ± 0.009	0.730 ± 0.022
	Particulate	2228 ± 39	10807 ± 177	19342 ± 900	0.206 ± 0.002	1.79 ± 0.09
Stn. #37 54°29.93'N 04°44.44'W	Filtrate	9.4 ± 0.7	47.9 ± 1.6	18.9 ± 0.7	0.197 ± 0.015	0.395 ± 0.020
	Particulate	33.6 ± 0.8	209 ± 3	286 ± 11	0.160 ± 0.004	1.37 ± 0.06
Stn. #46 54°16.96'N 05°14.94'W	Filtrate	15.2 ± 0.8	70.3 ± 1.9	11.2 ± 0.5	0.22 ± 0.13	0.159 ± 0.008
	Particulate	14.2 ± 1.3	87 ± 4	138 ± 5	0.164 ± 0.016	1.58 ± 0.09
Stn. #49 54°36.73'N 05°14.58'W	Filtrate	14.6 ± 0.8	70.7 ± 1.9	24.3 ± 0.8	0.206 ± 0.012	0.344 ± 0.015
	Particulate	20.0 ± 1.1	112 ± 3	203 ± 7	0.178 ± 0.010	1.81 ± 0.08

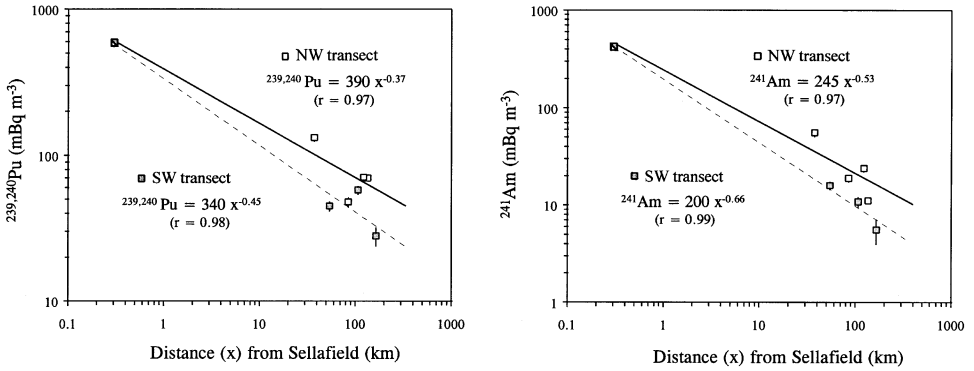


Fig. 15. Fall-off in $^{239,240}\text{Pu}$ and ^{241}Am concentrations ($\pm 2\sigma$) in filtered surface seawater with increasing distance from the Sellafield outfall (NW and SW transects).

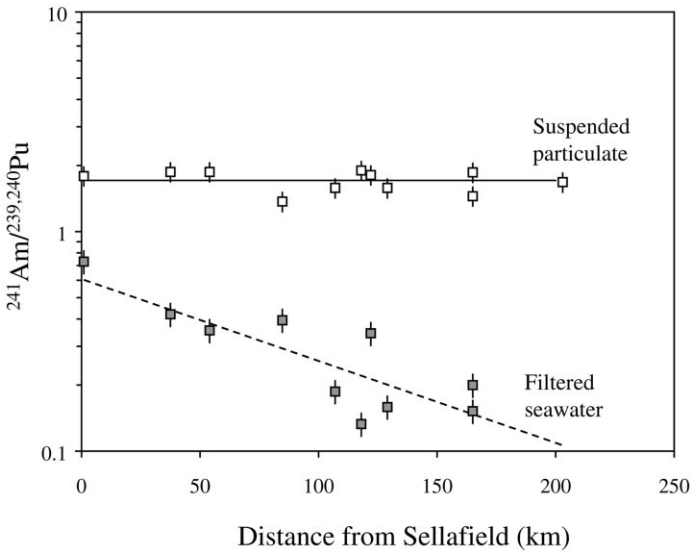


Fig. 16. Measured $^{241}\text{Am}/^{239,240}\text{Pu}$ activity ratios ($\pm 2\sigma$) in filtered seawater and suspended particulate with increasing distance from the Sellafield outfall.

$^{239,240}\text{Pu}$ and ^{241}Am concentrations in suspended particulate were also observed to diminish as power functions with increasing distance from Sellafield (Fig. 17). Again, a clear distinction was observed between the dispersion of particulate plutonium and americium in a northwesterly and a southwesterly direction, with a clear bias towards the former. This confirms the observation made in previous studies (Aston & Stanners, 1981; McDonald et al., 1990; Boust et al., 1996) that the advection of particle-bound plutonium is more active in a northerly direction.

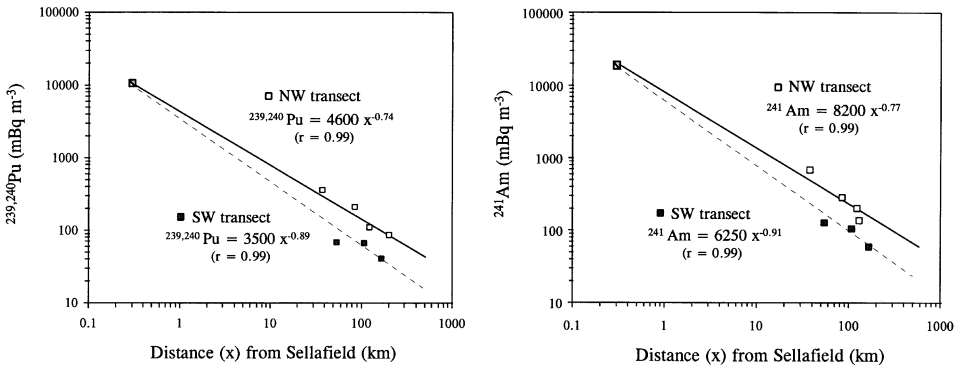


Fig. 17. Fall-off in $^{239,240}\text{Pu}$ and ^{241}Am concentrations in the suspended particulate fraction with increasing distance from the Sellafield outfall (NW and SW transects).

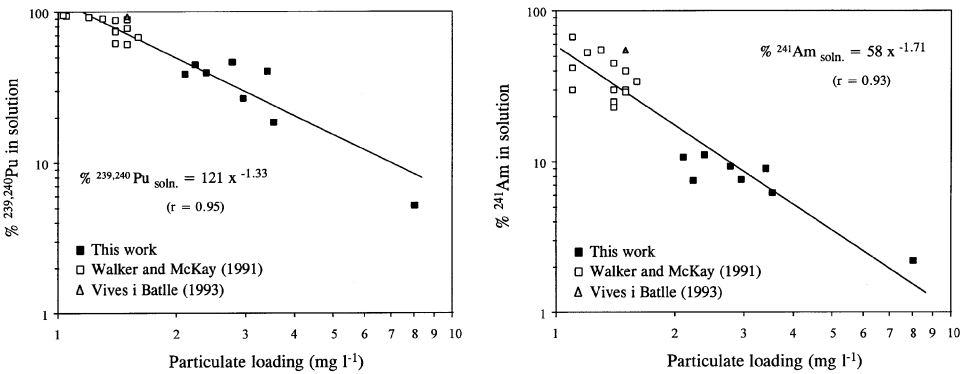


Fig. 18. Relationship between the percentages of $^{239,240}\text{Pu}$ and ^{241}Am in seawater in dissolved form ($<0.45\ \mu\text{m}$) and particulate loading.

The data in Table 6 show that 50–95% of the plutonium and 90–98% of the americium in waters sampled throughout the Irish Sea in December 1995 (following a heavy storm) were associated with the suspended particulate phase ($>0.45\ \mu\text{m}$). This contrasts with the partition observed in samples collected at Stations #7, #8 and #9 in the western Irish Sea in the period 1988–1995 (Table 4), when only 2–20% of the plutonium and 30–70% of the americium were found to be in particulate form. Similar variations within the same general zone have been reported by other workers (McKay & Pattenden, 1993; Vives i Batlle, 1993; Mitchell et al., 1995) and attributed to differences in the particulate loads at the time of sampling.

The role of suspended load in controlling the partitioning of transuranic nuclides between the filtered and suspended particulate fractions is illustrated in Fig. 18, where the proportions of plutonium and americium in solution are plotted against

particulate loading. It is obvious from these plots that temporal and spatial variations in the partitioning of plutonium and americium between the dissolved and particulate phases in open Irish Sea waters can largely be explained by variations in particulate loading. The latter, of course, depends on a number of factors including seasonality, meteorological conditions, currents, depth, nature of the sediment, etc.

Again, as in the case of the western Irish Sea mud basin (Section 3.1.3), there appears to be a small but significant difference between the mean $^{238}\text{Pu}/^{239}\text{Pu}$ activity ratio in the filtered and suspended particulate fractions at locations well removed from Sellafield (viz., Stations # 17, # 19, # 37, # 46 and # 49, all of which are located in the western/northwestern Irish Sea), reinforcing the view that most of the plutonium found in the western Irish Sea has been transported there in dissolved ($<0.45 \mu\text{m}$) form following resolubilisation from the heavily labelled eastern Irish Sea sediment pool. Some of the plutonium so transported is likely to have been in colloidal form (Mitchell et al., 1995).

3.3. Sediment-water distribution coefficients

Sediment-water distribution coefficients (K_{ds}) for $^{239,240}\text{Pu}$ and ^{241}Am in both the eastern and western Irish Sea zones have been deduced from the transect data and are given in Table 7. The mean K_{ds} for both nuclides are consistent with previously reported values for the Irish Sea (Pentreath et al., 1986; Mitchell et al., 1995). However, there is a suggestion in the data that the K_d for $^{239,240}\text{Pu}$ is slightly higher in the general vicinity of Sellafield than it is further afield. Such an observation has been made previously (Mitchell et al., 1995) and, if correct, may be due to the fact that plutonium is not in equilibrium within the sediment-water system of the eastern Irish Sea at the present time.

Table 7
Sediment-water distribution coefficients (K_{ds}) for plutonium and americium throughout the Irish Sea, December 1995. Uncertainties given to $\pm 1\sigma$

Location	K_d (total)	
	$^{239,240}\text{Pu}$	^{241}Am
Stn. # 17	$(4.3 \pm 0.4) \times 10^5$	$(3.1 \pm 0.5) \times 10^6$
Stn. # 19	$(4.1 \pm 0.2) \times 10^5$	$(3.5 \pm 0.3) \times 10^6$
Stn. # 27	$(6.4 \pm 0.5) \times 10^5$	$(3.4 \pm 0.2) \times 10^6$
Stn. # 33	$(9.3 \pm 2.7) \times 10^5$	$(4.1 \pm 1.2) \times 10^6$
Stn. # 35	$(2.3 \pm 0.1) \times 10^6$	$(5.6 \pm 0.3) \times 10^6$
Stn. # 37	$(1.2 \pm 0.1) \times 10^6$	$(4.3 \pm 0.3) \times 10^6$
Stn. # 46	$(5.5 \pm 0.3) \times 10^5$	$(5.5 \pm 0.3) \times 10^6$
Stn. # 49	$(7.6 \pm 0.3) \times 10^5$	$(4.0 \pm 0.2) \times 10^6$
Mean ($n = 8$)	$(9 \pm 6) \times 10^5$	$(4.2 \pm 0.9) \times 10^6$

3.4. Compartmental model predictions

The correspondence between predicted and measured $^{239,240}\text{Pu}$ concentrations in surface sediment and seawater in the Cumbrian and western Irish Sea regional compartments is shown in Fig. 19. It is evident from these plots that there is good agreement between measured and model-predicted concentrations for this nuclide. Preliminary analysis showed that the field data could not be reproduced by the model without the inclusion of the sedimentary processes discussed in Section 2.3.2 above. Overall, the agreement is satisfactory and gives confidence that the model can be used to provide realistic estimates of future concentrations in the various regional compartments.

Model predictions to the year 2100 of $^{239,240}\text{Pu}$ concentrations in surface sediment and seawater in the western Irish Sea compartment are given in Fig. 20. Clearly, $^{239,240}\text{Pu}$ concentrations are now just past their peak and are predicted to show a slow but steady decline into the future. In the case of the western Irish Sea, the model predicts mean availability times of *ca.* 100 yr for $^{239,240}\text{Pu}$ in seawater and surface

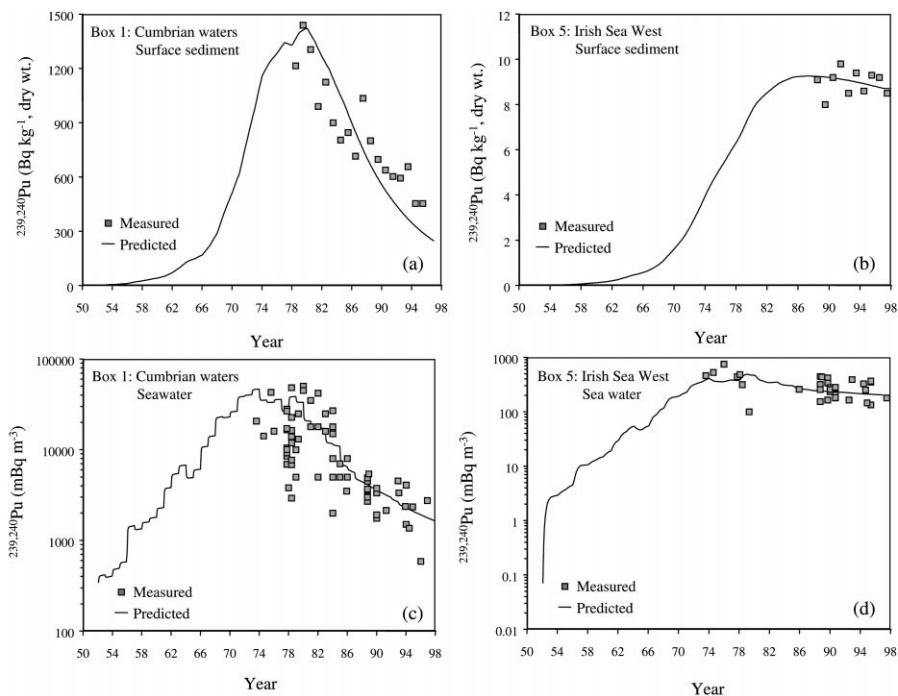


Fig. 19. Predicted (compartmental model) and measured $^{239,240}\text{Pu}$ concentrations in (a) surface sediment in the eastern Irish Sea; (b) surface sediment in the western Irish Sea; (c) filtered water in the eastern Irish Sea; and (d) filtered water in the western Irish Sea (measured concentrations taken from MAFF, 1978–1996; Hunt, 1985; Walker & McKay, 1991; McKay & Pattenden, 1993; Condren et al., 1996b; León Vintró, 1997; Leonard et al., 1999; this study).

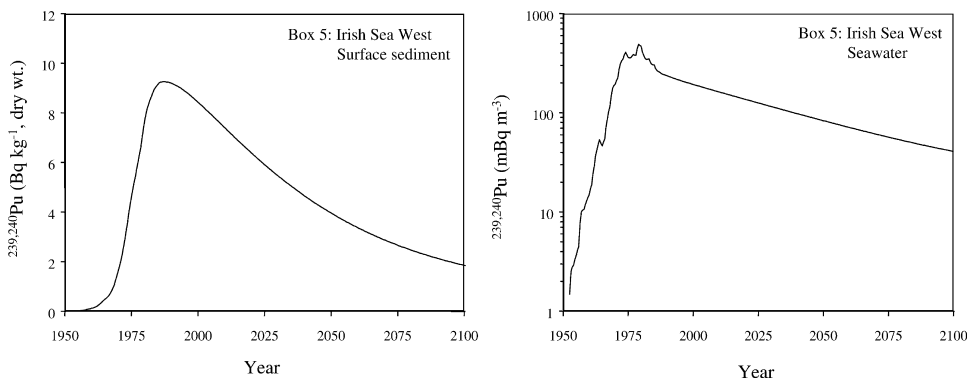


Fig. 20. Predicted (compartmental model) $^{239,240}\text{Pu}$ concentrations in surface sediment and seawater in the western Irish Sea for the period 1950–2100.

sediments. This is at the shorter end of the range predicted by the semi-empirical model, though the validity of using the latter to predict concentrations hundreds of years ahead is clearly questionable, given the large uncertainty in the estimated availability time for $^{239,240}\text{Pu}$ referred to in Section 3.1.1 above.

4. Conclusions

Our modelling results, supported by experimental observation, show conclusively that ^{137}Cs concentrations in western Irish Sea water and surficial sediment have already peaked and are now in steady decline, with estimated mean availability times for ^{137}Cs of ≈ 17 months and $\approx 7\text{--}16$ yr, respectively, at the present time. The total inventory in surface and deep sediments (combined) is also falling, with the somewhat longer mean availability time of ≈ 22 yr. These calculations are based on the assumption that discharges from Sellafield will remain at their present low level for several hundreds of years to come. At the present time, ^{137}Cs concentrations in seawater are little more than an order of magnitude higher than open ocean fallout levels, while concentrations in surface sediment are about two orders of magnitude higher.

In the case of $^{239,240}\text{Pu}$, our models show that concentrations in seawater and surface sediment in the western Irish Sea mud basin peaked in the late 1970s and early to mid-1980s, respectively. However, they predict that the fall-off in both compartments will be very much slower than for ^{137}Cs . A similar observation applies to ^{241}Am . Field measurements in the period 1988–97 are consistent with these predictions. In contrast, the $^{239,240}\text{Pu}$ inventory in deep sediment has not yet peaked and is not predicted to do so for at least several thousand years, provided these sediments are not subjected to significant physical disturbance (e.g., seismic activity).

It has been clear for some time that the decreases observed in ^{137}Cs and plutonium concentrations in the eastern Irish Sea can only be explained on the basis of

remobilisation from the seabed sediments in this region. It is now evident that the temporal evolution of ^{137}Cs and plutonium concentrations in the western Irish Sea is being driven by the rate at which these nuclides are being remobilised in the eastern Irish Sea and transferred to the western Irish Sea. Measurement of transuranium activity ratios in the western Irish Sea mud basin, as well as in filtered and suspended particulate sampled in east–west transects from Sellafield, indicate that desorption of these nuclides from the pool of well-mixed sediments in the eastern Irish Sea, followed by transfer, primarily in soluble form, to the western Irish Sea are the dominant mechanisms involved.

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