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An assessment of the availability of Tc-99 to marine foodstuffs from contaminated sediments

FSA Project R01062

Environment Report RL 09/08

An assessment of the availability of Tc-99 to marine foodstuffs from contaminated sediments

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List of contents **Page No.**

List of Tables **Page No.**

List of Figures Page No.

Executive summary

Technetium-99 is a long-lived ($t^{½}$ = 2.13 x 10^5 years) beta-emitting radionuclide and is an increasingly important component of high-level radioactive wastes. It is also present in the liquid effluent that has been discharged, under authorisation, into the north-east Irish Sea from the British Nuclear Fuels (BNF) reprocessing plant at Sellafield (Cumbria, UK) for over 50 years. The enhanced ^{99}Tc discharges to the Irish Sea between 1994 and 2003 have been the subject of national and international controversy, resulting from the perceived contamination of regional fisheries. The impact upon the Norway lobster, *Nephrops norvegicus*, is of particular concern given i) the relatively high bioaccumulation by this species, and ii) that it constitutes a most valuable fishery in the Irish Sea. Results from previous Food Standards Agency (FSA) projects (FSA, 2001) have provided preliminary indications of measurable ^{99}Tc uptake in Irish Sea sub-tidal sediments. The aim of the present project was to more fully investigate seabed accumulation and to assess the implications for seafood contamination. This was achieved via i) a program of sediment core sampling to estimate the inventory of ^{99}Tc currently residing in the sub-tidal sediments of the Irish Sea, and ii) tuning, validating and applying a multi-compartmental model to estimate the rate and extent of re-dissolution of ^{99}Tc into the overlying seawater, and hence the availability of ^{99}Tc to marine foodstuffs.

The inventory of ^{99}Tc currently residing in the sub-tidal sediments of the Irish Sea is estimated to be of the order of 37 TBq. The multi-compartmental model was optimised and validated using our detailed long-term datasets for ^{137}Cs, given that remobilisation is known to provide the major contribution towards present levels of this radionuclide in seawater and seafood. Further effort (outside the scope of the present study) was however identified as being necessary to improve the simulation of vertical mixing processes within the seabed. Technetium-99 seawater data, derived from model simulations, have subsequently been used to estimate levels in seafoods (and hence the dose to seafood consumers) using the concentration factor (CF) method. The impact of ^{99}Tc remobilisation from sediments upon levels in the water column is predicted to be minimal in the short to medium term (up to 2012). CF values for accumulation between individual species of shellfish are highly variable and complicate the comparison of environmental data and model

simulations. Although predicted doses are slightly lower than those provided in recent RIFE reports, the disparity is relatively small (< 3 fold) given the errors associated with both sets of values. It seems reasonable to conclude that discharges from Sellafield (hence levels in fish and shellfish in the Irish Sea) are likely to remain broadly similar to those in 2005 in the short to medium term (up to 2012). Consequently, levels in *Nephrops* are likely to persist at ~100 Bq/kg wet weight and ~10 Bq/kg wet weight in the eastern and western Irish Sea, respectively.

1. Introduction

Technetium-99 is a long-lived ($t^{½}$ = 2.13 x 10^5 years) beta-emitting radionuclide ($E_{\beta\ max}$ = 292 keV) and is an increasingly important component of high-level radioactive wastes (Wildung et al., 1979). It is also present in the liquid effluent that has been discharged, under authorisation, into the north-eastern Irish Sea from the British Nuclear Fuels (BNF) reprocessing plant at Sellafield (Cumbria, UK) for over 50 years. The elevated levels of ^{99}Tc released between 1994 and 2004 have been the subject of national and international controversy (Defra, 2002). The magnitude of the discharges had an immediate and well-recognised impact upon ^{99}Tc concentrations in some items of seafood and seaweed (Hunt et al., 1998; FSA, 2001; Smith et al., 2001).

Bio-accumulation in the Norway lobster, *Nephrops norvegicus*, is of particular concern given i) the extent of uptake and ii) that this species constitutes the most valuable fishery in the Irish Sea (ICES Sea Area VIIa) (http://statistics.defra.gov.uk/esg/publications/fishstat/; Briggs et al., 2002). Two separate populations of *Nephrops* exist in areas of muddy sediments in the eastern and western Irish Sea. The western population occupies a much larger area of mud than in the east, and provides the bulk of the commercial landings. Otter-trawl vessels from Northern Ireland and the Republic of Ireland are a considerable component of the *Nephrops* fishing effort. Otter trawl vessels use cone-shaped nets, trawled along the seabed to catch ground fish and prawns. The UK fleet obtained almost 5000 tonnes in 2004 with a first sale value of ~£8 million – these data are put into context by the fact that, in 2004, landings by the UK fleet of other species were ~20,000 tonnes with a first sale value of ~£16 million. Landings of *Nephrops* by the Irish Fleet in 2004 were of similar magnitude. Although the dose to man from seafood consumption is very low (Environment Agency et al., 2005), the socio-economic impact, due to perceived contamination, has been disproportionately large.

Another consequence of the enhanced ^{99}Tc discharges, which was less readily anticipated, was the accumulation of ^{99}Tc in the seabed sediments. Results from a previous FSA-funded project (FSA, 2001) have provided preliminary data indicating accumulation of ^{99}Tc in both surface sediment and sediment cores. One goal of this project was, therefore, to estimate the ^{99}Tc inventory in the sub-tidal sediments of the Irish Sea. This was achieved via an environmental survey involving the collection and analysis of sediment cores to produce ^{99}Tc depth profiles. The second objective was to assess the likely implications for future contamination of the food chain, due to remobilisation, for the most realistic discharge scenario. This was achieved using two different models. The model output was compared with new and existing ^{137}Cs sediment and seawater data (to provide validation of the model output).

2. Sampling and analysis

2.1 Sampling strategy

2.1.1 Previous investigations

The sampling design in the present study was informed by i) results from previous investigations (in 1978, 1988 and 1995) carried out to estimate the inventory of ^{137}Cs, ^{239,240}Pu and ^{241}Am in the sub-tidal sediments of the Irish Sea (Poole et al., 1997; Kershaw et al., 1999) and ii) operational factors, such as available ship time and the radioanalytical capacity of Cefas' Lowestoft laboratory.

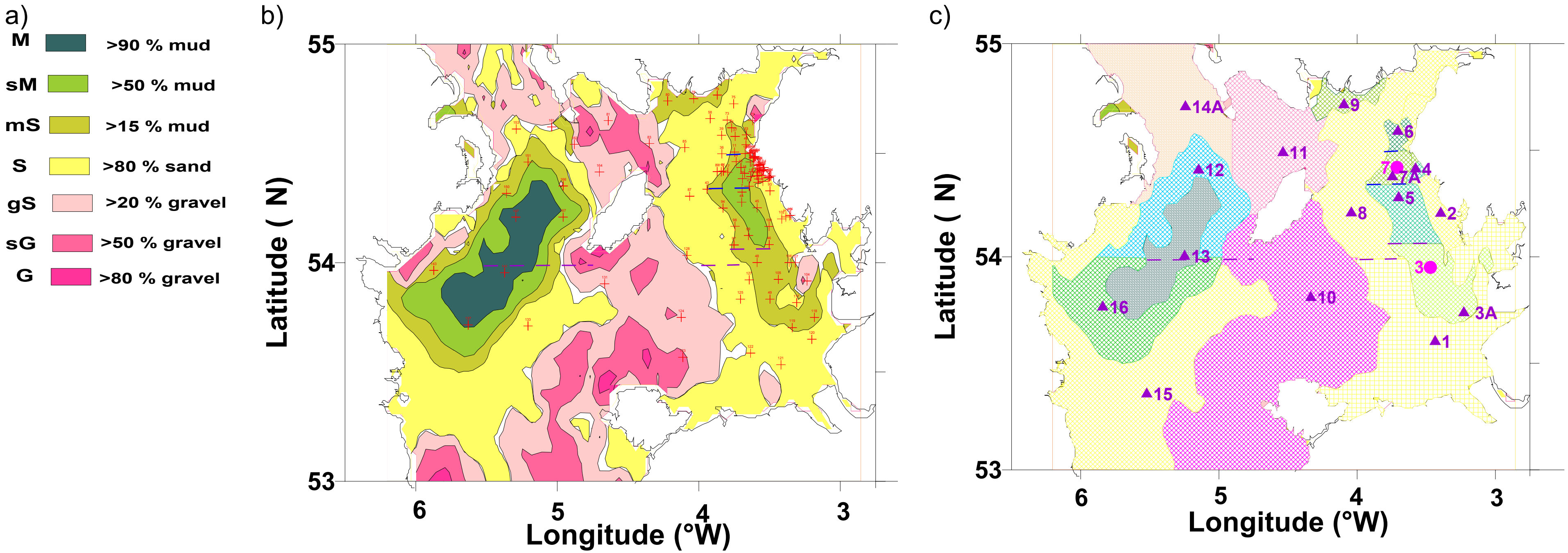
The radionuclide distribution in the sediments of the Irish Sea is greatly influenced by their particle size and distance from Sellafield, with the activity being greatest on fine-grained material close tothe Sellafield pipeline (Poole et al., 1997; Kershaw et al., 1999). Muddy sediments are confined to two main areas (Figure 1): a belt of sandy muds and muddy sands parallel to the Cumbrian coast, extending into Morecambe Bay in the south and partly across the mouth of the Solway Firth in the north; and a relatively deep (~100 m) basin between the Isle of Man and Ireland. Both areas coincide with zones of relatively weak tidal currents (Kershaw et al., 1992). Elsewhere the surface sediments are coarser grained. Gravely material, representing glacial lag deposits, predominates in the central Irish Sea to the north and south of the Isle of Man (and in St Georges Channel) grading into mobile sands in the east and south-west.

The vertical distribution of radionuclides within the seabed is markedly heterogeneous below depths of 5 -10 cm, particularly in muddy areas of the north-eastern basin, as a result of incomplete or episodic mixing processes (Kershaw et al., 1999 and references therein). The vertical mixing has been attributed to bioturbation, physical re-suspension (e.g. during storms and trawling) and settling processes (Kershaw et al., 1992). Traces of activity have been reported to occur at depths greater than ~70 cm in the eastern Irish Sea mud patch (Woodhead and Pentreath, 1992). Although radionuclide concentrations in replicate samples of surface sediment tend to be quite similar, in subsurface samples spaced a few cm apart levels can vary by more than two orders of magnitude. The disparities tend to increase with depth. This feature introduces considerable uncertainty in obtaining representative sediment core samples (i.e. the potential sampling error is large).

2.1.2 Current project

The most recent sub-tidal sediment inventory survey, prior to the present study, was undertaken over a period of ~10 days in June 1995, and involved the collection of over 100 cores from the sites shown in Figure 1b using a dedicated research vessel. In an attempt to reduce the uncertainty resulting from sampling error, a large number of cores were collected in the muddy sediments close to Sellafield. Unfortunately, dedicated ship time is extremely expensive. To reduce the cost to the FSA customer, sediment core sampling for the present study was carried out over a period of just five days using windows of opportunity aboard the research vessels Corystes and Cefas Endeavour, which were being used primarily for Defra funded fisheries surveys in the Irish Sea. The sampling strategy for the present study (Figure 1c) was therefore significantly less extensive than previous surveys, and involved the planned collection of just 16 cores representing individual sectors of the Irish Sea (Table 1).

Figure 1. *Sampling strategy for collection of cores to estimate radionuclide inventories in the sub-tidal sediments of the Irish Sea. a) Legend indicating composition of surface substrate (for Figure 1b), b) Most recent study to assess the inventory of ^{137}Cs, ^{239,240}Pu and ^{241}Am (June 1995, Cir 5/95). ^{137}Cs data for the sites shown here have been reworked to estimate likely sampling error (Table 1). c) Present study. Triangles and circles indicate sampling sites in June 2006 (CEnd 13/06) and September 2005 (Cory 3/05), respectively.*



The distribution of sampling sites in the present study (Figure 1c) covers all the major surface sediment substrates. The intensity of sampling was designed to be greatest on muddy material close to Sellafield. This is because results from the previous surveys (Poole et al., 1997; Kershaw et al., 1999) indicated that the bulk of the radionuclide inventories were located in the 'muddy' sediments close to the Cumbrian coastline. The objective of the present strategy was to obtain a balance between an even geographical coverage and the possibility that the majority of the ^{99}Tc is also likely to reside close to the Cumbrian coastline.

2.1.3 Reworking historic data to assess likely sampling error in present study[1]

The raw ^{137}Cs data from the June 1995 survey were reworked to: i) estimate the inventory in the individual sectors sampled in the present study and ii) compare the value for the sum in all sectors with the previously published value derived using the full dataset. It was anticipated that this could provide a useful indicator of the additional sampling errors that are likely to result from our reduced coring programme. The results are provided in Table 1. These data show that, for a given sector, the variation in ^{137}Cs inventories between individual cores could be significant (typically by an order of magnitude but as high as two orders of magnitude in sector 3).

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[1] Historic data were previously obtained from a number of research cruises (note, references to Cir, Clione and CEnd in text, figures and tables refer to Research Vessels, RV Cirolana, RV Clione and RV Cefas Endeavour, respectively).

Table 1. *Sampling strategy for collection of cores to estimate ^{99}Tc inventory in the sub-tidal sediments of the Irish Sea. Sectors covered by individual sediment cores, along with estimates of ^{137}Cs inventories in June 1995, derived from locations shown in* Figure 1c.

Site No.	Sector description (1)	Area of sector (km^2)	Fraction of total area	Number of sediment cores	Estimated ^{137}Cs inventory, (Bq/m^2) (2)		^{137}Cs inventory (TBq)	Fraction total ^{137}Cs inventory
					Average±Stdev	Range		
1	EIS Sand South	4088	11%	5	36,388±29,060	9,176-85,76	149±119	14%
2	Sellafield shore	391	1.1%	6	55,607±64,618	6,249-155,803	22±25	2.0%
3	EIS Muddy Sand South	1050	3%	8	128,571±126,396	1,391-334,392	135±133	13%
4	Sellafield PLZ	73	0.2%	20	391,795±547,537	23, 479-2,100,498	29±42	2.7%
5	EIS Mud Patch Central	635	2%	10	192,853±115,630	29,474-351,911	122±73	11%
6	EIS Muddy Sand North of ~54.5°N	159	0.4%	8	429,304±351,609	39,309-1,068,203	68±56	6.4%
7	Sellafield offshore	305	1%	14	373,974±258,871	32,291-703,293	114±79	11%
8	EIS Sand North	2795	8%	10	61,254±64,507	1,469-197,442	171±180	16%
9	Scottish coast	317	0.9%	3	25,648±80,755	38,566-171,532	25±26	2.3%
10	CIS South	7933	22%	3	3,433±1011	2,631-4,569	27±8	2.5%
11	CIS North	2246	6%	4	11,711±13,607	3,817-32,014	26±31	2.5%
12	WIS North	1611	4%	4	14,825±2,795	10,886-17,199	24±5	2.2%
13	WIS Mud	1587	4%	3	36,366±23,834	11,513-59,037	58±38	5.4%
14	North Channel	2612	7%	2	6,058±1,364	5,093-7,023	16±4	1.5%
15	WIS Sand	5577	15%	1	2,698	2,698	15	1.4%
16	WIS South	1953	5%	1	35,014	35,014	68	6.4%
	Not sampled	~3027	8%					
Sum		36, 359	100%				1069±291	

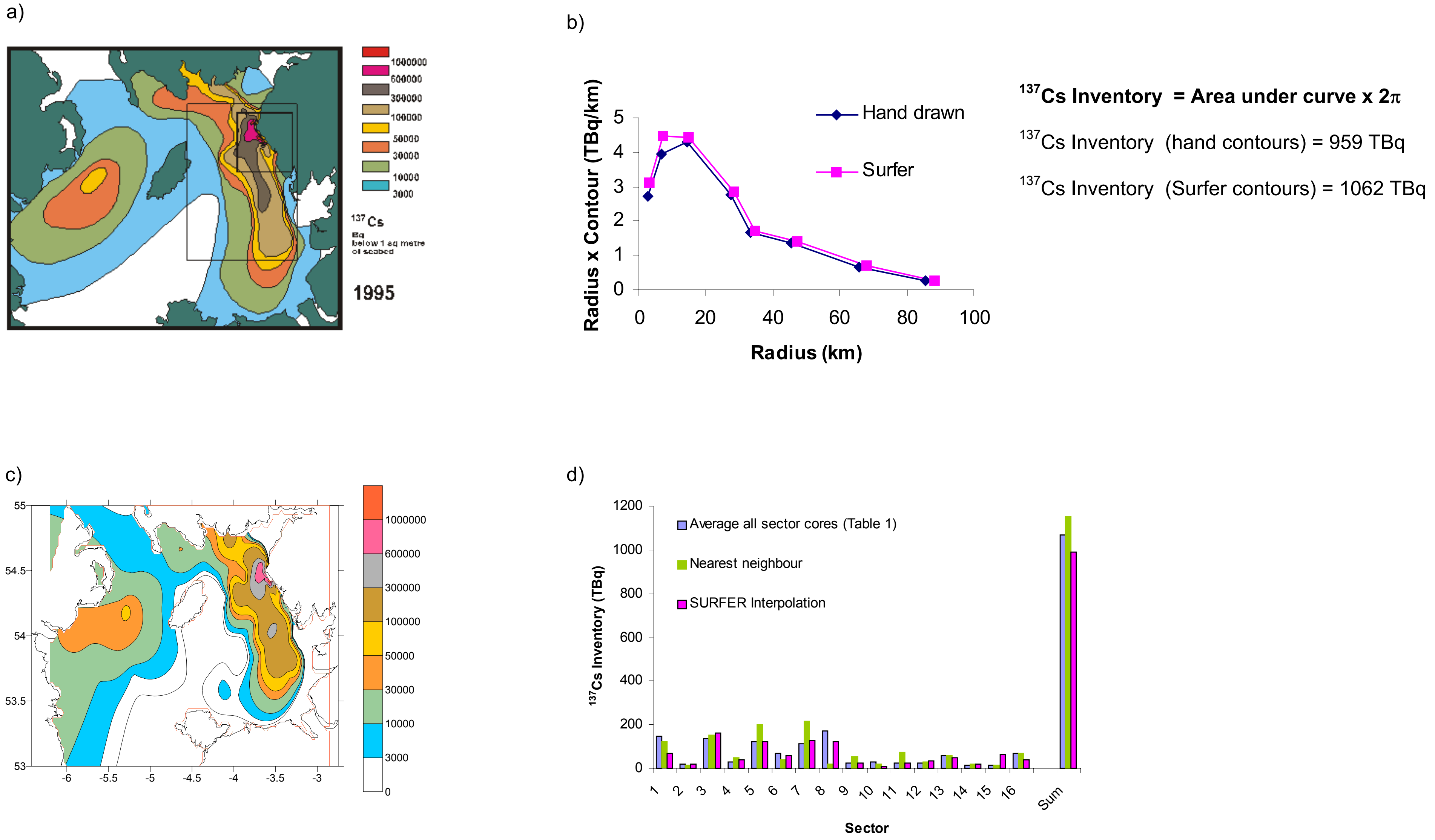
(1) EIS, CIS and WIS denote Eastern Irish Sea, Central Irish Sea and Western Irish Sea, respectively.

(2) Average and standard deviation estimated from cores collected in June 1995 (Figure 1b) in sectors shown in Figure 1c. No value for standard deviation is provided where data is only available for one core.

The derived value for the total ^{137}Cs inventory in the sub-tidal sediments in the Irish Sea in June 1995, obtained by calculating the mean inventory of all cores in a given sector and provided in Table 1 (1069 TBq), is slightly greater (by ~10% or 110 TBq) than the previously reported value (959 TBq; Poole et al., 1997). It is worth noting that, had only a single 1995 core been used, selected on the basis of being the closest to the 2006 sampling location, the derived value for the total ^{137}Cs inventory would have been 1150 TBq (see Figure 2d), which is ~20% greater than the published value.

Unfortunately, no attempt was made by the authors (i.e. Poole et al., 1997) to quantify the error associated with their inventory estimate. An attempt was, therefore, made to assess the likely error allied to the published value by re-examining the original (source) data. Inspection of the raw data (Denoon, pers. comm.) indicates these authors considered two alternative methods to estimate the ^{137}Cs inventory. In the first, results were manually contoured from individual cores (Figure 2a). The contours were drawn (by hand), using a consistent protocol to decide their position relative to the adjacent data points, taking into account the coastal boundary and being guided by the known sediment grain-size distribution where inventory data were sparse. The areas encompassed by adjacent contours were then measured manually using a planimeter. These results were subsequently interpolated (Figure 2b) by constructing a plot of rP versus r (where r is the equivalent radius of circle for the area encompassed between individual contours and P is the activity represented by each contour line). The inventory estimate (959 TBq) was derived by measuring the area beneath this plot (in Bq) using a planimeter and multiplying by 2π. The uncertainty associated with the derived value is, therefore, a summation of the error associated with the contouring and interpolation process. Their second method (Figure 2c) consisted of contouring the raw sediment core data using a commercial software package (SURFER®). For consistency, the areas encompassed by adjacent contours were once again measured manually using a planimeter and plotted (Figure 2c) to derive an alternative total inventory estimate (1062 TBq).

Figure 2. *Derivation of estimate for ^{137}Cs inventory in the sub-tidal sediments of the Irish Sea in 1995 (Poole et al., 1997). a) Hand drawn contour plot, b) plot of rP verus r to interpolate between contours, c) Contour plot drawn using SURFER® package, d) Independent ^{137}Cs inventory estimates in individual sectors.*



^{137}Cs Inventory = Area under curve x 2π

^{137}Cs Inventory (hand contours) = 959 TBq

^{137}Cs Inventory (Surfer contours) = 1062 TBq

It was considered that the first method (i.e. hand drawn contours) provided a better representation of the ^{137}Cs distribution in the Cumbrian coastal zone (Poole et al., 1997). Primarily, this was because the relative paucity of data posed problems at the boundary (i.e. the beach). Accuracy in this region was considered critical because of the relatively high seabed inventories and steep concentration gradients. Whatever the most appropriate method the discrepancy between the two inventory estimates was ~11%, providing an indication of the error associated with contouring the raw data. It is also possible to derive a crude estimate of the error associated with the second process (i.e. interpolating between contour areas by plotting rP vs r to estimate the total inventory). When the raw sediment data are contoured using SURFER®, a grid file is created that can be used to directly calculate the sediment inventory (i.e. obviating the need to manually measure areas between contours and interpolate by plotting rP vs r). For the purposes of the current study, the SURFER® grid file was used to derive a total inventory estimate of ~991 TBq. Comparison of the two SURFER® estimates (i.e. 991 TBq and 1062 TBq) indicates the error associated with interpolating between individual contours (i.e. ~7%) was less than that in contouring the data. If the combined error is (simplistically) estimated by propagating the two individual estimates in quadrature, then the overall error associated with the estimate provided by Poole et al. (1997) is ±13% (i.e. 959 ± 125 TBq).

The error associated with both the reported estimate and our reworked value (1069 ± 291 TBq or ±27%, derived by propagating the standard deviation of values for all cores within a given sector, see Table 1) suggests that the disparity between the two values is not statistically significant. It is, however, acknowledged that our estimate of the error associated with our very limited sampling programme (i.e. almost 30%) probably represents a lower limit.

Finally, it is worth noting that historical sediment cores have been collected using a variety of coring devices in previous investigations, dependent upon the substrate being sampled and equipment availability. Unfortunately, the successive coring programmes have consistently failed to reach the limit of the radionuclide contamination, particularly in the sandy and gravelly sediments (Kershaw et al., 1999). In an attempt to address this problem, sampling for the present study was carried out using a geological corer (vibrocorer).

2.2 Sediment sampling methods

Deep (~ 2 m) and near surface (<40 cm) sediment cores were obtained by deploying a vibrocorer and NIOZ corer. These are specialist and standard items of equipment used in geological and benthic research, respectively. The NIOZ core was sub-sampled using a 10 cm diameter plastic tube. All cores were subsequently sliced. The sections were freeze-dried and thoroughly mixed prior to sub-sampling for radiochemical analysis.

2.3 Radionuclide analysis

To determine the concentrations of ^{99}Tc in the sediment samples, rhenium carrier (10 mg), a chemical analogue of technetium, was added as a yield monitor. The sediment was subsequently leached with 6M HCl. The ^{99}Tc in the acid extract was separated from gravimetric and radiometric interferences by ion exchange and selective co-precipitation. Following purification both technetium and rhenium were precipitated as tetraphenyl arsonium complexes, collected on a filter paper and beta counted against commercially available referenced standards of ^{99}Tc obtained from National Physical Laboratory (NPL). The detection limit was ~ 0.3 Bq/kg. Full details of the analytical procedures for ^{99}Tc are reported elsewhere (Harvey et al., 1991; 1992). For a few selected samples, an additional characterisation was carried out, by counting γ emitting radionuclides (including ^{137}Cs) on a high purity Ge detector.

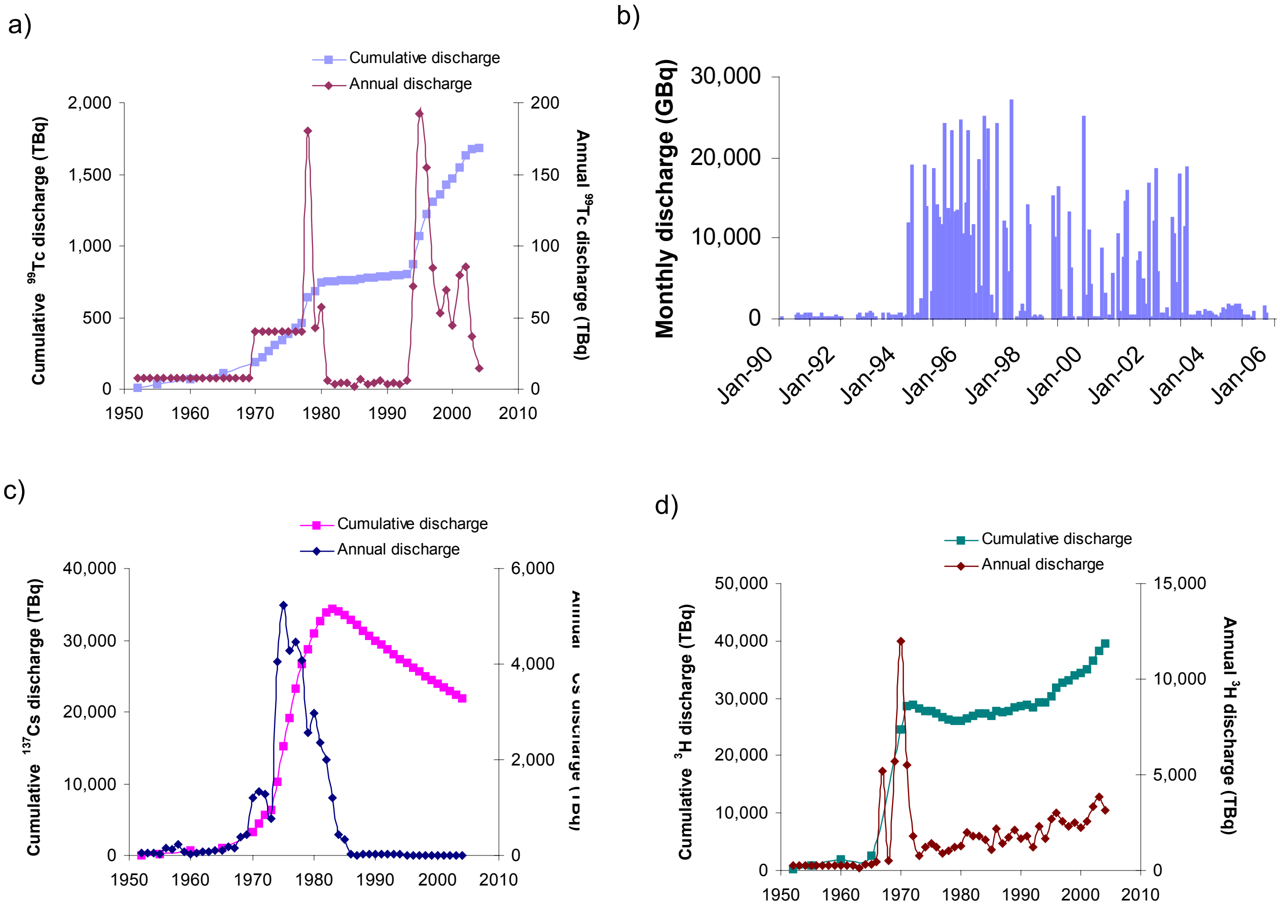
3. Results

3.1 Chronology of liquid discharges into the Irish Sea from Sellafield

Since liquid discharges to sea began in 1952, a range of radionuclide determinations has been carried out on Sellafield liquid effluent including ‘total beta’ (Gray et al., 1995). The latter radiochemical analysis would exclude the contribution from low energy beta emitters, but some nuclides such as ^{99}Tc would be included (albeit with lower counting efficiency). Therefore, discharges of ^{99}Tc in the years 1952 to 1977 have been estimated by extrapolation from available measurements. In 1978, the operators expanded their radioanalytical survey to incorporate a number of specific nuclides including ^{99}Tc. The annual discharges of ^{99}Tc for 1952 to 2005, based on published data (CEC, 1990; NRPB, 1995; BNF, 1979-2006), are given in Figure 3a. Technetium-99 discharges during the 1970s were significantly greater than those in the 1980s. In 1994 the discharge of ^{99}Tc returned to the previous higher levels. This increase followed the commissioning and operation of the Enhanced Actinide Removal Plant (EARP), an additional treatment plant designed to reduce alpha and beta activity in effluents prior to discharge. The installation of this plant allowed the reprocessing of medium active concentrate (MAC) wastes, which had previously been accumulating on site, but necessitated the discharge of ^{99}Tc that is not significantly removed by the EARP treatment process. The backlog of stored MAC has now been processed. In addition, substantial progress has recently been made in reducing ^{99}Tc releases from Sellafield following the introduction of new abatement technology and by diverting some MAC arisings into vitrification; thus reducing the amount to be treated in EARP (Environment Agency et al., 2005; Mayall et al., 2005). The new treatment uses TPP (tetraphenylphosphonium bromide) to complex the ^{99}Tc in the MAC treatment plant discharge so that it is stored as a solid. Trials in 2003 showed 95% removal of ^{99}Tc from this waste stream (arising from Magnox spent fuel reprocessing, which provides the dominant source for this radionuclide in liquid effluent released to sea). Consequently in 2005, Sellafield were able to achieve an overall reduction in liquid discharges of ^{99}Tc from the site of ~90% compared with 2002 levels.

A more detailed chronology of the ^{99}Tc discharges (monthly), from January 1993 to June 2006 (BNFL, pers. comm.) is provided in Figure 3b. The monthly ^{99}Tc data show the extent, and pulsed nature, of elevated levels of discharge, commencing in March 1994 and ending in October 2003.

Figure 3. *Liquid discharges of selected radionuclides into the Irish Sea from Sellafield. a) Annual and cumulative discharges of ^{99}Tc (1952-2005), b) Monthly discharges of ^{99}Tc (January 1993 - June 2006), c) Annual and cumulative discharges of ^{137}Cs (1952-2005), d) Annual and cumulative discharges of ^{3}H (1952-2005).*



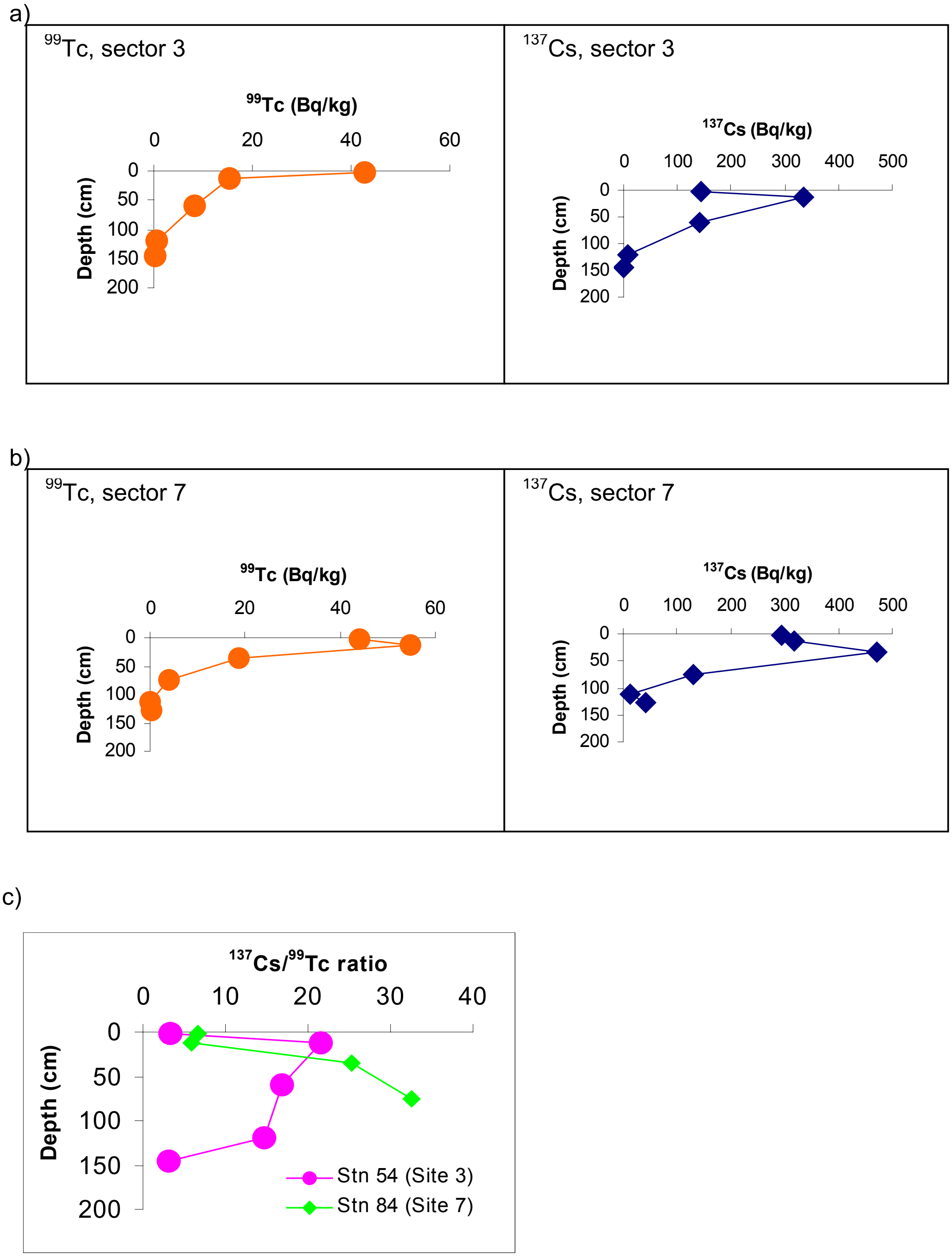
Data for the annual and cumulative discharges of ^{137}Cs and ^{3}H are also provided, in Figure 3c and Figure 3d respectively, as the environmental behaviour of these radionuclides is also considered in this report. Releases of ^{137}Cs peaked in 1975. They were drastically reduced (by ~ two orders of magnitude) between 1983 and 1986, following the installation and commissioning of the Site Ion Exchange waste treatment Plant (SIXEP). Over the last two decades releases have remained extremely small, in relation to the high discharges of the 1970s. Consequently, the cumulative ^{137}Cs discharge reached its maxima in 1984 and has slowly decreased with time as a result of radioactive decay. The temporal variation in releases of ^{3}H (Figure 3d) has been significantly less than those exhibited by ^{99}Tc and ^{137}Cs.

3.2 Inventory of ^{99}Tc in sub-tidal sediments of the Irish Sea

3.2.1 Preliminary survey (September 2005)

An initial programme of sampling was carried out in September 2005 aboard the research vessel, RV Corystes. Unfortunately, the weather conditions restricted collection of deep cores (i.e. use of the vibrocorer) to just two sites in the eastern Irish Sea. Other demands upon the ship's programme severely reduced the flexibility afforded by the dedicated vessel time available to previous surveys carried out between 1978 and 1995. The analysis of the two cores (from sites 3 and 7) was brought forward to gain a preliminary insight into the success of the sampling strategy in reaching the limit of ^{99}Tc contamination and the likely sub-tidal sediment inventory. The results are provided in Figure 4. Additional cores (NIOZ) were collected, including the collection of relatively shallow cores at sites 4 and 13 (Figure 7).

Figure 4. *Vertical distribution of radionuclides down sediment cores from the Irish Sea in September 2005 (Survey: Corystes 3/05). a) Site 3 (EIS Muddy Sand South), b) Site 7 (Sellafield offshore, c) ^{137}Cs/^{99}Tc ratio*



To a first approximation, the ^{99}Tc distribution in both cores was broadly similar in that i) the maximum activity was observed in the top 20 cm and ii) below 20 cm the activity decreased exponentially such that levels of ^{99}Tc were below the limit of detection (~0.3 Bq/kg dry weight) beneath a depth of 1 m. The ^{137}Cs distribution differed slightly in that the profile was broader with a distinct subsurface peak in both cores. Consequently, the ^{137}Cs/^{99}Tc ratio increased from <7 in the top 5 cm up to >20 in subsurface material. The average ^{137}Cs/^{99}Tc ratio in the whole core, determined from the inventory values, was ~16 in both samples and almost identical to that observed in the cumulative Sellafield discharge (~13).

The values obtained for the ^{99}Tc inventory at each site (~1.5 x 10^4 Bq/m^2 and ~1.9 x 10^4 Bq/m^2 for sites 3 and 7, respectively), may be used to estimate the inventory in the particular sector that the core represents (Table 2).

The inventory of ^{99}Tc in sectors 3 and 7 was estimated to be ~16 TBq and 6 TBq, respectively. Comparable values for ^{137}Cs were ~246 TBq and 96 TBq, respectively. If it is assumed that the spatial distribution of the ^{137}Cs inventory was unchanged from 1995 (see data in Table 1 indicating that ~13% and 11% were present in sectors 3 and 7, respectively), then the sector inventories presented in Table 2 suggest that the total ^{137}Cs sub-tidal inventory in 2005 was of the order 10^3 TBq. Assuming that the sub-tidal ^{99}Tc is similarly distributed, Table 2 suggests a total inventory of the order 10^2 TBq.

Table 2. *Estimates of radionuclide inventories in individual sectors of the Irish Sea in September 2005, derived from the data in Figure 4.*

Sector	Radionuclide inventory (Bq/m^2)	Sector area (km^2)	Sector inventory (TBq)
	^{99}Tc		
3	1.5 x 10^4	1050	16
7	1.9 x 10^4	305	5.9
	^{137}Cs		
3	2.3 x 10^5	1050	246
7	3.1 x 10^5	305	96

3.2.2 Main survey (June 2006)

The main programme of sampling was carried in June 2006 aboard the research vessel, Cefas Endeavour, by staff from a specialist subcontractor (Alluvial Mining). Favourable weather conditions allowed the collection of deep (>0.9 m) cores from all 16 sectors, albeit that penetration and recovery were variable dependent upon the nature of the substrate. Selected details from the operational logs are provided in Table 3.

Table 3. *Vibrocore penetration and recovery for deep core samples in June 2006. Samples were obtained by staff from Alluvial Mining aboard Cefas Endeavour.*

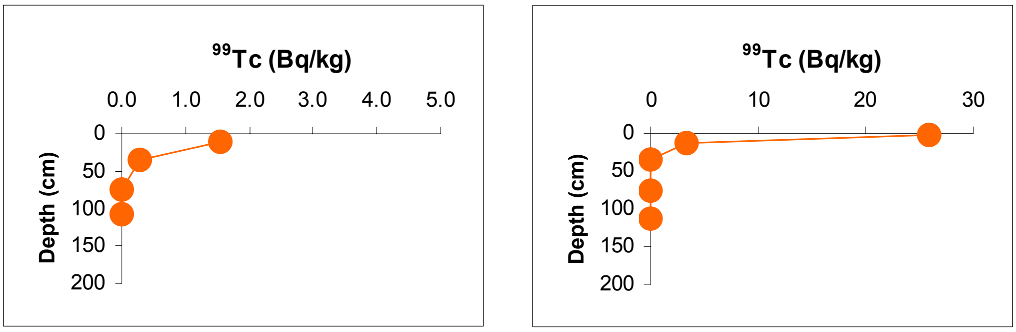
Site	Date	Time GMT	Water depth (m)	Vibration Time (mins)	Operator comments	Penetration (m)	Recovery (m)
3A	22-Jun-06	23:42	17.5	04:30	Very small current reading, vibration stopped after 4.5mins. Bagged top 0.05m of sample	1.25	1.05
1	23-Jun-06	08:49	21.1	13:00	Vibration continued to 13 minutes. Bagged top 0.17m & catcher samples	2.45	2.22
10	23-Jun-06	23:42	63.0	10:00	Stiff to very stiff sandy clay. Unlikely to achieve further penetration on retest.	1.40	1.12
8	23-Jun-06	00:48	28.1	10:00		2.17	1.65
2	24-Jun-06	20:37	13.4	10:00	Soil - medium sand. Unlikely to be able to achieve greater recoveries.	1.30	1.24
5	24-Jun-06	23:38	36.4	10:00		4.30	2.50
7A	24-Jun-06	02:32	34.5	10:00		4.30	3.30
4	24-Jun-06	03:20	24.3	10:00		4.30	4.00
6	24-Jun-06	05:03	24.4	10:00		4.30	3.32
9	24-Jun-06	07:21	30.2	10:00		4.30	3.20
11	25-Jun-06	08:52	37.3	10:00	Very hard clay, with gravel. Tube damaged along bottom 30-40cm	1.33	1.22
14	25-Jun-06	21:08	265.8	10:00	260m water depth - insufficient cable to perform coring. VC14A performed at alternative location.	ABORTED	
14A	25-Jun-06	23:12	171.5	10:00	Alternate site, 1 n.mile west of station 14. Water depth - 167m. Hard ground, unlikely to achieve greater recoveries.	1.36	0.86
12	25-Jun-06	01:27	120.8	10:00	Corer failed due to water ingress in plug. Penetration due to self weight only.	2.10	2.02
13	25-Jun-06	04:23	78.3	10:00		3.80	3.15
16	26-Jun-06	05:18	53.3	10:00		4.30	2.46
15	26-Jun-06	08:50	87.8	10:00	Extremely fluid medium to coarse sand. Core catcher unable to hold sample. Recovery unlikely to improve on repeat attempt.	2.72	1.14

Samples were successfully retrieved at all but one of the planned sites. In the North Channel (site 14) greater than expected water depths were encountered, necessitating the selection of an alternative location at which to collect this core (site 14A, 1 nautical mile west of the original site). A few cores were limited by hard ground conditions (compared with soft muddy sites) such that penetration was variable. At one site (sector 15), very loose sand was encountered that could not be completely retained in the sampling tube. Despite these difficulties, the penetration at all sites was fairly good (> ~0.9 m) and considered to be fit for the purpose of the current project. Results arising from the analysis of these cores are provided in Figure 5.

Figure 5. *Vertical distribution of radionuclides down sediment cores from the Irish Sea in June 2006 (Survey: Cefas Endeavor 13/06). a)* ^{99}*Tc: Sectors 1-16, b)* ^{137}*Cs: Sectors 1-16*

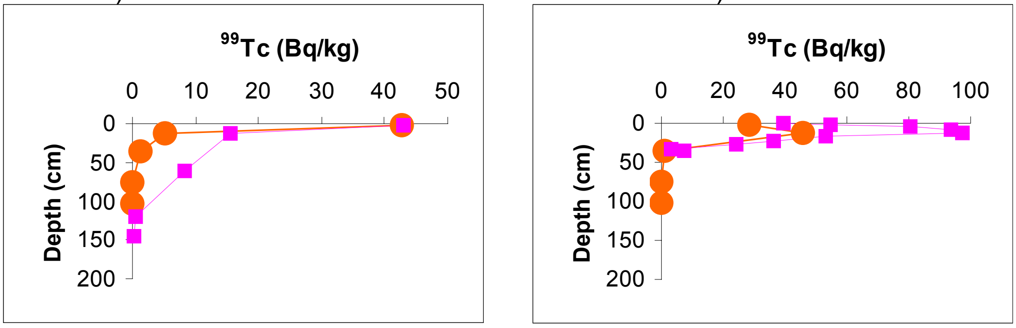
Sector 1

Sector 2



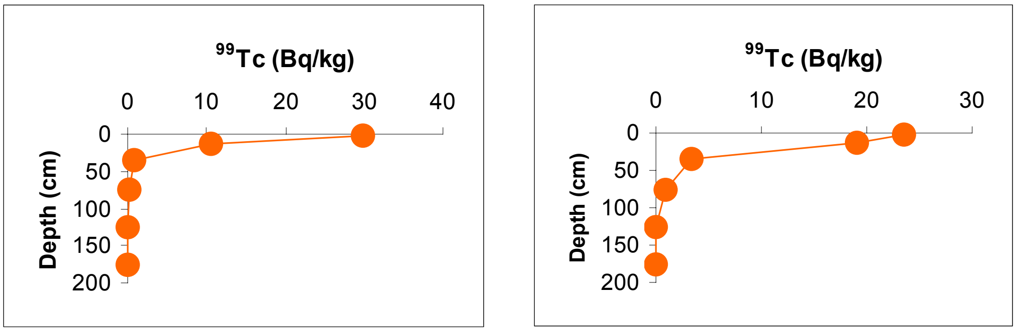
Sector 3 (pink squares represent Cory 3/05 data)

Sector 4-(pink squares represent Cory 3/05 NIOZ data)



Sector 5

Sector 6



Sector 7 (pink squares represent Cory 3/05 data)

Sector 8

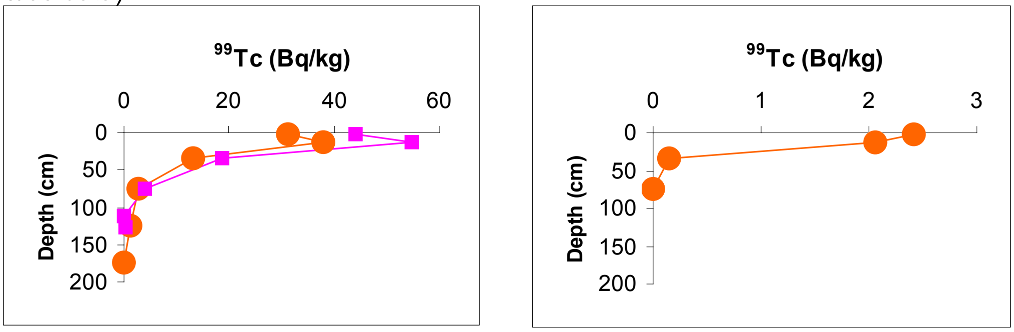
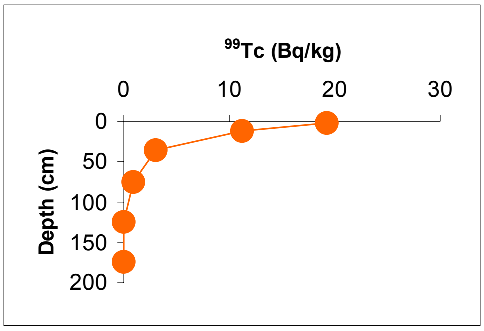
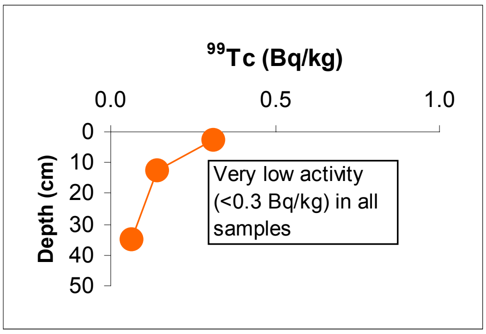


Figure 5a contd.

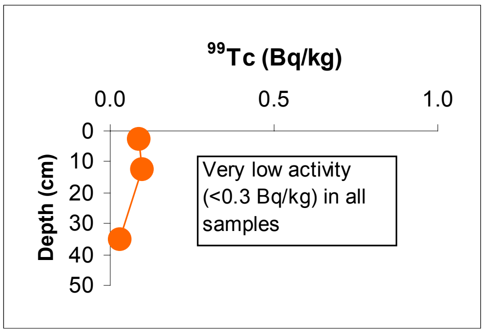
Sector 9



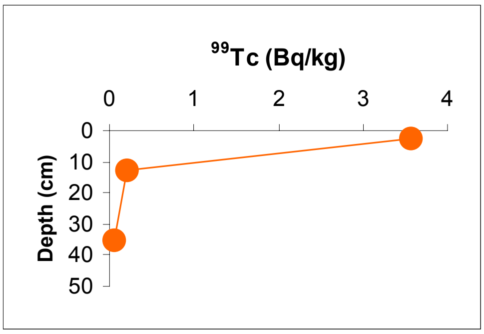
Sector 10



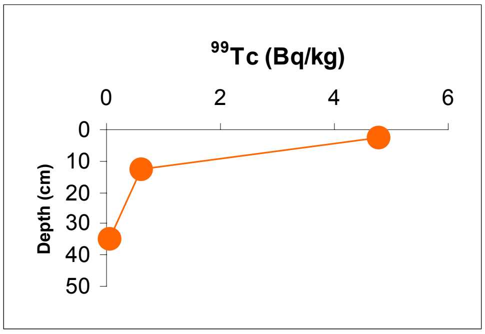
Sector 11



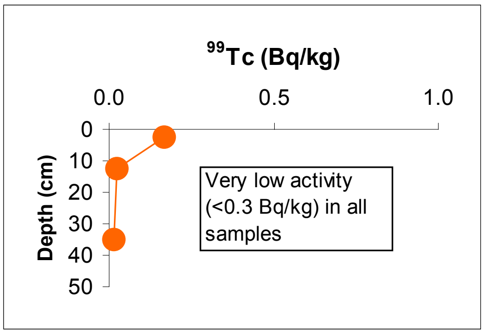
Sector 12



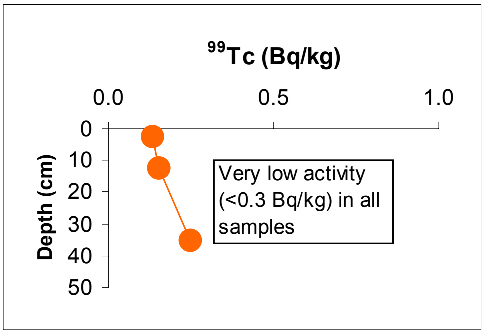
Sector 13



Sector 14



Sector 15



Sector 16

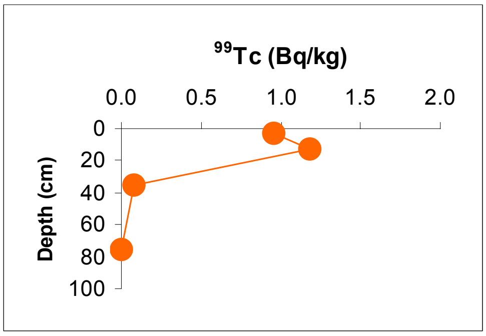
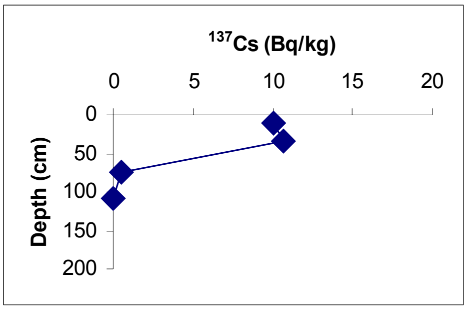
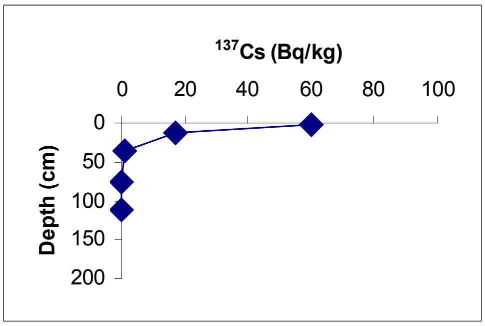


Figure 5b

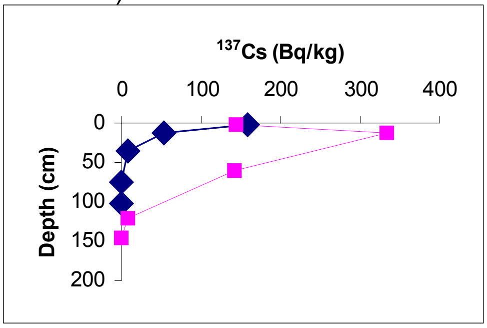
Sector 1



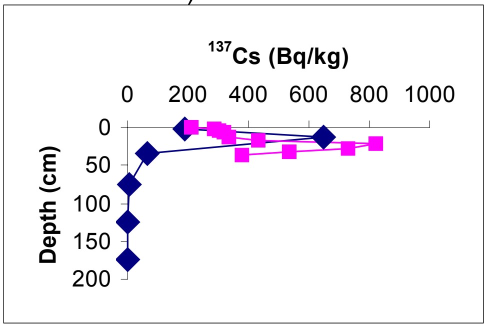
Sector 2



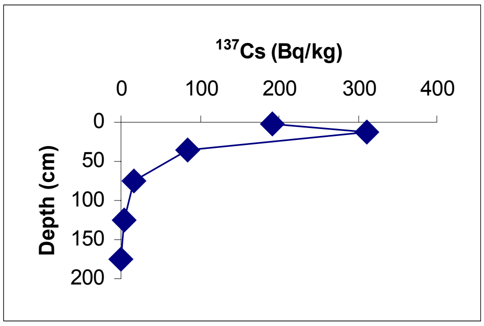
Sector 3 (pink squares represent Cory 3/05 data)



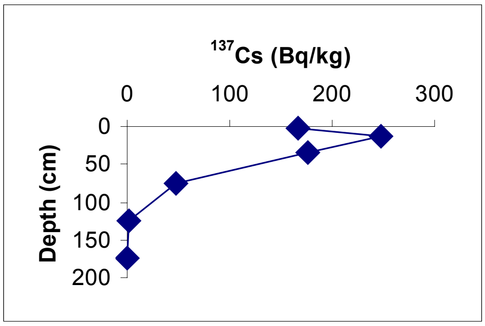
Sector 4 (pink squares represent Cory 3/05 NIOZ data)



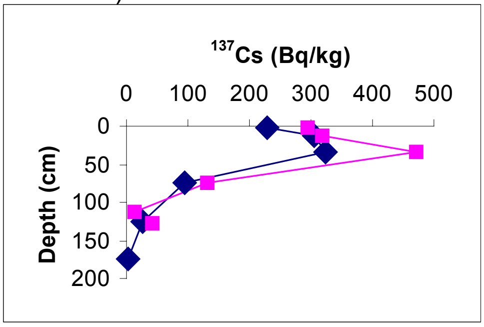
Sector 5



Sector 6



Sector 7-(pink squares represent Cory 3/05 data)



Sector 8

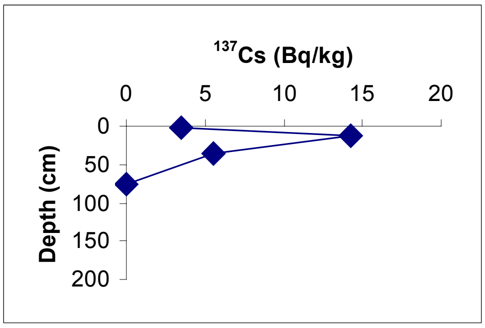
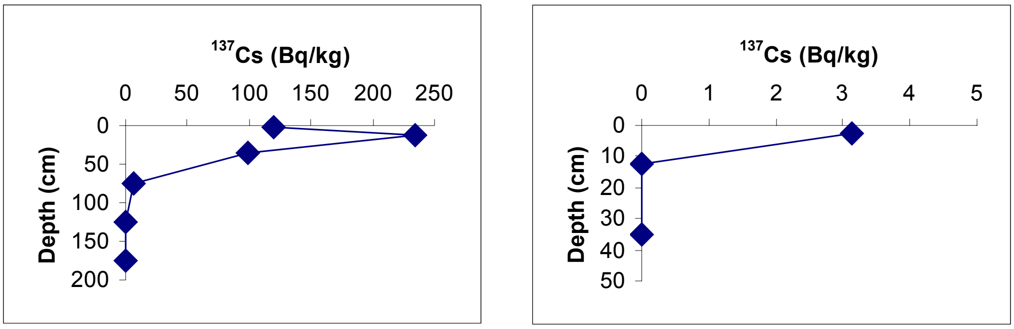
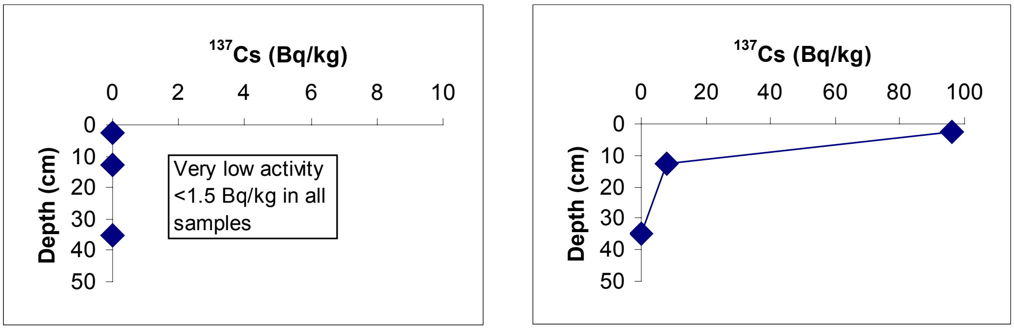


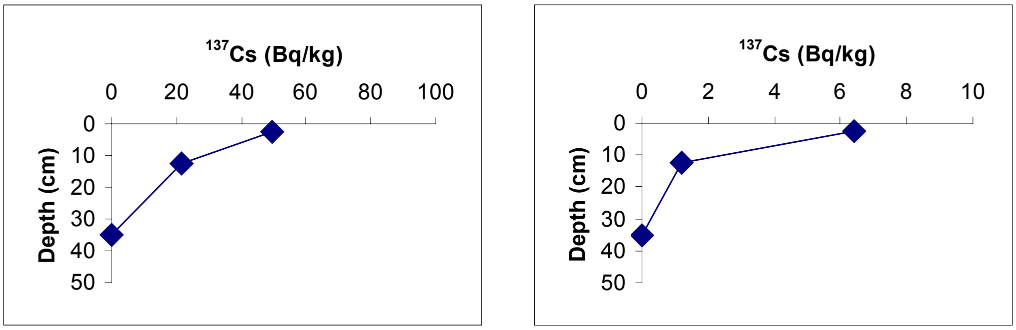
Figure 5b contd.


Sector 9

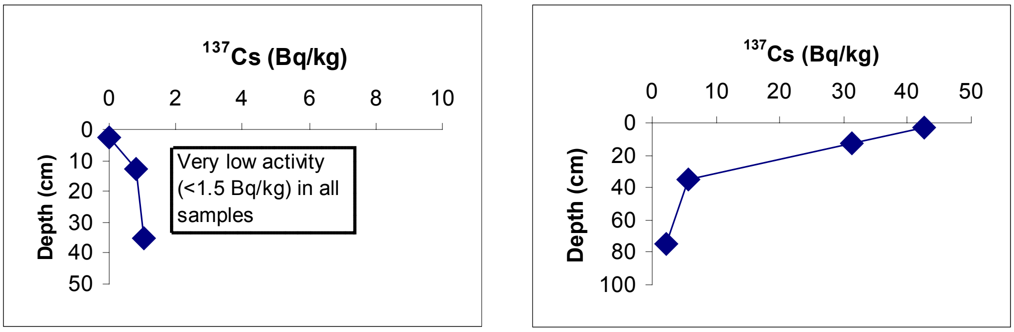
Sector 10


Sector 11

Sector 12


Sector 13

Sector 14

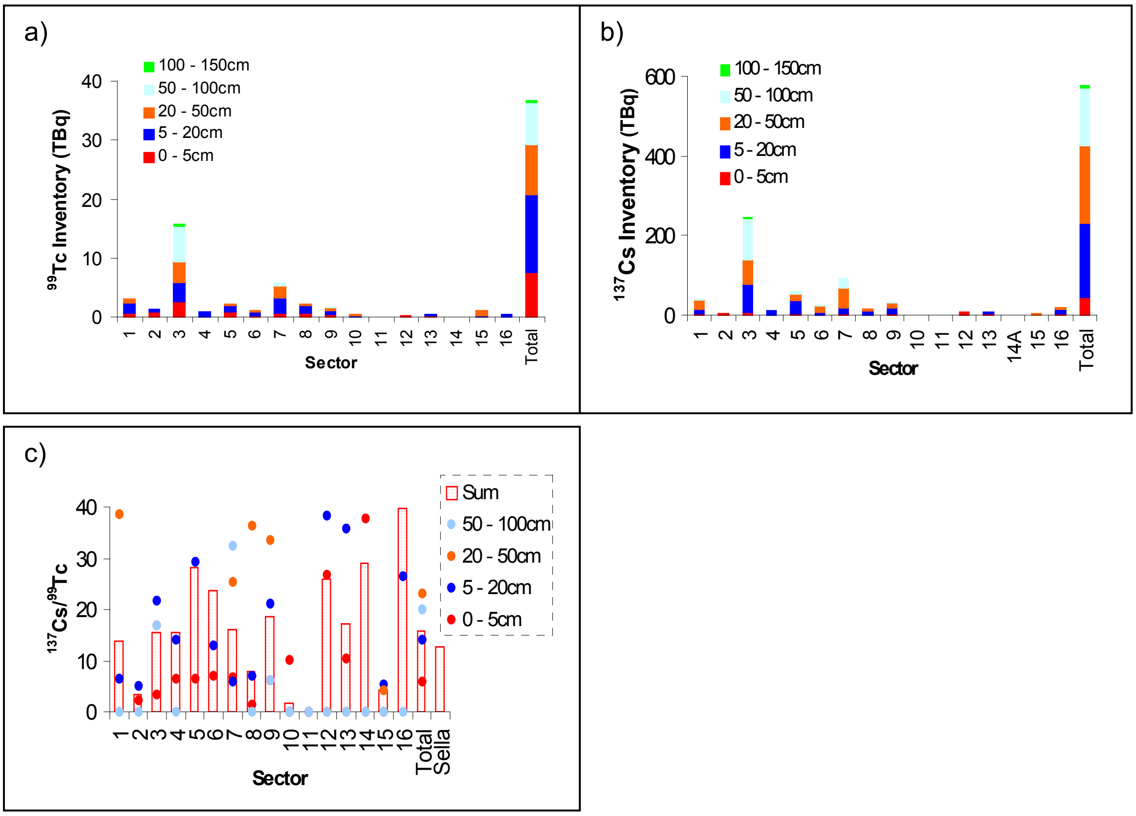

Sector 15

Sector 16

The data in Figure 5 indicate significant variation between i) the absolute radionuclide concentrations in both surface and subsurface material and ii) the shape of the individual depth profiles. As anticipated, levels tended to decrease with distance with Sellafield, and to be greater on fine-grained material. Concentrations tended to decrease with depth, although the rate of decline varied markedly. At some sites (e.g. at Site 4 in the vicinity of the Sellafield pipeline), there was a pronounced subsurface maximum whereas other cores (e.g. Site 2) exhibited an approximately exponential decrease in levels with depth. At the base of all our cores, concentrations were below detection, meaning it is possible to derive realistic inventory values as compared with a lower boundary in the event that the bottom core sections contained measurable activity.

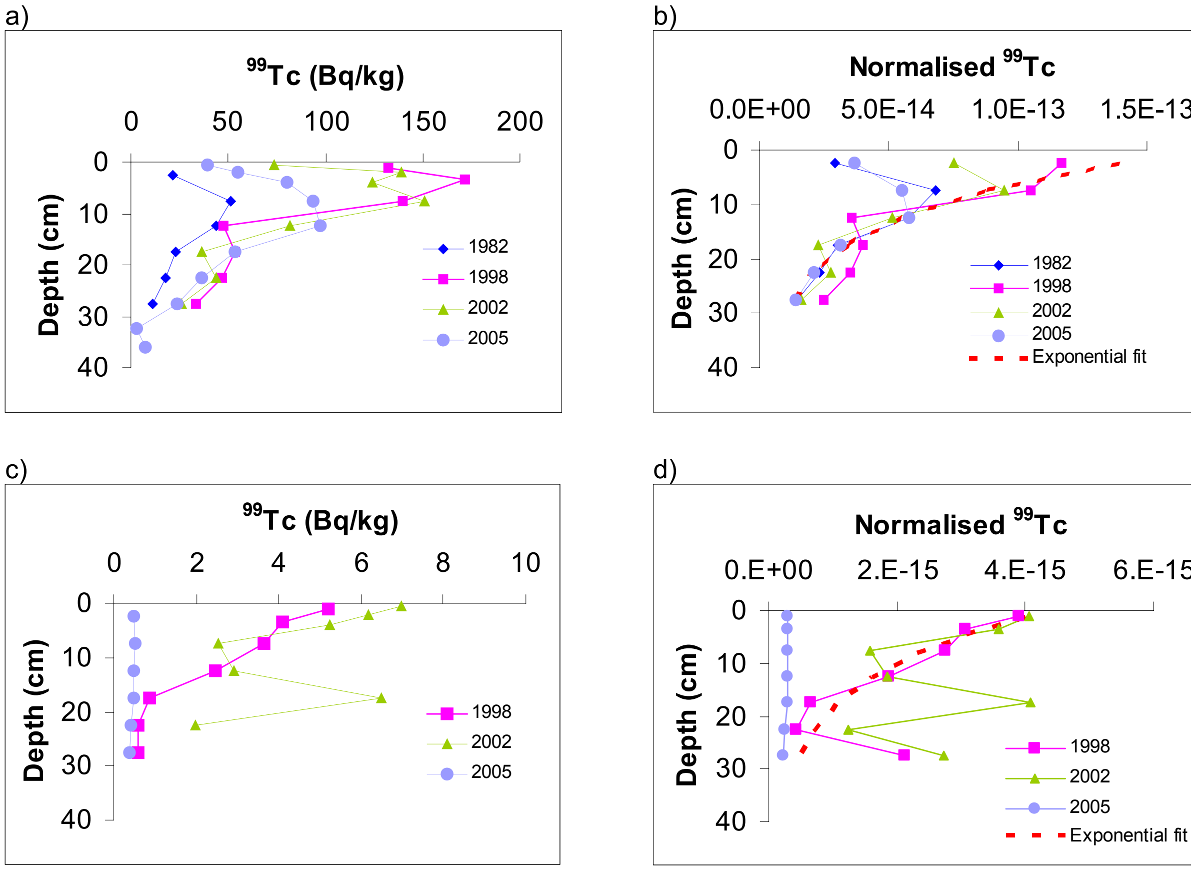
Due to the relatively small number of available cores, very limited data are available to assess reproducibility of core data within each sector. Two cores were collected from both sector 3 and sector 7. The first cores (sites 3 and 7) were collected in September 2005 (Cory 3/05) and the second cores (sites 3A and 7A) were collected in June 2006 (CEnd 13/06), with distances between the two sampling locations being ~28 km and 5 km in sector 3 and 7 respectively. The data in Figure 5a and Figure 5b indicate that levels of both radionuclides in surface sediment were broadly comparable in a given sector. However, as noted in previous surveys (e.g. Kershaw et al., 1999), there were readily measurable differences in the subsurface material. Consequently, there was a very significant difference between the estimates of the ^{137}Cs inventory in sector 3 derived from the cores obtained from site 3 (September 2005, Cory 3/05) and site 3A (June 2006, CEnd 13/06). The value derived from the core collected at site 3 (246 TBq) was almost an order of magnitude greater than derived from the core collected at site 3A (28 TBq). It is perhaps fortuitous that the discrepancy between estimates for ^{99}Tc (16 TBq and 4.8 TBq for sites 3 and 3A, respectively) was rather less (~3 fold). The agreement between inventory estimates in sector 7 was rather better than for sector 3 (disparity less than 2 fold). Data for sites 3 and 7 were used in preference to those for sites 3A and 7A for the purpose of estimating total sub-tidal radionuclide inventories as the former locations were most central within each sector. Derived values for the radionuclide inventories in individual sectors, estimated using the data in Figure 5, are provided in Figure 6.

Figure 6. *Derived values for radionuclide inventories in individual sectors of the Irish Sea in June 2006 (CEnd 13/06), derived from the data in Figure 5. Results for sectors 3 and 7 derived from cores collected at sites 3 and 7 in September 2005 (Cory 3/05). a)* ^{99}*Tc, b)* ^{137}*Cs, c)* ^{137}*Cs/*^{99}*Tc ratios. Dots indicate isotopic ratio in individual core sections and bar the value averaged throughout the core.*



The data in Figure 6a and Figure 6b indicate that the total sub-tidal Irish Sea sediment inventory of ^{99}Tc and ^{137}Cs in June 2006 was ~37 TBq and ~577 TBq, respectively. The proportion of the cumulative Sellafield discharge residing in sub-tidal sediment in 2006 is therefore estimated to be 2.2 % for ^{99}Tc and 2.7 % for ^{137}Cs. The total ^{137}Cs/^{99}Tc ratio (~15.7) compares with a ratio of ~12.6 in the cumulative Sellafield discharge between Jan 1952 and December 2005. The proportion of the total ^{137}Cs sediment inventory in surface material (i.e. in the top 5 cm) and thereby readily susceptible to re-dissolution or re-suspension in storms is small at ~8% (45 TBq). Although the fraction of ^{99}Tc in the top layer appears greater (~21 %, 7.7 TBq), nevertheless the majority is associated with subsurface material (i.e. below 5 cm).

Figure 7 *Comparison of* ^{99}*Tc sediment core profile at Site 4 (vicinity Sellafield pipeline) and Site 13 (middle Western Irish Sea mud patch) in September 2005 with previously published data. Results for May 1982, September 1998 and July 2002 profiles taken from Harvey and Kershaw (1984), Leonard et al. (2004) and McCubbin et al. (2006) respectively. a)* ^{99}*Tc activity concentrations at Site 4, b)* ^{99}*Tc activities at site 4 normalised to cumulative Sellafield discharge at time of sampling. Dotted line represents fit of monoexponential curve to combined data for depths >10 cm and extrapolated to predict values in surface layers, c)* ^{99}*Tc activity concentrations at Site 13, d)* ^{99}*Tc activities at site 13 normalised to cumulative Sellafield discharge at time of sampling. Dotted line represents fit of monoexponential curve to combined data for depths <25 cm.*



3.2.3 NIOZ time series

Data are provided in Figure 7 to illustrate the temporal variability in ^{99}Tc vertical profiles off the Sellafield pipeline (Site 4) and in the western Irish Sea mud patch (Site 13) for shallow (NIOZ) cores.

The data in Figure 7a indicate that the magnitude of the ^{99}Tc sediment activities off the Sellafield pipeline throughout the sediment core varied markedly between the pre-EARP sample (May 1982) and those collected in September 1998 and July 2002 (post-EARP). The latter were significantly greater compared with the levels observed pre-EARP (by ~ 6 fold in the top 5 cm and ~2 fold between 5-30 cm). Subsurface maxima were apparent in all three cores, albeit that the position showed some variation. The pre-EARP data indicate that the greatest activity occurred in the 5-15 cm section. The ^{99}Tc activity in the surficial sediment (0-5 cm section) was approximately half of that in the immediate underlying sediment between 5 cm and 15 cm. Below 15 cm there was a step change in ^{99}Tc activities (decrease of ~ 3 fold from 48 Bq/kg in the 5-15 cm section to an average value of 17 Bq/kg between 15 cm and 30 cm). The first post-EARP core obtained in September 1998 (~4½ years after the commencement of the enhanced ^{99}Tc discharges) showed a marked peak in the 2-5 cm section. Below a depth of 10 cm, there was a step decrease in ^{99}Tc activities (down from an average value of 148 Bq/kg in the top 10 cm to 45 Bq/kg between 10 cm and 30 cm). The second post-EARP core (obtained ~ 4 years later in July 2002) showed a profile intermediate between that observed pre-EARP and the first post-EARP core. The activity on surficial sediment in July 2002 was approximately half of that observed in September 1998, despite the increase in the cumulative Sellafield discharges (Figure 3a). It is also noticeable that the sub-surface maxima appeared to be significantly broader than that observed in September 1998. Activities between 1-10 cm were, within experimental error, remarkably similar with an average value of 139 Bq/kg. The most recent core (obtained in September 2005) exhibited a remarkably similar profile to the pre-EARP core, albeit with significantly enhanced activities throughout.

Data are provided in Figure 7b to show the effect of normalising the results in Figure 7a to the cumulative ^{99}Tc discharge at the time of sampling. The marked disparity between pre-EARP and post-EARP activities (Figure 7a) is significantly reduced following normalisation (Figure 7b). In fact, below 10 cm, values were remarkably similar for a given depth. The dotted line indicates that it was possible to fit a monoexponential decay curve to the combined data such that normalised values halved, concomitant with an increase in depth of ~7 cm. If this curve is extrapolated to predict normalised values in the surface layer (see dashed line), then activities in May 1982 and July 2002 were noticeably lower than that indicated by this model. It is tentatively suggested that the disparity is a result of re-dissolution processes in the surface layer, although it is acknowledged that sediment transport could provide an alternative explanation.

The availability of data to evaluate trends at site 13 is more limited. In contrast to the behaviour observed at Site 4, to a first approximation the profiles exhibit an exponential decrease in concentration with depth. Normalised to the cumulative ^{99}Tc discharge at the time of sampling, the activities were, once again, broadly similar. It was possible to fit a monoexponential decay curve to the combined data such that values halved, concomitant with an increase in depth of ~9 cm.

3.3 Assessment of availability of sediment bound ^{99}Tc to marine foodstuffs

3.3.1 Approaches used in current project

An assessment of the availability of ^{99}Tc residing in the bed sediments to marine foodstuffs involves the application of a suitable model. A stepwise approach has been taken in the current project. The predominant pathway for ^{99}Tc accumulation by seafood appears to be uptake from surrounding seawater (transfer factors for accumulation of Tc from exposure of benthic organisms to contaminated sediment are low (Fowler et al., 1983; Germain et al., 1984)). Therefore, estimates have firstly been made of the likely rate and extent of re-dissolution of ^{99}Tc from the seabed sediments into the overlying seawater. The seawater data have subsequently been used to estimate levels in seafoods. This was achieved using the biological concentration factor (CF) method. The concept of an equilibrium CF for marine biota, which indicates the apparent bioaccumulation of radionuclides from seawater, has gained wide acceptance as a pragmatic measure despite the problems inherent in deriving and interpreting such CFs (Lowman et al., 1971; IAEA, 2004). A range of 'standard' values, fit for the purposes of the present project, have now been compiled from environmental observations and laboratory experiments (IAEA, 2004).

Remobilisation back into the water column can occur by three principal mechanisms. The first mechanism is diffusion of ^{99}Tc from sediment pore-water into the overlying water column. The second mechanism is porewater exchange driven by tidal pumping and the presence of burrowing biota. The third mechanism is physical re-suspension of contaminated bed sediment into the water column, followed by re-dissolution from the suspended particles into the dissolved phase. The relative importance of each mechanism is governed by the partitioning between solid and liquid phases. In turn, the partitioning is governed by the ratio of the rates of the chemical reactions controlling sorption to, and desorption from, sediment particles. The partitioning between phases is commonly expressed as a distribution coefficient (K_d) and is normally obtained from environmental observations (K_d = solid phase concentration divided by aqueous phase concentration). Although

K_d data are available for ^{99}Tc (McCubbin et al., 2006) in the Irish Sea, the number of measurements is small and there is significant scatter between individual values.

The development and application of sophisticated numerical models, such as CSERAM (Aldridge, 2003), to simulate the fate of sediment bound ^{99}Tc in the Irish Sea requires a good understanding of the chemical reactions involved in its uptake and release by particulate material in the environment (sorption/desorption processes) along with accurate knowledge of seawater-sediment exchange processes. Unfortunately, information concerning both processes remains insufficient to provide robust predictions. Indeed, results from attempts to model the transfer of radionuclides other than ^{99}Tc between the water column and the seabed sediments layer in the Irish Sea were variable (FSA, 2003). Consequently, it was considered to be inappropriate, for the present project, to use a sophisticated numerical model such as CSERAM requiring detailed meteorological data. Instead, we have compared results from two alternative and simpler approaches.

In the first instance an established low-resolution compartmental model, originally formulated by Jefferies and Steele (1989) to simulate the distribution of waterborne ^{137}Cs, discharged from Sellafield, throughout the Irish Sea was used to predict ^{99}Tc behaviour. Other workers (e.g. Nicholson and MacKenzie, 1988; Mitchell et al., 1999; Simmonds et al, 2002) subsequently made refinements to the original model to enable it to be used for other purposes (e.g. to simulate remobilisation from seabed sediments). The original model (and subsequent refinements) have been critically assessed here and further improvements made in line with current knowledge of water-sediment exchange processes. Model simulations were then compared with available ^{137}Cs seawater and sediment data to assess the 'goodness of fit'. The revised model was subsequently used to predict ^{99}Tc activities in seabed sediment and the water column, in order to assess likely seafood contamination for a range of future discharge scenarios.

The critical assessment perhaps inevitably indicated limitations in our ability to realistically simulate the fate of radionuclides in the environment using this relatively simple compartmental model. In the second instance we have, therefore, developed a semi-empirical model by extrapolating the long time series of data available for ^{137}Cs in the Irish Sea. It is useful to compare and contrast results from the two approaches to derive credible conclusions regarding the future ^{99}Tc behaviour.

Finally, our predictions from both these models regarding the relative contribution from current Sellafield discharges and remobilisation have been compared with estimates derived from data for dissolved ^{3}H, ^{99}Tc and ^{137}Cs in shoreline seawater using the NAC approach (Baxter and Camplin, 1994). Given that caution is required in extrapolating the trends between individual radionuclides, we have also carried out a general review of findings from other investigations concerning i) chemical reactions controlling the rates of uptake and release from sediment particles (i.e. sorption/desorption processes) and ii) physical processes controlling porewater exchange and sediment mixing in the Irish Sea. The objective of these reviews was to better understand the uncertainties involved in extrapolating trends between ^{137}Cs and ^{99}Tc behaviour.

3.3.2 Sorption/desorption processes

3.3.2.1 Technetium-99

Almost all the ^{99}Tc discharged from Sellafield, pre-EARP, appeared to be in 'a truly dissolved form', as the pertechnetate (TcO_4^-) anion (Leonard et al., 1995). It seems reasonable to conclude this is also true of later post-EARP releases. Particulate releases of ^{99}Tc from Sellafield were not found to be significant. From thermodynamic considerations, the TcO_4^- anion is predicted to be the dominant species in an environment with high ionic strength and dissolved oxygen content such as the open sea (Garland, 1983). The pertechnetate anion is also highly soluble (i.e. poorly sorbed by sedimentary material). However, it has been shown that Tc may be removed from aqueous solution by reduction of the pertechnetate anion into less soluble Tc(IV) species by both abiotic (Cui and Ericksen, 1996; Farell et al., 1999; Wharton et al., 2000) and biotic (Lloyd et al., 2000; Wildung et al., 2000; De Luca et al., 2001) processes. More recently, detailed work has been carried out to assess ^{99}Tc fixation by estuarine sediment containing indigenous microbial populations (Burke, 2005). TcO_4^- removal from solution occurred during active Fe(III) reduction resulting in the formation of sediment-bound hydrous $Tc(IV)O_2$. Diagenetic studies of the Cumbrian mud patch suggest that these sediments are mildly reducing, with redox driven mobilisation of Fe and Mn occurring around 4-10 cm depth (Harvey, 1981; Malcolm et al., 1990), although the overlying water remains well-oxygenated throughout the year (Kershaw et al., 1992). Consequently, the uptake of ^{99}Tc now residing in the seabed sediments of the Irish Sea was probably due to biogeochemical reduction of dissolved $^{99}TcO_4^-$ in subsurface (anoxic) sediments.

Laboratory investigations of ^{99}Tc remobilisation behaviour in uncontaminated (oxic) seawater, show the desorption rate is variable between different sediment types (Germain et al., 1984). Desorption from an oxidising carbonate sediment has been reported to be rapid (Germain et al., 1984) with less than 5 % remaining bound to the sediment after 24 hours. In contrast, when reducing sediments contaminated with Tc were returned to flowing seawater, 50% of Tc was found to be eliminated within 24 hours; the remainder was completely fixed throughout the 3-month experimental period. Similar trends were reported in a more recent study (Burke et al., 2006). When radiolabelled slurries of both Fe(II) and sulphate reducing sediments were exposed to air, rapid initial remobilisation of ~40% of the bound Tc occurred within 8 days rising to ~60% after ~2 months. At the end of their experiment ~40 % of the Tc remained bound to sediment indicating a significant fraction was recalcitrant to remobilisation. A qualitatively similar observation has been reported for Tc bound to a well-characterised monomineralic phase, as compared with heterogeneous poorly characterised natural materials (Wharton et al., 2000). Upon reoxidation of a suspension of Tc (initially existing as TcS_2) bound to mackinawite (FeS), the technetium remained in an insoluble TcO_2-like phase (i.e. the Tc(IV) failed to reform into TcO_4^- on reoxidation and remained insoluble). Therefore, although solid phase hydrous TcO_2 oxidises to soluble Tc species in oxic circumneutral solutions (unpublished results outlined in Fredrickson et al., 2004), sorption to some minerals appear to buffer oxidation processes.

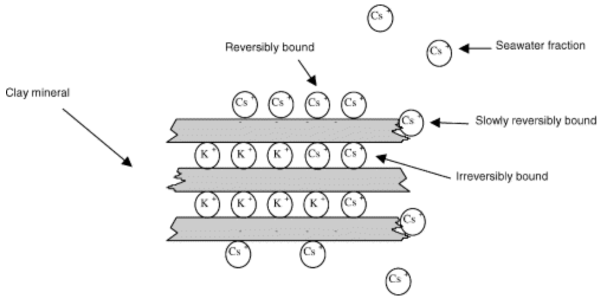
Overall, the information from these studies show that the partitioning of ^{99}Tc between solid and liquid phases is dependent upon the relative rates of the reduction and oxidation reactions, controlling sorption and re-dissolution behaviour, respectively. Bacterial reactions may be important in governing uptake behaviour. It is very difficult to extrapolate data from laboratory experiments to behaviour in the marine environment where bacterial populations may exhibit large fluctuations in activity. To date, there appears insufficient information to construct a credible model of reactions controlling ^{99}Tc sorption/desorption behaviour in the Irish Sea (as required for CSERAM and other numerical models).

In contrast, all the modelling carried out for the present project was only reliant on the pragmatic (and simpler) concept of equilibrium partitioning between solid and liquid phases in seawater (as determined from environmental K_d data). Observed ^{99}Tc K_d values in the Irish Sea range from ~3 x 10^2 – 3 x 10^3, with an average value of ~2 x 10^3 (McCubbin et al, 2006). This average ^{99}Tc value is more than an order of magnitude greater than the presently recommended value of 1 x 10^2 (IAEA, 2004), but is similar to that reported for ^{137}Cs (Kershaw et al., 1992).

3.3.2.2 Caesium-137

Caesium-137 is usually present as the simple monovalent cation (Cs^+) in seawater. Results from laboratory experiments indicate its partitioning between solid and liquid phases is a function of sediment–tracer contact time and that it is progressively ‘fixed’ to sediment particles (i.e. it becomes less and less susceptible to re-dissolution) as the contact time increases (e.g. Børretzen and Salbu, 2002 and references therein). Various models have been proposed to account for the observed behaviour. For example, binding of ^{137}Cs by clay minerals has been suggested to occur at three different sites (Figure 8): i) sorption to surface and planar sites from which ^{137}Cs is generally exchangeable; ii) sorption to wedge sites where ^{137}Cs exchange is sterically limited to cations of similar size and charge; and iii) interlayer sites from which ^{137}Cs is not readily exchanged and can be regarded as ‘irreversibly’ fixed.

Figure 8. *Schematic diagram of* ^{137}*Cs binding sites on clay minerals (from Evans et al., 1983)*



Apparent K_d values were observed to reach an asymptotic plateau after ~40 days and this behaviour was suggested to be due to rapid sorption of Cs^+ ions to surface and planar sites (Børretzen and Salbu, 2002). When models are developed to assess which reaction scheme may provide the best fit for radiotracer sorption and desorption data, the reaction rate constants are typically considered as variable parameters. Using this approach (Børretzen and Salbu, 2002) it has been estimated that the rate of fixation of Cs^+ ions to 'irreversible' binding sites is very slow (e.g. 50% after 3 years). Given the typically short period of time over which laboratory experiments are carried out, errors associated with estimates of slow reaction rates are high. Unfortunately, differences between models that appear rather small in fitting data obtained from laboratory experiments may be drastically amplified when they are used in numerical models (such as CSERAM) to simulate radionuclide behaviour in the environment (Periáñez, 2004).

In summary, a large number of studies have been carried out to assess the rate and extent of ^{137}Cs uptake by, and release from, sediment material. Estimates of the rate and extent of uptake by interlayer (i.e. so called irreversible) sites are uncertain since the kinetics is very slow. The chemical reactions involved (i.e. ion exchange) are completely different to those controlling ^{99}Tc behaviour (i.e. redox reactions). The similarity between average observed ^{99}Tc and ^{137}Cs K_d values in the Irish Sea (~2 x10^3), therefore, appears to be coincidental.

3.3.2.3 Tritium

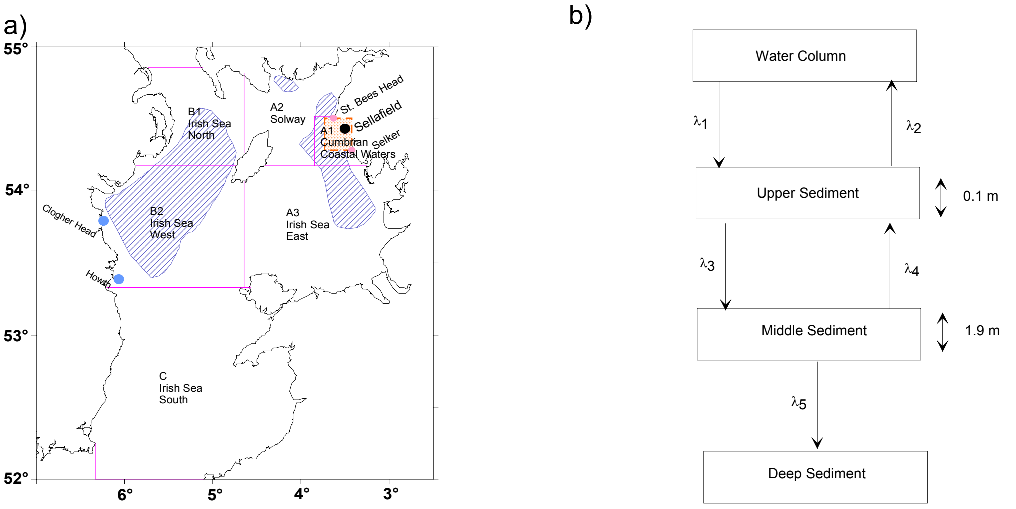
The tritium (^{3}H) discharged from Sellafield is likely to be predominantly in the form of $^{3}H_2O$. Uptake of ^{3}H by sediment from exposure to $^{3}H_2O$ is typically minimal (Blaylock et al., 1986), albeit that some binding to particulate organic material may occur by physicosorption on to surfaces through hydrogen bridges and/or by chemisorption through exchange reactions with OH-, SH- or NH-groups. Indeed, 'high' ^{3}H concentrations have been found in Hudson River (USA) sediments and this was suggested to be due to synthesis of organic material following the introduction of weapons testing material into the environment and the long turnover time of ^{3}H associated with the organic residue in sediments (Bogen and Welford, 1976). Measurable ^{3}H concentrations may therefore be present in the inter-tidal and sub-tidal sediments of the Irish Sea, due to chronic contamination of the local environment with ^{3}H over a long period of time. Information to confirm or discount this hypothesis is currently lacking. The accepted K_d value of ^{3}H in seawater is 1 (IAEA, 2004), and two to three orders of magnitude less than for ^{137}Cs and ^{99}Tc. The extent of ^{3}H incorporation into seabed sediment is, therefore, expected to be minimal in comparison with that of ^{137}Cs and ^{99}Tc.

3.3.3 Compartmental modelling

3.3.3.1 Compartmental modelling

The compartment 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 shown in Figure 9a. It consists of a small number of interconnected compartments representing various sea areas within the Irish Sea (see also Table 4).

Figure 9. *Structure of the low-resolution compartmental model of the Irish Sea. a) Sea areas (from Jefferies and Steele, 1989). See Table 4 for detailed information The shaded and dotted areas indicate the estimated locations of the Irish Nephrops harvesting effort and the 'Sellafield Coastal Area', respectively. The landing sites in Ireland where RPII collect fish and shellfish for radionuclide analysis are also shown, b) Vertical structure of each compartment in the model (from Simmonds et al., 2002).*



As mentioned previously, the impact of the ^{99}Tc discharges upon the *Nephrops* fishery is of particular concern. The shaded areas in Figure 9a, indicating the location of the *Nephrops* populations in the eastern and western Irish Sea, show these fall primarily in boxes A1 and B2 and model predictions for these compartments are therefore particularly important. It is also worth noting that most fish and shellfish consumed by the local critical group in the vicinity of Sellafield is obtained from the 'Sellafield Coastal Area' (Environment Agency et al., 2005). This area, indicated by the dotted rectangular box, extends 15 km to the north and to the south of Sellafield, from St Bees Head to Selker, and 11 km offshore and falls entirely within the A1 compartment.

Radionuclide transport by water movement due to advection and dispersion processes is simulated by exchanges between compartments that are represented by a set of transfer (rate) coefficients. Jefferies and Steele (1989) optimised these coefficients (constrained by their knowledge of residual circulation patterns) using survey data for ^{137}Cs concentrations in seawater throughout the Irish Sea. Oceanographic measurements indicate water circulation patterns in UK coastal waters can exhibit significant temporal variation (e.g. McCubbin et al., 2002 and references therein). Therefore, it is perhaps not surprising that Jefferies and Steele (1989) reported that it was necessary to use time dependent water transfer coefficients. More specifically, the agreement was optimised between model simulations and survey data (for the period 1970-1985) by changing the water flow between compartments in September 1976. The change required was substantial (e.g. the net flow rate out of the Irish Sea via the North Channel was assumed to double from 800 $km^3\ y^{-1}$ up to 1600 $km^3\ y^{-1}$). This approach has been adopted here (i.e. the use of two flow patterns). Unfortunately, there is insufficient information to justify adding further sets of flow patterns that could help improve the match between survey data and model simulations after 1985.

The vertical structure to each compartment (Figure 9b) is based on that used recently in the MARINA II model by Simmonds et al. (2002) to simulate dispersion of radionuclides in North European waters. It consists of three sediment layers, subject to a number of exchange processes. More specifically, these authors represented the transfers between water and sediment compartments (presented in Figure 9b) as:

λ_1 = Particle scavenging + Molecular diffusion + Porewater mixing + Particle mixing

$$\lambda_1 = [S.K_d/WD.(1+K_d.SP_c)] + [D/L_t.WD.(1+K_d.SP_c)] + [R_T.\varepsilon.L_t/ WD.(1+K_d.SP_c)] + [R_w.\rho.K_d.(1-\varepsilon)/ WD.(1+K_d.SP_c)]$$

λ_2 = Molecular diffusion + Porewater mixing + Particle mixing

$$\lambda_2 = [D.F_s/L_t^2.\varepsilon] + [R_T.F_s] + R_w(1-F_s)/L_t$$

λ_3 = Molecular Diffusion + Sedimentation

$$\lambda_3 = D.F_s/L_t^2 + [(1-F_s).S/\rho.L_t.(1-\varepsilon)]$$

λ_4 = Molecular Diffusion

$$\lambda_4 = Fs.D/L_m.L_t$$

λ_5 = Sedimentation

$\lambda_5 = (1\text{-}Fs).S/L_m.(1\text{-}\varepsilon).\rho$

where:

K_d = sediment distribution coefficient ($m^3\ t^{-1}$)

S = sedimentation rate ($t\ m^{-2}\ y^{-1}$)

SP_c = suspended particle concentration ($t\ m^{-3}$)

D = diffusion coefficient ($m^2\ y^{-1}$)

WD = Water layer depth (m)

L_t = upper sediment thickness (m)

L_m = middle sediment depth (m)

ε = sediment porosity

R_T = Pore-water turn over rate (y^{-1})

R_W = sediment reworking rate ($m\ y^{-1}$)

ρ = Density ($t\ m^{-3}$)

$F_s = 1/1+K_d.\rho.\{(1-\varepsilon)/\varepsilon\}$

The parameter values used to calculate the transfer coefficients in the MARINA II model (Simmonds et al., 2002) are provided in Table 4 and Table 5.

Table 4. *Model compartments (*Figure 9*a) and basic model parameters (from Simmonds et al., 2002)*

Compartment	Sea area	Volume (m^3)	Water Depth (WD) (m)	Sedimentation rate (S) ($t\ m^{-2}\ y^{-1}$)	Suspended particle concentration (SP_c) ($t\ m^{-3}$)
A1	Cumbrian Waters	2.7×10^{10}	26	6×10^{-3}	10×10^{-6}
A2	Solway	1.2×10^{11}	26	1×10^{-4}	3×10^{-6}
A3	Irish Sea East	3.3×10^{11}	33	1×10^{-4}	2×10^{-6}
B1	Irish Sea North	2.7×10^{11}	61	1×10^{-4}	2×10^{-6}
B2	Irish Sea West	5.8×10^{11}	65	1×10^{-3}	3×10^{-6}
B3	Irish Sea South	1.1×10^{12}	57	1×10^{-4}	1×10^{-6}

Table 5. *Model parameters describing the transfer of radionuclides between seawater and sediments (from Simmonds et al., 2002)*

Parameter	*Value*
Diffusion coefficient (D) (m^2 y^{-1})	0.0315
Depth of surface sediment layer (L_t) (m)	0.1
Depth of middle sediment layer (L_m) (m)	1.9
Sediment porosity (ε)	0.75
Pore-water turn over rate (R_T) (y^{-1})	1.0
Sediment reworking rate (R_W) (m y^{-1})	0.005
Density (ρ) (t m^{-3})	2.6
K_d (^{137}Cs) (m^3 t^{-1})	230
K_d (^{99}Tc) (m^3 t^{-1})	100

Derived ^{137}Cs rate constants $^{(1)}$

Compartment	λ_1 (y^{-1})	λ_2 (y^{-1})	λ_3 (y^{-1})	λ_4 (y^{-1})	λ_5 (y^{-1})
A1	9.7E-02	7.6E-02	1.1E-01	8.3E-04	4.8E-03
A2	4.5E-02	7.6E-02	1.7E-02	8.3E-04	8.1E-05
A3	3.5E-02	7.6E-02	1.7E-02	8.3E-04	8.1E-05
B1	1.9E-02	7.6E-02	1.7E-02	8.3E-04	8.1E-05
B2	2.1E-02	7.6E-02	3.1E-02	8.3E-04	8.1E-04
B3	2.0E-02	7.6E-02	1.7E-02	8.3E-04	8.1E-05

(1) Allowance was also made for radioactive decay.

3.3.3.2 Critical assessment and amendments to model parameters

When assessing output from any model it is important to critically review the underlying assumptions associated with the representation of complex and heterogeneous environmental processes. Inspection of the parameters listed in Table 5, describing the transfer of radionuclides between seawater and sediments, indicates that the only one that varies between individual radionuclides are K_d values. Moreover, it is implicitly assumed that the K_d value representing partitioning between suspended particulate material and seawater is the same as that for partitioning between seabed sediment and interstitial water. In practice, the highest concentrations of most radionuclides in bulk Irish Sea sediments are associated with fine-grained deposits (McCartney et al., 1994). The grain-size distribution of surface sediments in the Irish Sea is extremely heterogeneous (Williams et al., 1981). Therefore, partitioning between seabed sediment and interstitial water is likely to be variable according to the relative proportions of mud, sand and gravel, and different to that in the water column. In our revised model, an attempt was made to take this into account by using variable values for seabed sediment distribution coefficients adopting the approach used by Nicholson and MacKenzie (1988):

$$K_{ds} = K_{dsw} (0.9\alpha + 0.1)$$

where K_{ds} and K_{dsw} represent the distribution coefficient for partitioning in the seabed sediment and water column, respectively, whilst α is the fraction (by weight) of the seabed sediment finer than 63 μm. The values for α, listed in Table 6, were the same as those used by Nicholson and MacKenzie (1988).

With respect to incorporation of radionuclides into the seabed as a result of particle scavenging, the value for λ_1 (Table 5) is greatest in the Cumbrian coastal box (A1) as a result of the relatively high parameter values recommended for sedimentation rate (S) and suspended load (SP_c). In contrast, environmental observations indicate net sedimentation in the north-eastern Irish Sea is extremely low (<~0.1 mm y^{-1}) (Kirby et al., 1983; Kershaw et al., 1988). Therefore in practice, particle scavenging is probably not a significant mechanism towards radionuclide incorporation into the seabed in the eastern Irish Sea. Information from ^{210}Pb dating does, however, indicate significant sedimentation in the western Irish Sea mud basin (Mitchell et al., 1999). In our revised model, the sedimentation rate in box A1 was thus decreased to 10^{-4} t m^{-2} y^{-1}, consistent with that in the other compartments of the eastern Irish Sea (Table 6).

The parameter representing sediment reworking, $R_{w,}$ is an attempt to provide a combined representation of a number of sediment resuspension and settling processes caused by bioturbation and episodic events such as storms and trawling. Deep burrowing animals such as the thalassinidean crustacean *Callianassa subterranea* or the echiuran worm *Maxmuelleria lankesteri* can transfer considerable quantities of sediment between surface and underlying layers (Swift, 1993; Hughes et al., 1996). The extent of bioturbation is variable between different sediment types, meaning that it is difficult to set a single representative value for R_w for the whole Irish Sea. It is perhaps not surprising that a review of the literature regarding values of R_w has shown these can vary by almost three orders of magnitude in coastal waters (from $6x10^{-4}$ m y^{-1} up to $3x10^{-1}$ m y^{-1}) (Nicholson and MacKenzie, 1988). Changing the value of R_w in numerical models can have a significant effect on the interaction between the water column and the top sediment, in both directions. In the MARINA II model (Simmonds et al., 2002) transfer between the top and middle layers, represented by the rate constants λ_3 and λ_4, due to particle mixing is ignored. In the current study, the model was modified to include the effects of particle mixing between the surface and middle layers. The combined effect of these changes was such that the equations describing λ_1 – λ_5 read:

λ_1 = Particle scavenging + Molecular diffusion + Porewater mixing + Particle mixing

$$\lambda_1 = [S.K_{dsw}/WD.(1+K_{dsw}.SP_c)] + [D/L_t.WD.(1+K_{dsw}.SP_c)] + [R_T.\varepsilon.L_t/ WD.(1+K_{dsw}.SP_c)] + [R_w.\rho.K_{ds}.(1-\varepsilon)/ WD.(1+K_{dsw}.SP_c)]$$

λ_2 = Molecular diffusion + Porewater mixing + Particle mixing

$$\lambda_2 = [D.F_s/L_t^2.\varepsilon] + [R_T.F_s] + R_w(1-F_s)/L_t$$

λ_3 = Sedimentation + Molecular Diffusion + particle mixing

$$\lambda_3 = [(1-F_s).S/\rho.L_t.(1-\varepsilon)] + D.F_s/L_t^2 + R_w (1-F_s)./3.L_t.$$

λ_4 = Molecular Diffusion + particle mixing

$$\lambda_4 = Fs.D/L_m.L_t + R_w(1-F_s)/3.L_m$$

λ_5 = Sedimentation

$$\lambda_5 = (1-Fs).S/L_m.(1-\varepsilon).\rho$$

In the eastern Irish Sea mud patch, radionuclides have been estimated to be almost completely mixed within the top 10 cm by reworking processes within ~ 1 year (MacKenzie et al., 1998). The mixing efficiency does, however, decrease with depth. Following Aldridge et al. (2003), particle mixing between the surface and middle layers (affecting values of λ_3 and λ_4) was assumed to be ~3 fold less than that between the water column and surface sediment.

Table 6. *Changes made to basic model parameters listed in* Table 4 *for individual model compartments (Figure 9a)*

Compartment	Volume (m^3), Water Depth (m) and Suspended sediment load (SP_c) ($t\ m^{-3}$)	Sedimentation rate (S) ($t\ m^{-2}\ y^{-1}$)	Fraction seabed sediment less than 63 µm diameter (α)	Derived ^{137}Cs partitioning coefficient seabed sediment (K_{ds}_Cs) ($m^3\ t^{-1}$)
A1	No change	1×10^{-4}	0.5	1100
A2	No change	No change	0.07	320
A3	No change	No change	0.2	560
B1	No change	No change	0.2	560
B2	No change	No change	0.5	1100
B3	No change	No change	0.05	290

Revised values for the basic model parameters and rate constants λ_1 - λ_5 used in the model for the present project, as a result of the combined modifications described above, are provided in Table 6 and Table 7, respectively.

The model, using the revised basic model parameters and rate constants, listed in Table 6 and Table 7, was implemented with the aid of a commercially available software package (MODELMAKER®, FamilyGenetix Ltd.) in which linear first-order differential equations are used to describe the transfer between compartments. It is, however, acknowledged that, whatever the success or otherwise of this compartmental model in simulating historic survey data, its application to predict future trends should always be treated with caution or otherwise independently corroborated. In view of the uncertainties in attempting to use existing models to predict future remobilisation of ^{99}Tc from contaminated seabed sediments, it was decided to use a semi-empirical approach based upon extrapolating trends from the existing, and much larger, sets of environmental data for ^{137}Cs to compare and contrast with the model simulations. This is described in more detail below.

Table 7. *Modifications made to model parameters describing the transfer of radionuclides between seawater and sediments. Values used in MARINA II model (Simmonds et al, 2002) are provided in* Table 5*.*

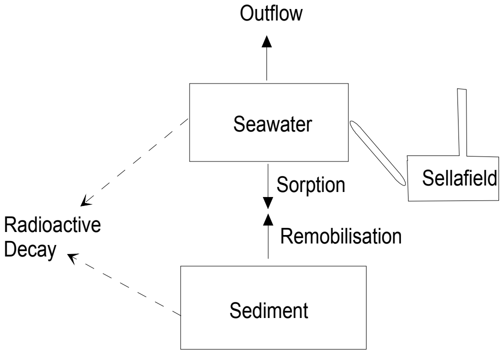
<table>
<tr><td colspan="3"><i>Parameter</i></td><td colspan="3"><i>Value</i></td></tr>
<tr><td colspan="3">K_{dsw} (^{137}Cs) ($m^3\ t^{-1}$)</td><td colspan="3">2000</td></tr>
<tr><td colspan="3">K_{dsw} (^{99}Tc) ($m^3\ t^{-1}$)</td><td colspan="3">2000</td></tr>
<tr><td colspan="6"><i>Revised rate ^{137}Cs constants</i>$^{(1)}$</td></tr>
<tr><td>Compartment</td><td>λ_1 (y^{-1})</td><td>λ_2 (y^{-1})</td><td>λ_3 (y^{-1})</td><td>λ_4 (y^{-1})</td><td>λ_5 (y^{-1})</td></tr>
<tr><td>A1</td><td>1.6E-01</td><td>5.5E-02</td><td>2.1E-02</td><td>1.0E-03</td><td>8.1E-05</td></tr>
<tr><td>A2</td><td>6.3E-02</td><td>6.8E-02</td><td>2.9E-02</td><td>1.5E-03</td><td>8.1E-05</td></tr>
<tr><td>A3</td><td>7.3E-02</td><td>6.1E-02</td><td>2.5E-02</td><td>1.2E-03</td><td>8.1E-05</td></tr>
<tr><td>B1</td><td>3.9E-02</td><td>6.1E-02</td><td>2.5E-02</td><td>1.2E-03</td><td>8.1E-05</td></tr>
<tr><td>B2</td><td>9.1E-02</td><td>5.5E-02</td><td>3.5E-02</td><td>1.0E-03</td><td>8.1E-04</td></tr>
<tr><td>B3</td><td>2.7E-02</td><td>7.0E-02</td><td>3.1E-02</td><td>1.5E-03</td><td>8.1E-05</td></tr>
</table>

(1) Allowance was also made for radioactive decay.

3.3.4 Semi-empirical modelling

Survey data for ^{137}Cs in the water column and sub-tidal sediments of the Irish Sea were empirically fitted to a single box model (Figure 10).

Figure 10. *Semi-empirical model used to fit survey data for the temporal variation of ^{137}Cs in the water column and sub-tidal sediments of the Irish Sea. "Sellafield" is a Lookup Table containing data for monthly liquid radionuclide discharges to sea.*



The fate of ^{137}Cs (and by implication ^{99}Tc) discharged into the Irish Sea is considered to be governed by just three competing reversible first order reactions, instead of the multiple processes considered in the compartmental model (Figure 9). Flows between compartments (Figure 10) were represented by the equations:

Outflow = $k_{outflow}$ x $^{137}Cs_{seawater}$

Sorption = $k_{sorption}$ x $^{137}Cs_{seawater}$

Remobilisation = $k_{remobilisation}$ x $^{137}Cs_{sediment}$

where $^{137}Cs_{seawater}$ and $^{137}Cs_{sediment}$ represent the inventory of ^{137}Cs in the water column and sub-tidal sediments of the Irish Sea, respectively. $k_{outflow}$ represents the first-order rate constant for the transfer of ^{137}Cs out of the Irish Sea by the residual flow. Similar considerations apply to the other rate constants. Allowance was also made for radioactive decay of ^{137}Cs ($t_{½}$ ~ 30.07 y) in both the water column and sediments.

To fit the survey data, $k_{sorption}$ and $k_{remobilisation}$ were considered as variable parameters. Given that the mean residence half-time of water in the Irish Sea has been reported to be in the order of 1 year (Jefferies et al., 1982), $k_{outflow}$ was set as ~0.69 y^{-1}. The equations were once again solved numerically using the software package MODELMAKER®. Initial estimates of $k_{sorption}$ and $k_{remobilisation}$ (0.08 y^{-1} and 0.08 y^{-1}, respectively) were derived to allow ~10% of each years annual discharge to be transferred from the water column to the seabed. The initial values were subsequently refined to achieve better agreement between the model simulations and the survey data.

3.3.5 Normalised Activity Concentrations (NACs)

The concept of Normalised Activity Concentrations (NACs) has proved extremely useful to empirically link measured discharges from a site to observed environmental activity concentrations (Baxter and Camplin, 1994). A NAC is defined as the activity concentration per unit discharge rate, and for a particular radionuclide R in material M is calculated using the equation:

$$NAC_{RM} = C_{RM}/DR$$

where,

C_{RM} = annual mean concentration of radionuclide R in material M (Bq/kg or Bq/l) and

DR = annual mean daily discharge of radionuclide, R (TBq/day)

Defined this way, a NAC has a unit of Bq/kg (or l) per TBq/day.

The usefulness of the NAC concept is based on the assumption that an observed annual mean radionuclide concentration in a given material is directly proportional to the annual discharge from the nuclear site in the sample vicinity. It is assumed that the equilibrium between discharge and concentration is has been reached within that year. Normally, individual NACs are calculated from data for several years to evaluate consistency, and then averaged. Having established a NAC for a given radionuclide and material, concentrations of radionuclides in that material can be simply predicted (for a given discharge scenario) by multiplying the NAC by the discharge (e.g. Hunt and Jefferies, 1981; Baxter and Camplin, 1994; Hunt et al, 2000).

3.3.6 Environmental observations of ^{137}Cs behaviour

There exists a long-term series of environmental observations from which it is possible to assess the rate and extent of ^{137}Cs remobilisation into the water column of the Irish Sea, following the dramatic reduction of discharges from Sellafield between 1983 and 1986. Although the combined environmental observations were obtained from a large number of different investigations (i.e. they do not represent the culmination of an integrated research programme) the composite data set provides an excellent opportunity to assess ^{137}Cs behaviour. Data are available for both sedimentary material and seawater. Given the inevitable scatter in results for single materials, it was considered important to assess results for both solid and liquid phases in order to corroborate individual rate estimates/model simulations.

3.3.6.1 Sub-tidal sediments

Surveys to estimate radionuclide inventories in the sub-tidal sediments of the Irish Sea are extremely time consuming and labour intensive (hence costly). Consequently, results from which to estimate the temporal variations in activity residing in the seabed are extremely sparse. Historic data is limited to results for ^{137}Cs (and ^{239,240}Pu/^{241}Am) derived from surveys in 1978, 1988 and 1995 (Table 8). Moreover, these results probably represent minimum estimates given that the sediment core sampling did not always reach the limit of radionuclide contamination (Poole et al., 1997; Kershaw et al., 1999).

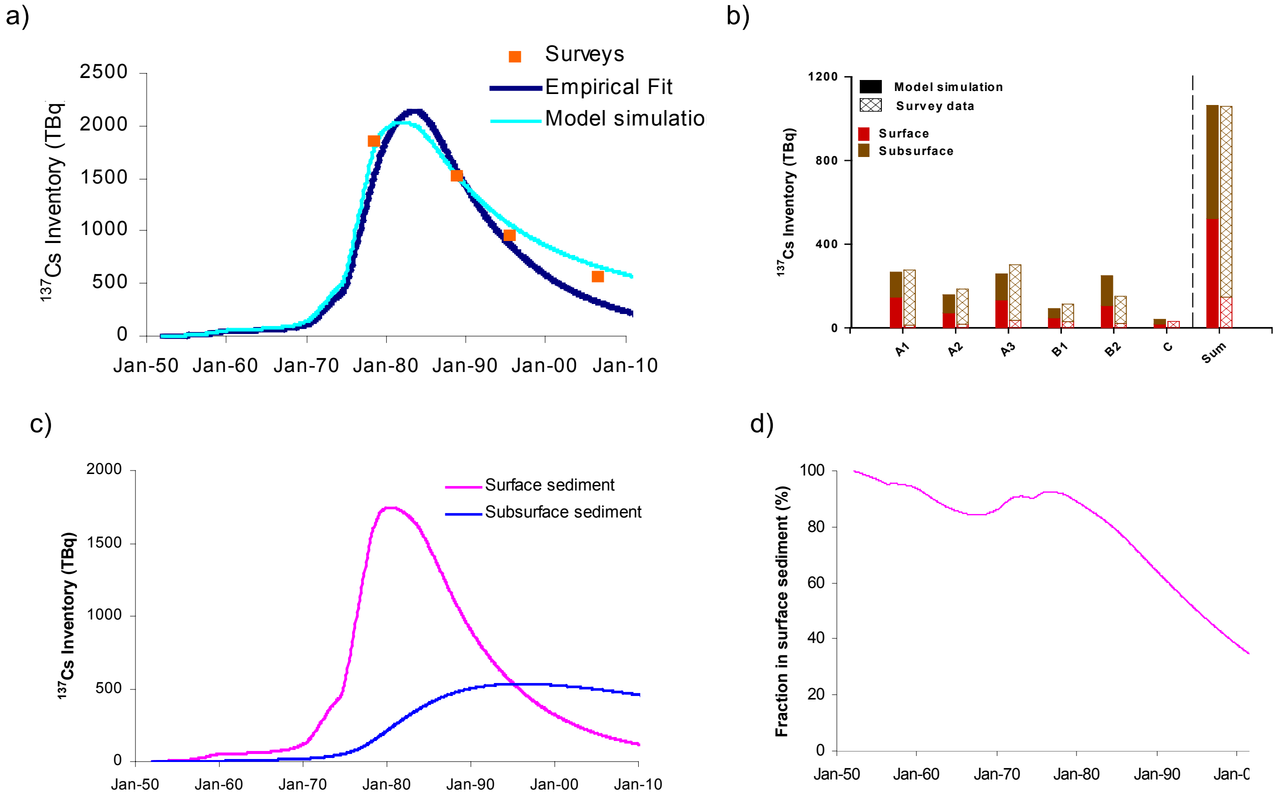
Table 8. *Estimated inventory of ^{137}Cs in sub-tidal sediments of the Irish Sea (historic data 1978, 1988 and 1995 is from Poole et al., 1997).*

	1978	1988	1995	2006
Cumulative Sellafield discharge (TBq)	26,750	31,349	26,799	21,348
Total sub-tidal sediment inventory (TBq)	1861	1532	959	577
Fraction cumulative Sellafield discharge (%)	7.0	4.9	3.6	2.7
Surficial (0-5 cm) sediment inventory (TBq)		134	110	45
Fraction total sub-tidal inventory in surface layer (%)		9.1	12	7.8

The results in Table 8 indicate that the sub-tidal sediments of the Irish Sea acted initially as an effective sink for a small but measurable fraction of ^{137}Cs during the period of maximum discharges from Sellafield. However, significant re-dissolution of ^{137}Cs occurred following the major reduction in releases between 1983 and 1986. The proportion of the cumulative Sellafield discharge residing in the sub-tidal sediments decreased to ~3.6% by 1995 and 2.7% in 2006.

Results from both the compartmental model (Figure 9) and the semi-empirical single box model (Figure 10) are provided in Figure 11a to compare with the survey data provided in Table 8.

Figure 11. *Simulating the temporal variation in the inventory of* ^{137}*Cs in sub-tidal sediments of the Irish Sea. a) Comparison of survey data and results from the semi-empirical fit (Figure 10) and multi-compartmental box model (Figure 9) simulation, b) predicted distribution between individual compartments and sediment layers in 1995 using the multi-compartmental model, c) predicted temporal variation in surface and subsurface layers using the multi-compartmental model. Dashed line represents fit of exponential decay curve to surface data after 1986, d) predicted proportion in surface layer using the multi-compartmental model.*



The results in Figure 11a indicate that a good empirical fit to the survey data was achieved using values for both $k_{sorption}$ and $k_{remobilisation}$ of ~0.077 y^{-1}. Results from the multi-compartmental model simulation indicated an almost identical pattern of behaviour up to 1979. However, the predicted maxima (in 1983), and subsequent rate of decrease (due to remobilisation) were less pronounced. If values from both simulations after 1986, following the decrease in Sellafield discharges, are fitted to monoexponential decay curves, the effective half-time for ^{137}Cs residing in the seabed sediments is predicted to be ~8 and 14 years for the empirical and multi-compartmental models, respectively. Consequently, a noticeable disparity between the empirical fit and multi-compartmental models developed after 1995 (e.g. predicted inventory in 2004 using the multi-compartmental model was ~3.2% of the cumulative Sellafield discharge and almost double that of the empirical fit). Although not shown here, results from the multi-compartmental simulation were sensitive to both changes in the water flow patterns as well as the ^{137}Cs K_{ds} value.

The data in Figure 11b provide the predicted distribution between individual compartments (and the sum of compartments, as indicated by the data given beyond the dashed line). The results indicate that the majority (~65 %) of the total ^{137}Cs sediment inventory is predicted to reside in the eastern Irish Sea (compartments A1-A3). This is broadly in line with the survey data (Poole et al., 1997).

Estimates of the inventory in surficial (0-5 cm) sediment are also provided in Table 8. These data indicate that the majority of the ^{137}Cs activity (~90 %) resides in subsurface material. The vertical structure of the multi-compartmental model allows predictions to be made of the distribution between surface (top 10 cm) and underlying sediment. Results from the multi-compartmental simulation (Figure 11c) indicate that the inventory in surface sediment is predicted to attain a maximum value of ~1590 TBq in 1981 and decrease thereafter. In contrast, changes in the inventory in subsurface material are predicted to differ significantly such that the maximum value of ~503 TBq is attained in 1996. Consequently, the proportion predicted to be in surface sediment shows a steady decrease with time (e.g. down from ~90 % in 1979 to ~50 % in 1995). Overall, the model appears to provide a significant overestimate of the proportion in surficial material. The disparity between model simulation and environmental observation (see also the data in Figure 11b) presumably reflects the difficulty of modelling the complex vertical sediment mixing processes (hence remobilisation). Although results are not provided here, preliminary application of the multi-compartmental model to predict behaviour of the particle reactive ^{239,240}Pu indicates the simulation overestimates the proportion incorporated into the seabed compared with survey data (Kershaw et al., 1999). Further work (outside the scope of the present study) is required to construct a more accurate model of vertical radionuclide mixing processes within the seabed.

It is worth noting that different rates of re-dissolution have been reported for ^{137}Cs bound to surface and subsurface sediment (MacKenzie et al., 1998). From a comparison of data for ^{137}Cs/^{241}Am activity ratios in inter-tidal sediment in 1978/1979 and a sediment core collected close to Sellafield in 1992, they suggested that up to 77% of the ^{137}Cs had been re-dissolved from surface (< 10 cm depth) material and some 15% from deeper layers within a period of ~13 years. If we extrapolate their two data points and assume first-order kinetics, their results imply that the effective residence half-time of ^{137}Cs in surficial sediment is ~6 years compared with ~50 years in ‘subsurface’ material.

Similar trends are apparent in the results for surface sediment from our multi-compartmental model simulation (Figure 11c) with a predicted decrease in the inventory between 1979 and 1992 of ~56%. It is also worth noting that the surface sediment data points after 1986 can be successfully fitted to a monoexponential decay curve, indicating that the effective residence half-time of ^{137}Cs in the top layer is ~7 years. If a similar analysis is carried out on data for subsurface sediment after 1996, the effective residence half-time of ^{137}Cs in the subsurface layers is predicted to be ~80 years. The effective residence half-time of 14 years, derived from the combined sediment inventory data (Figure 11a), therefore represents a composite value resulting from differential release rates concomitant with depth.

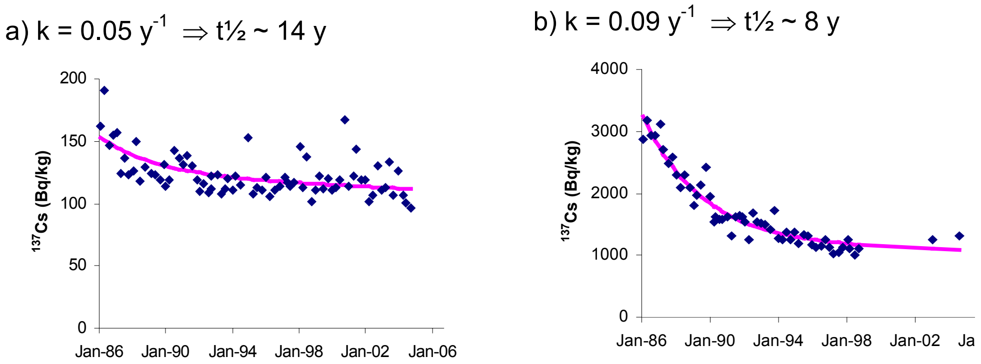
In addition to the limited inventory data, results arising from the analysis of a large number of surface sediment samples between 1968-1988 have been reported elsewhere (McCartney et al., 1994). There was a general increase in levels of ^{137}Cs over the period 1968-1983 concomitant with an increase in the cumulative Sellafield discharge. Subsequent to 1983, reductions were observed in the level of ^{137}Cs in surficial sediments coinciding with a sharp decrease in the annual discharges (from ~1200 TBq in 1983 down to ~12 TBq in 1988). Concentrations in the top 5 cm of sediments near Sellafield decreased by ~75% within this 5 year period, compared with a decrease of just 10% in the cumulative Sellafield discharge, and tend to corroborate model predictions of relatively rapid re-dissolution from surface material.

Time-series data (between 1988-1995) on ^{137}Cs concentrations in surficial sediments at three different sites in the western Irish Sea mud basin have been modelled in an attempt to estimate a representative mean availability time in this zone (Mitchell et al., 1999). Concentrations of ^{137}Cs were found to fall continuously over this period, resulting in overall decreases of between 30-70%. Mean availability times were found to be in the range 7- 16 years, corresponding to half-times in the range 5-11 years (i.e. also in broad agreement with the value of ~7 years derived from modelling our sub-tidal inventory data). Variations between the three stations were suggested to reflect differences in physical dispersion and dilution processes that, in turn, are dependent on local hydrological conditions such as currents and depth.

3.3.6.2 *Inter-tidal sediments*

Detailed time series are available for a limited number of sites, arising from the UK RIFE monitoring programme, from which it is possible to assess the temporal variation of ^{137}Cs in surficial inter-tidal sediments. However, the RIFE dataset is derived from the combination of four independent programmes with contributions from the Environment Agency, the Environment and Heritage Service (Northern Ireland), the Scottish Environment Protection Agency as well as the Food Standards Agency. For a variety of practical reasons, their contractors collect and analyse samples in different ways. Data provided in the RIFE report is, moreover, confined to publication of average values, in instances where more than one sample is collected in a given year. Given the variety of potential confounding factors, care needs to be taken in interpreting the RIFE data. Selected data are provided in Figure 12 for ^{137}Cs activities in surface sediment at two locations within the vicinity of Sellafield (sand from the beach at St Bees and mud from Whitehaven Yacht Basin).

Figure 12. *^{137}Cs activities in inter-tidal sediment. Data (provided as dots) have been decay corrected to a standard collection date of January 1st 1986. Lines represent fit of data to monoexponential curves. a) St Bees sand, b) Whitehaven Yacht Basin mud.*

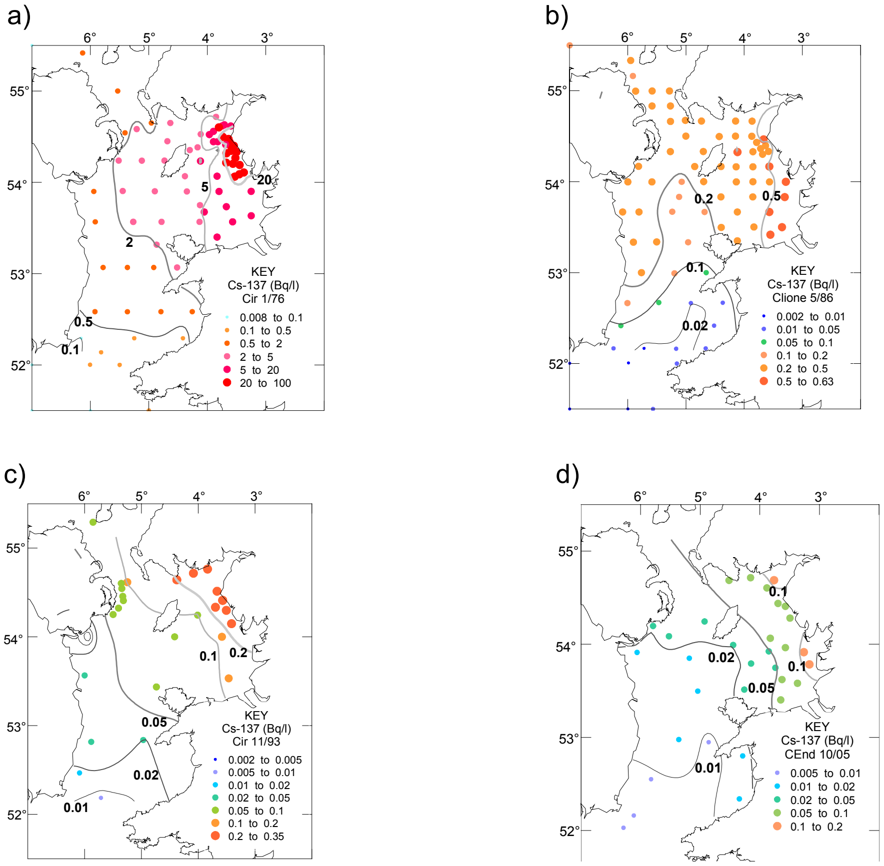


The activities of ^{137}Cs bound to surface sediment have declined in an exponential manner with time, for both materials. Both sets of decay corrected data can be fitted more or less equally well to a family of exponential curves of the form $C_{Cs(t)}$ = A*exp(-kt), A*exp(-kt) + resid., or A*exp(-k_1t) + B*exp(-k_2t), where $C_{Cs(t)}$ is the ^{137}Cs activity bound to sediment at time t and k represents the first order rate constant for re-dissolution into seawater. The scatter in the data about all the curves is noticeably less for mud, meaning the uncertainty associated with best fit parameter values is less than those derived for the sand data. The best fit values for k (monoexponential decay curve, with residual set to zero) for St Bees Sand and Whitehaven mud are ~0.05 y^{-1} and ~0.09 y^{-1}, respectively. These first order rate constants indicate that the specific activity decreases by a factor of 2 every 14 and 8 years in sand and mud, respectively. The importance of this information is that it provides support for the application of a value for $k_{remobilisation}$ of ~0.08 y^{-1} in the single box empirical model (Figure 10). It is worth noting that if the results for Whitehaven mud had instead been fitted to a biexponential decay curve then best fit values for k_1 and k_2 would have been ~0.3 y^{-1} and ~0.005 y^{-1}, respectively (indicating half-times for 'fast' and 'slow' reactions of ~2.4 and ~135 years, respectively).

3.3.6.3 Water column inventories

A reasonably comprehensive set of data is available for dissolved ^{137}Cs in the water column of the Irish Sea, arising from a programme of surveillance into the distribution of radionuclides in surface UK waters maintained by Defra. This programme includes biennial sampling in the Irish Sea, and is extremely useful to corroborate the interpretation of the sediment dataset. All these seawater results are reported elsewhere including in the RIFE reports. Selected data, abstracted from these sources, are provided in Figure 13.

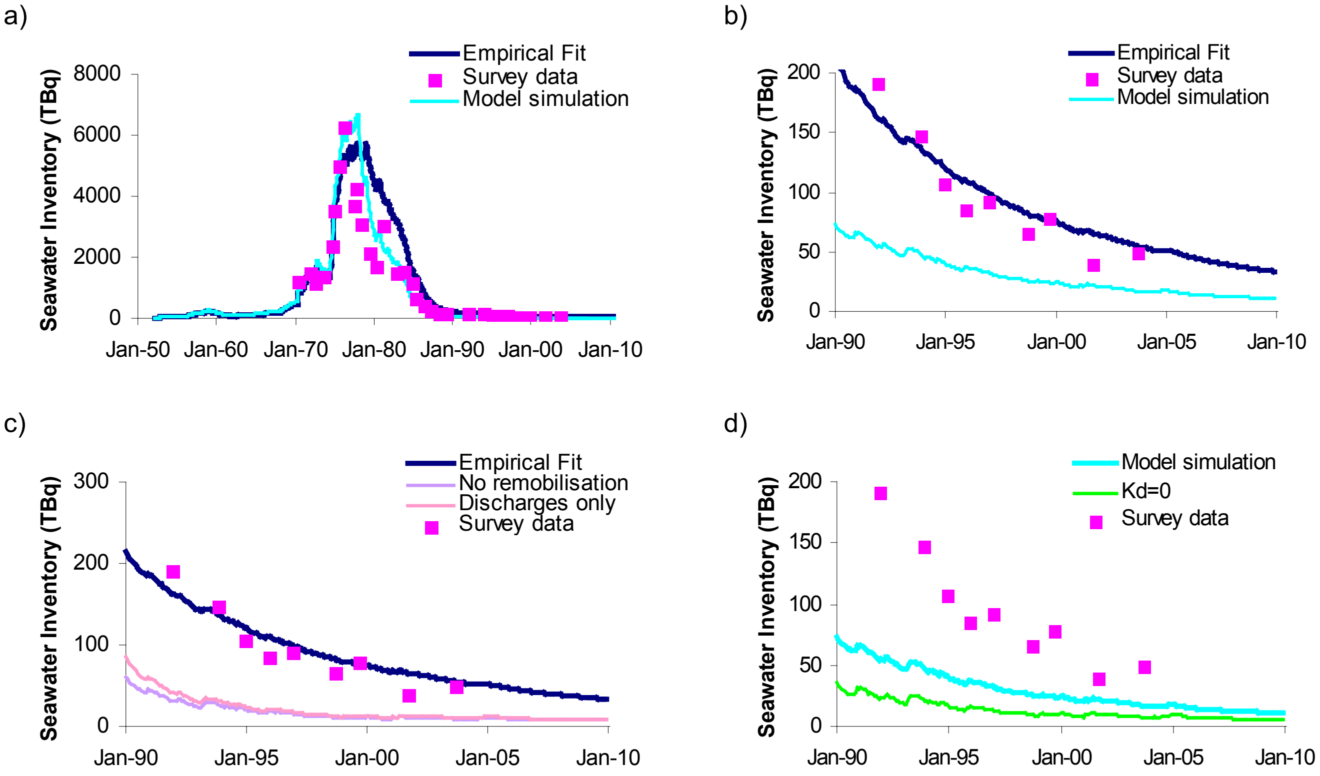
Figure 13. *Spatial distribution of dissolved ^{137}Cs in surface seawater throughout the Irish Sea. a) January 1976, b) April 1986, c) November 1993, d) June 2005*



The results in Figure 13 show that ^{137}Cs activities in surface seawater have significantly decreased with time since the late 1970s. Levels of over 20 Bq/l were observed in the vicinity of the Sellafield outfall during the period of maximum discharges in the late 1970s, compared with ~0.1 Bq/l in 2005. To a first approximation, the spatial distribution has remained broadly similar with time. Caesium-137 concentrations along a large section of the British coastline, extending from Liverpool Bay in the south to the Mull of Galloway in the north, have been consistently greater than those observed along the Irish coastline over the period of these surveys. The contours extend parallel to the Cumbrian coastline. The overall distribution of ^{137}Cs is in line with that expected from our knowledge of mean surface water circulation in the Irish Sea (Dickson, 1987). The predominant flow of water is northward via input of Atlantic water from St. George's Channel, passing to the west of the Isle of Man. A minor component of the flow enters the eastern Irish Sea to the north of Anglesey and moves anti-clockwise round the Isle of Man before rejoining the main flow to exit through the North Channel. Closer inspection of the data does, however, indicate that the gradient in concentrations between the vicinity of the outfall and far-field areas has become less pronounced, due to the declining influence of ^{137}Cs releases from Sellafield.

It is possible to use these surface water data to estimate ^{137}Cs inventories in the Irish Sea if we assume complete vertical mixing of radionuclides throughout the water column. During winter months this is almost certainly true (e.g. Leonard et al., 2004). Inventories have been calculated using results for the bathymetry of the region combined with interpolation of radionuclide data using a commercial software package (SURFER®). The results are provided in Figure 14 along with simulations from the multi-compartmental (Figure 9a) and empirical single box (Figure 10) models.

Figure 14. *Simulating the temporal variation in the inventory of ^{137}Cs in the water column of the Irish Sea: comparison of survey data and output from empirical and multi-compartmental box models a) 1952-2004, b) Expanded y-axis for period 1990-2004, c) application of empirical single box model to assess influence of Sellafield discharges and remobilisation upon water column inventory, d) application of multi-compartmental box model to assess influence of Sellafield discharges and remobilisation upon water column inventory.*



The results in Figure 14a show good agreement between survey data and the multi-compartmental model simulation up to ca 1985. The empirical fit provided a reasonable match to the survey data over the entire period considered here (1952-2004), albeit that close inspection of the data in Figure 14a indicates environmental observations are clustered below the line between 1976 and 1984. Since 1990 (Figure 14b), the multi-compartmental model simulation provided values that were consistently lower (average of ~ 3 fold) compared with the environmental observations. There is significantly less disparity between the environmental ^{137}Cs observations and the empirical ^{137}Cs simulation. If values from both ^{137}Cs simulations after 1986, following the decrease in Sellafield discharges, are fitted to monoexponential decay curves, then the effective half-time for ^{137}Cs in the water column is predicted to be ~6 and 5 years for the empirical and multi-compartmental models, respectively.

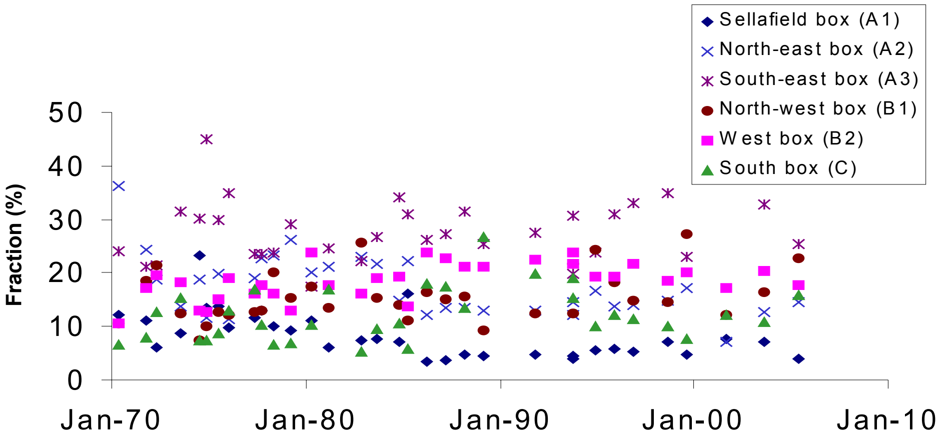
The empirical model was run to assess i) the influence of the Sellafield discharges only (i.e. by setting both $k_{sorption}$ and $k_{remobilisation}$ to zero) and ii) the influence of remobilisation (i.e. by comparing output with $k_{remobilisation}$ set to zero and the best fit value of 0.077 y^{-1}).

Output from other runs, to assess the relative influence of discharges and sediment remobilisation upon the water column inventory, was broadly similar up to 1984, indicating the influence of sediment interactions was relatively minor when discharges remained elevated. However, the data in Figure 14c indicate that, since 1990, measured ^{137}Cs seawater inventories have been consistently in excess of those predicted from annual Sellafield discharges. Although results are not provided here, the contribution from other sources such as global fallout and Chernobyl can be shown to be minor. The average contribution due to remobilisation between 1990 and 2004, estimated by difference between the individual runs, was ~80%. A broadly similar result was derived from the difference between two model runs carried out using the multi-compartmental model (Figure 14d), with an average contribution due to remobilisation between 1990 and 2004 estimated to be ~60%.

As mentioned previously, the multi-compartmental model underestimates (by ~ 3 fold) the actual ^{137}Cs water column inventory when remobilisation is the most significant source term (Figure 14b). Although results are not provided here, preliminary application of the multi-compartmental model to predict behaviour of the particle reactive ^{239,240}Pu indicates that, in contrast, the simulation consistently overestimates the water column inventory (by 2-6 fold) compared with survey data (Leonard et al., 1999). The disparity between model simulation and environmental observation for both nuclides is presumably also a consequence of the difficulty of adequately modelling the complex vertical sediment mixing processes occurring within the Irish Sea.

As mentioned previously, the data in Figure 13 indicate that there has been a small but noticeable shift in the spatial distribution of dissolved ^{137}Cs since releases from Sellafield were drastically reduced between 1983 and 1986. The seawater inventory data were, therefore, examined further to assess whether the decrease with time was uniform throughout the Irish Sea. This was achieved by evaluating inventories in individual areas of the Irish Sea, based on the multi-compartmental

Figure 15. *Selected survey data to illustrate temporal variation in the distribution of dissolved* ^{137}*Cs between individual sectors of the Irish Sea*.



box-model described (Figure 9a). Results for the fraction of the total inventory in individual sectors of the Irish Sea are provided in Figure 15.

The fraction of the total water column inventory in any given sector was significantly variable (Figure 15). For example, that in the Cumbrian coastal box (A1) ranged from ~3 % up to 23 %. Statistical analysis indicated that the average proportion in this sector between 1986-2005 (~ 5%, range 3%-8%) was noticeably less than during the period of maximum discharges (~12%, range 6%-23%) and corroborates the conclusion derived from qualitative inspection of maps showing spatial distribution of dissolved ^{137}Cs (Figure 13). Values for average proportion in each sector (derived from data after 1986 in Figure 15) can be combined with results from the semi-empirical box model for the total ^{137}Cs seawater inventory to produce estimates of inventories in individual compartments.

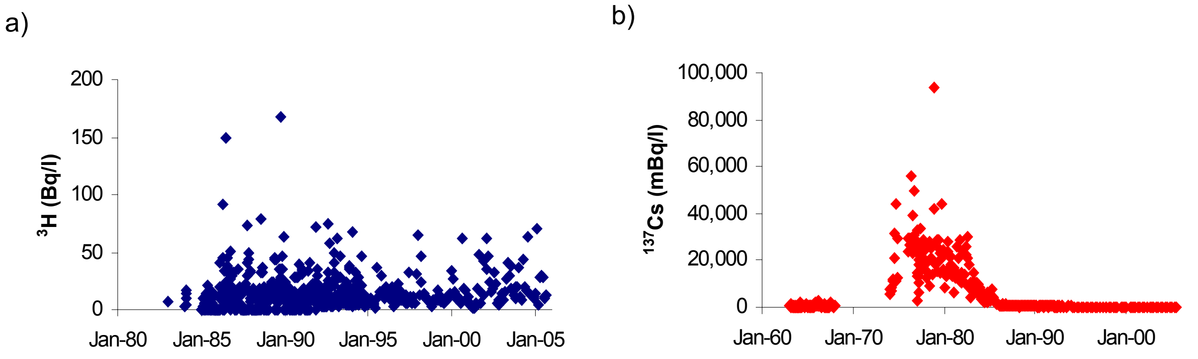
Despite the apparent change in the spatial distribution after 1986, it was not possible to identify any significant difference in the rate of decrease in inventory values between individual sectors of the Irish Sea. This is perhaps to be expected given the large fluctuations in water flow that are known to occur in the Irish Sea, concomitant with variations in wind and tide. The uncertainties associated with detailed spatial and temporal analysis of data from these snapshot surveys are, therefore, very large.

3.3.6.4 Shoreline seawater

The RIFE monitoring programme includes analyses of shoreline seawater and assessment of some of the resulting data is useful for the purposes of the present study, to corroborate interpretation of the offshore dataset. In addition to the large set of data available for ^{137}Cs, a more limited number of seawater samples are also analysed for ^{3}H (and ^{99}Tc). ^{3}H data are also considered here, to compare and contrast with those for ^{137}Cs and to verify model predictions, using the NAC approach, that the majority of ^{137}Cs found in the Irish Sea since 1986 is due to remobilisation (see Figure 16b).

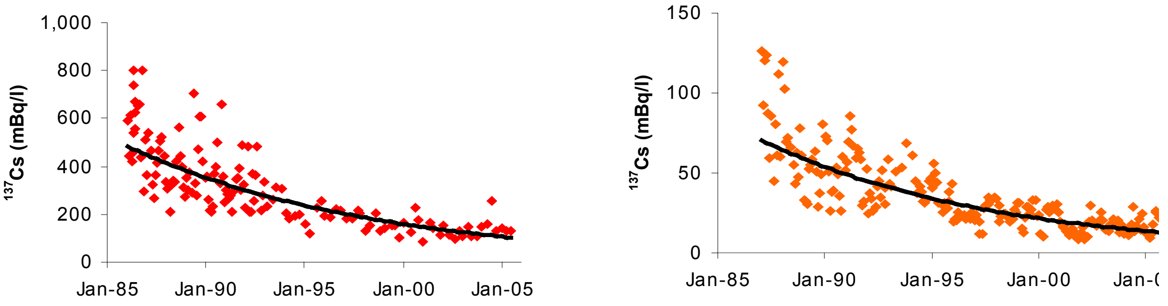
Routine measurements of ^{3}H and ^{137}Cs in shoreline seawater at St Bees, ca 10 km to the north of Sellafield (Figure 16), are carried out by Cefas (as a contractor of the Food Standards Agency). A long-term dataset for ^{137}Cs is also available from samples collected at North of Larne in Northern Ireland, which provides a good indication of the radionuclide activity in seawater exiting the Irish Sea via the North Channel (Figure 16d). Unfortunately ^{3}H analyses are not carried out for these samples.

Figure 16. *Radionuclide concentrations in shoreline seawater from the Irish Sea (provided as dots), a) ^{3}H in water from St Bees, b) ^{137}Cs (1963-2004) in water from St Bees, c) ^{137}Cs (1986-2004) in water from St Bees. Results have been decay corrected to a standard collection date of January 1st 2004. Line indicates best fit exponential curve to these data, d) ^{137}Cs (1986-2004) in water from North of Larne Results are decay corrected to a standard date of January 1st 2004. Line indicates best fit exponential curve to these data.*



c) k = 0.09 yr^{-1} ⇒ t½ ~ 8 y

d) k = 0.09 y^{-1} ⇒ t½ ~ 7.5 y

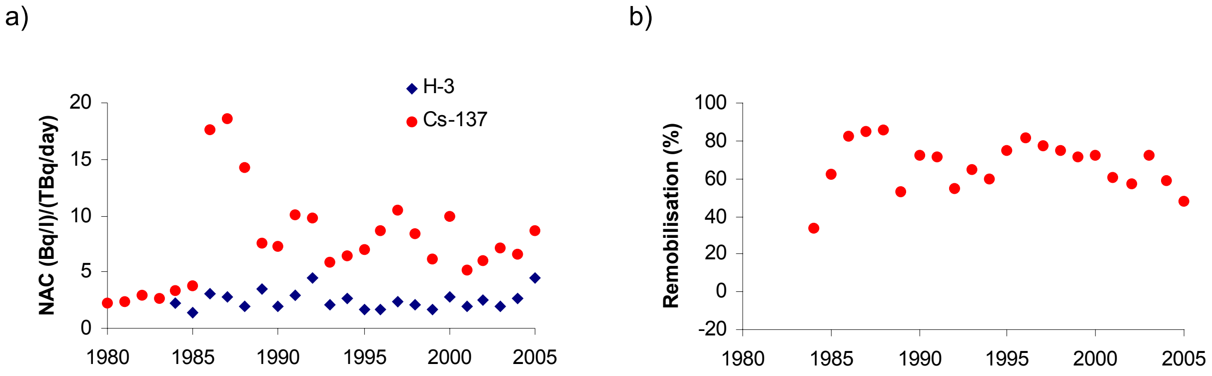


The period for which data are available varies between radionuclides, being greatest for ^{137}Cs with results going back over 40 years. Concentrations have varied widely (by ca three orders of magnitude) in response to, amongst other factors, differing discharges from Sellafield with time (see Figure 3). More specifically, the decay corrected data in Figure 16c and 16d indicate that, since 1986, levels of dissolved ^{137}Cs have declined in an exponential manner with time, due to the very low annual releases from Sellafield (discharges in any given year being <0.1% cumulative discharge). As noted with the data for inter-tidal sediment, the decay corrected seawater data can be fitted to a family of exponential curves of the form C_{Cs} = A*exp(-kt), A*exp(-kt) + resid. or A*exp(-k_1t) + B*exp(-k_2t). The best fit value for k (monoexponential decay curve) is ~0.09 y^{-1}, indicating that ^{137}Cs concentrations halved about every 8 years between 1986 and 2004 (i.e. the identified trend is very similar to that derived from analysis of data for Whitehaven mud and the empirical model simulation). If the data in Figure 16c were instead fitted to a biexponential decay curve then it would be possible to identify a ‘fast’ and ‘slow’ component represented by decay constants k_1 and k_2 with values of ca 1.5 y^{-1} and 0.08 y^{-1}, respectively corresponding to reaction half-times of ~0.5 and 9 years.

The data provided in Figure 16d show that trends in ^{137}Cs behaviour at Larne, away from the vicinity of Sellafield, are similar to those identified for St Bees. If a monoexponential decay curve is fitted to the ^{137}Cs data, the best fit value for the reaction rate constant was ~0.09 y^{-1}, resulting in decay corrected ^{137}Cs concentrations halving about every 7.5 years.

Comparison of the NAC values derived for ^{3}H and ^{137}Cs (Figure 17a) have been used to infer the proportion of dissolved ^{137}Cs in St Bees seawater due to remobilisation from seabed sediments in the Irish Sea (Figure 17b).

Figure 17. *Normalised activity concentrations for radionuclides in seawater at St Bees close to Sellafield and associated estimates of contribution due to remobilisation. a) NAC values for ^{3}H and ^{137}Cs, b) proportion of ^{137}Cs due to remobilisation (estimated as [NAC ^{137}Cs - NAC ^{3}H].[100/ NAC ^{137}Cs])*



NAC values for ^{3}H in St Bees seawater ranged from 1.4-4.5 Bq/l per TBq/day discharged with an average value of 2.5±0.8 Bq/l per TBq/day discharged (Figure 17a). The influence of remobilisation upon concentrations of dissolved ^{3}H is assumed to be almost zero, given that uptake by sediment is thought to be minimal. NAC values for ^{137}Cs showed significant temporal variation, concomitant with the changing discharges from Sellafield. For the period 1963-1984, NAC values ranged from 1.5-3.3 Bq/l per TBq/day discharged with an average value of 2.3±0.6 Bq/l per TBq/day discharged and almost identical to that derived for ^{3}H. Discharges from Sellafield decreased rapidly after 1985 (Figure 3) resulting from the operation of the Site Ion Exchange Plant (SIXEP). For the period 1986-2004 NAC values were significantly greater (range 4-19 Bq/l per TBq/day discharged). The data in Figure 17b, derived from the difference between the ^{137}Cs and ^{3}H values, indicate that remobilisation from the seabed has accounted for the majority (average of ~70%) of the dissolved ^{137}Cs in seawater close to Sellafield since 1986. These data, derived from environmental observations, substantiate the estimates of 60-80% derived from the model simulations.

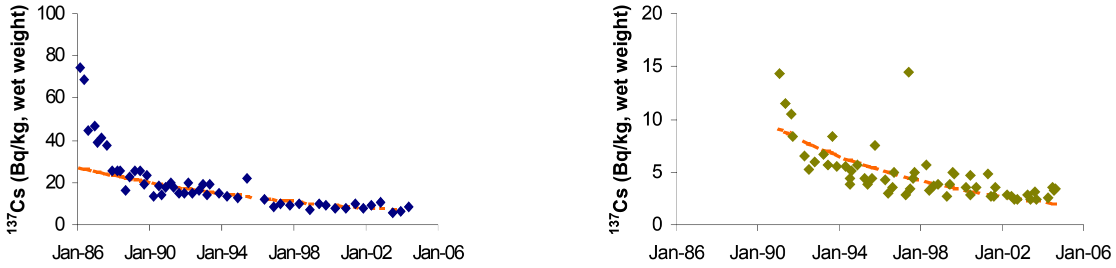
3.3.6.5 Temporal variation in seafood

There is a wealth of data available from the RIFE monitoring programme to assess the temporal variation in the specific activity of ^{137}Cs in a range of seafoods, including fish, crustaceans and molluscs. Selected ^{137}Cs data are provided in Figure 18.

Figure 18. *^{137}Cs concentrations in seafood from the Irish Sea, a) Sellafield offshore area Plaice b) Sellafield pipeline Crabs, c) Whitehaven commercial Nephrops, d) St. Bees Seamill Winkles. Results have been decay corrected to a standard date of January 1st 1986. Lines indicate best fit exponential curve to these data.*

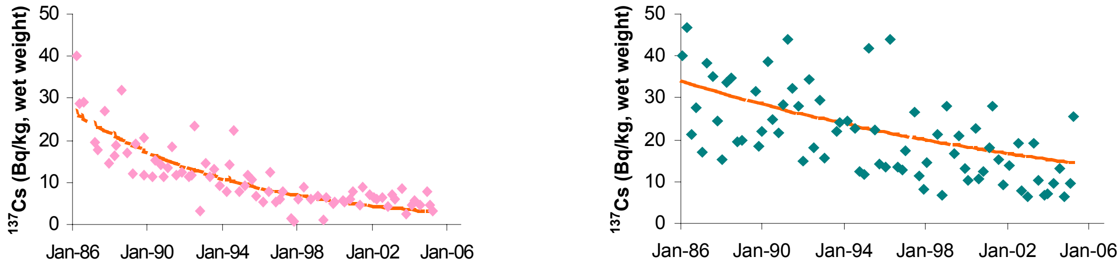
a) *Sellafield offshore area Plaice*
k = 0.08 yr^{-1} ⇒ t½ ~ 9 y

b) *Sellafield pipeline Crabs*
k = 0.11 yr^{-1} ⇒ t½ ~ 6 y



c) *Whitehaven commercial Nephrops*
k = 0.11 yr^{-1} ⇒ t½ ~ 6 y

d) *St. Bees Seamill Winkles*
k = 0.04 yr^{-1} ⇒ t½ ~ 16 y



The data provided in Figure 18 show that the trends in the specific activity of ^{137}Cs in all four items of seafood are broadly similar to those identified for seawater. If monoexponential decay curves are fitted to the ^{137}Cs data, the best fit values for the first order rate constants were in the range 0.04-~0.11 y^{-1}, resulting in decay corrected ^{137}Cs concentrations halving about every 6-16 years.

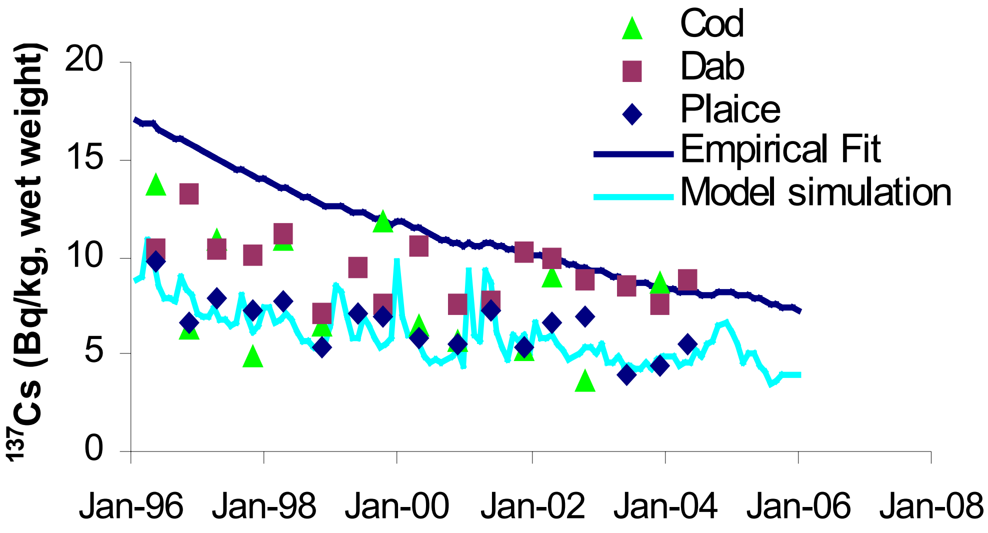
Studies of ^{137}Cs excretion from fishes (Jefferies and Hewett, 1971) indicate that the results may be fitted to a single exponential function that indicates the biological half-time is of the order of 140-180 days (i.e. 0.4 - 0.5 years). The biological half-life varies greatly among different ecological groups of organisms, being inversely dependent on the size of the organisms (Thomann, 1981). Therefore, the turnover time in shellfish is likely to be significantly less than that reported in fish. It seems reasonable to conclude that the reason for the similar rate of decrease in ^{137}Cs activity in seawater and seafood from the Irish Sea (see Figure 16 and Figure 18) is that the turnover time in biota is significantly faster than the rate of remobilisation from seabed sediments. Consequently, the fact that a significant proportion of the environmental body burden of ^{137}Cs in demersal fish, such as plaice and rays, is due to absorption from food rather than the uptake from seawater does not appear to have a significant impact on the long-term trends identified here.

3.3.6.6 Modelling ^{137}Cs seafood data to predict dose to man

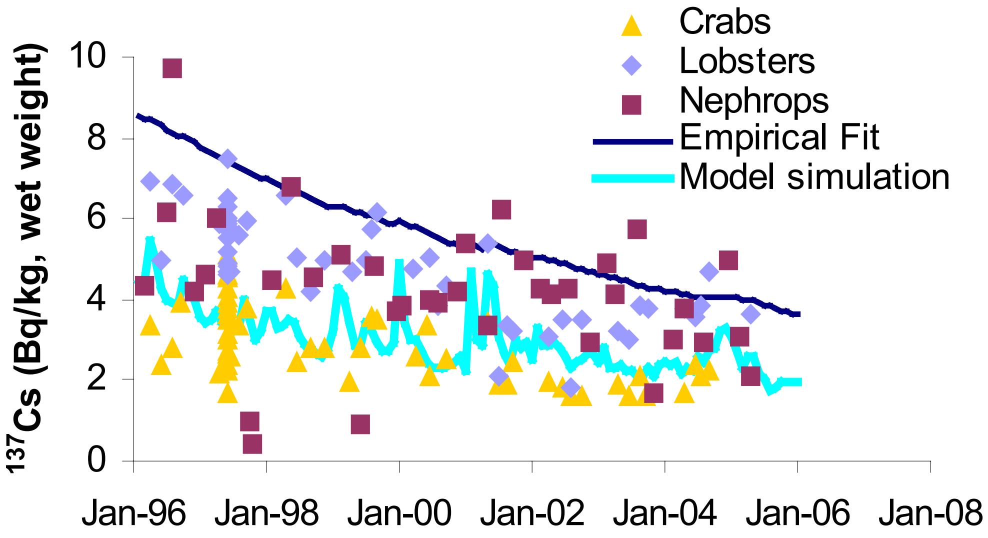
The results in Figure 11 and Figure 14 indicate that both the multi-compartmental and semi-empirical models can more or less adequately simulate survey data for the inventory of ^{137}Cs in both the sub-tidal sediments and water column of the Irish Sea, albeit that that there are inevitably some disparities. In turn, the model values allow predictions to be made of seawater concentrations and therefore seafood catches by applying appropriate CF values (IAEA, 2004). Selected results from both models, showing predicted ^{137}Cs concentrations in fish, molluscs and crustaceans in the Cumbrian coastal box, are provided in Figure 19, for comparison with routine monitoring data.

Figure 19. *Comparison of predicted values and monitoring data for ^{137}Cs concentrations in seafood obtained from the Cumbrian coastal box (A1), a) Fish (CF = 100). Monitoring data are for fish caught within the Sellafield offshore area; b) Crustaceans (CF =50). Crabs and lobster were caught in vicinity of Sellafield pipeline. Nephrops are Whitehaven commercial landing, c) Molluscs (CF = 60). Winkles and Mussels were obtained from St. Bees Seamill. Whelks are Whitehaven commercial landing, d) Predicted dose from seafood consumption due to presence ^{137}Cs (assuming consumption rates of 50 kg/a, 25 kg/a and 30 kg/a for fish, crustaceans and molluscs, respectively and a dose per unit intake of 1.3 x 10^{-8} Sv/Bq). Data for the Cumbrian critical group, derived from assessments undertaken in conjunction with the RIFE reports, are shown for comparison. Consumption rates were slightly variable from year to year.*

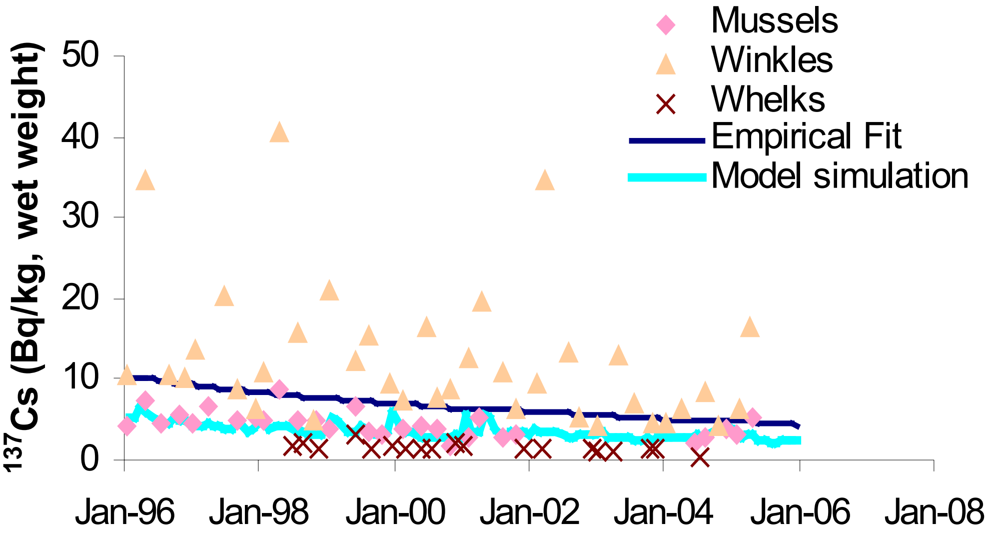
a) *Fish (CF = 100). Monitoring data are for fish caught within the Sellafield offshore area*



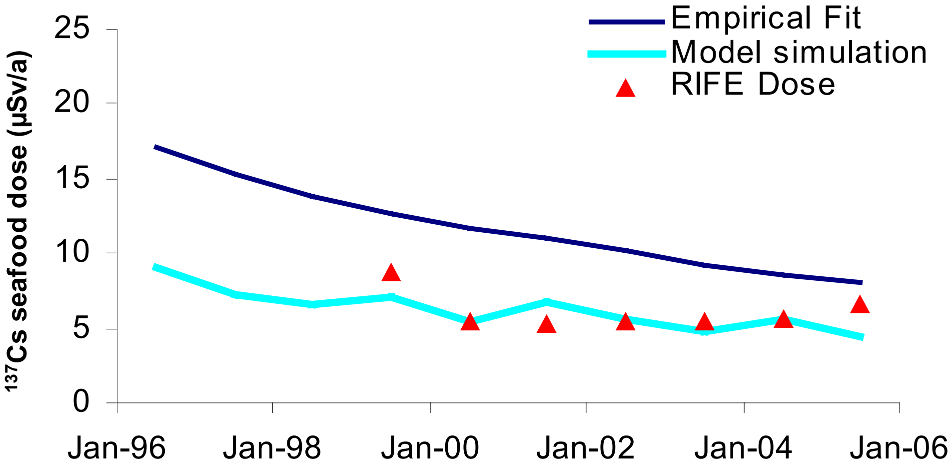
b) *Crustaceans (CF =50). Crabs and lobster were caught in vicinity of Sellafield pipeline. Nephrops are Whitehaven commercial landing*



c) *Molluscs (CF = 60). Winkles and Mussels were obtained from St. Bees Seamill. Whelks are Whitehaven commercial landing*



d) *Predicted dose from seafood consumption due to presence ^{137}Cs (assuming consumption rates of 50 kg/a, 25 kg/a and 30 kg/a for fish, crustaceans and molluscs, respectively and a dose per unit intake of 1.3 x 10^{-8} Sv/Bq). Data for the Cumbrian critical group, derived from assessments undertaken in conjunction with the RIFE reports, are shown for comparison. Consumption rates were slightly variable from year to year*



The monitoring data in Figure 19 are significantly scattered as a result of variable ^{137}Cs accumulation between individual species of fish and shellfish (most notably for winkles and whelks). Overall, the data provided in Figure 19 show that the model predictions for all three items of seafood broadly capture the trend in the monitoring data. It is noticeable that predicted values for fish and crustaceans from the empirical single box model appear conservative. It is suggested that agreement between model predictions and monitoring data is sufficient for the purpose of dose calculations, where the uncertainties are inevitably quite large due to i) the scatter in the environmental data between individual species and ii) highly variable interannual seafood consumption data (Environment Agency et al., 2005). Data from the model simulations have been used to predict the dose arising from consumption of fish and shellfish, assuming constant consumption rates (Figure 19d). The predicted doses, due to ^{137}Cs seafood contamination, both show a gradual decrease with time (down from ~17 μSv/a in 1996 to ~9 μSv/a in 2004 and down from ~9 μSv/a in 1996 to ~4 μSv/a in 2004, using the empirical single box and multi-compartmental models, respectively). These values are in broad agreement with the values derived from assessments carried out for recent RIFE reports (Environment Agency et al., 2005).

3.3.6.7 Summary ^{137}Cs data

Model simulations provide a reasonable approximation to the limited survey data for the inventory of ^{137}Cs residing in the sub-tidal sediments of the Irish Sea. Closer inspection of the results does, however, indicate that the compartmental model provides a significant overestimate of the proportion in surface material. This means that further work (outside the scope of the present study) is required to construct a more accurate model of vertical radionuclide mixing processes within the seabed. The greater proportion (60-80%) of dissolved ^{137}Cs present in the waters and seafood of the Irish Sea since 1986 is predicted to be due to remobilisation from contaminated sediments. An improved capability towards simulating vertical mixing within the seabed could also help in providing more accurate predictions of remobilisation back into the water column, a parameter that is currently underestimated and overestimated for ^{137}Cs and ^{239,240}Pu, respectively. Throughout all areas of the Irish Sea, ^{137}Cs survey data indicates levels in seawater have declined in an exponential manner with a half-time of ~ 8 years. It is possible to use output from a simple empirical box model and a multi-compartmental model to predict ^{137}Cs concentrations in the water column (and hence in fish and shellfish) of the Irish Sea up to 2005. The difference between the two models' predicted dose due to seafood consumption by the Cumbrian critical group in 2005 was ~ 2 fold. Given the inevitable scatter in the monitoring data between individual species, both model predictions appear fit for the purpose of estimating dose from ^{137}Cs contamination to man via the seafood consumption pathway. More importantly, the broad agreement with monitoring data validates the application of either of the models considered here to simulate present and future ^{99}Tc behaviour.

3.3.7 Predicted ^{99}Tc behaviour

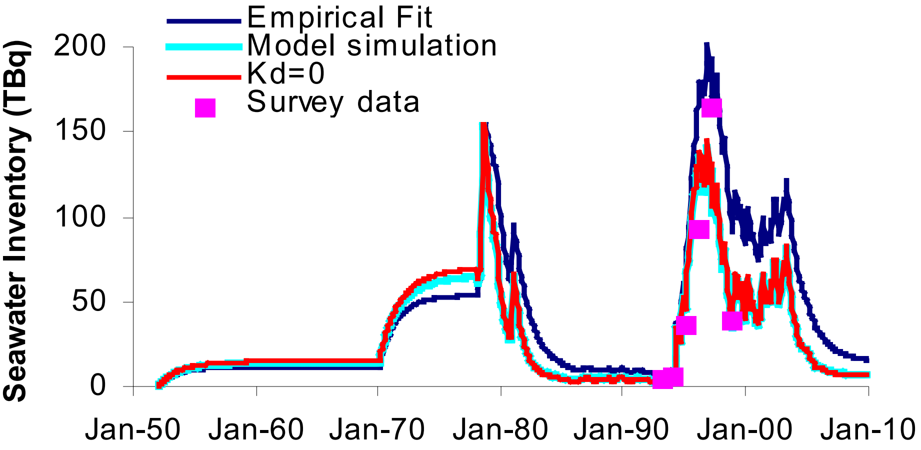
It appears reasonable to use the multi-compartmental and semi-empirical models to predict ^{99}Tc behaviour, given that they can both simulate the fate of ^{137}Cs.

3.3.7.1 Predicted sediment and water column inventories

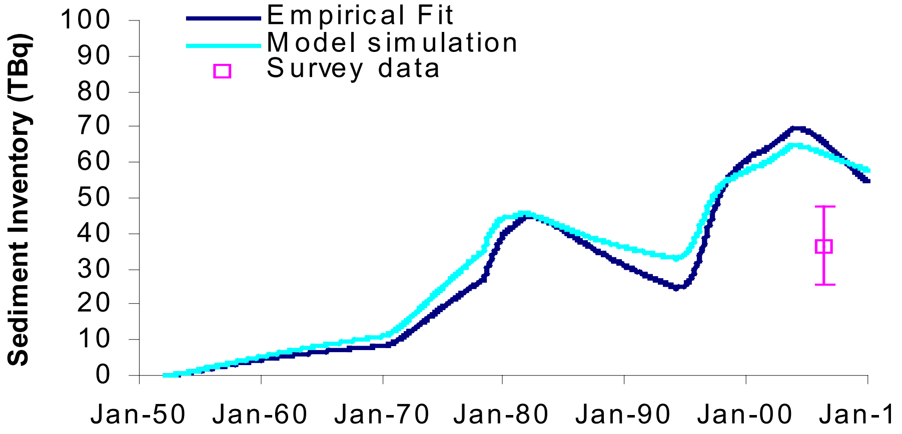
There are limited amounts of data available from seawater surveys with which to derive values for ^{99}Tc inventories in the Irish Sea (McCubbin et al., 2002). As noted previously, these data are for surface waters and it was necessary to assume complete vertical mixing of radionuclides throughout the water column. The results are provided in Figure 20a along with output from model simulations.

Figure 20. *Comparison of survey data and model predictions for inventory of ^{99}Tc in water column and sediments of the Irish Sea a) Seawater b) Seabed sediment*

a)



b)



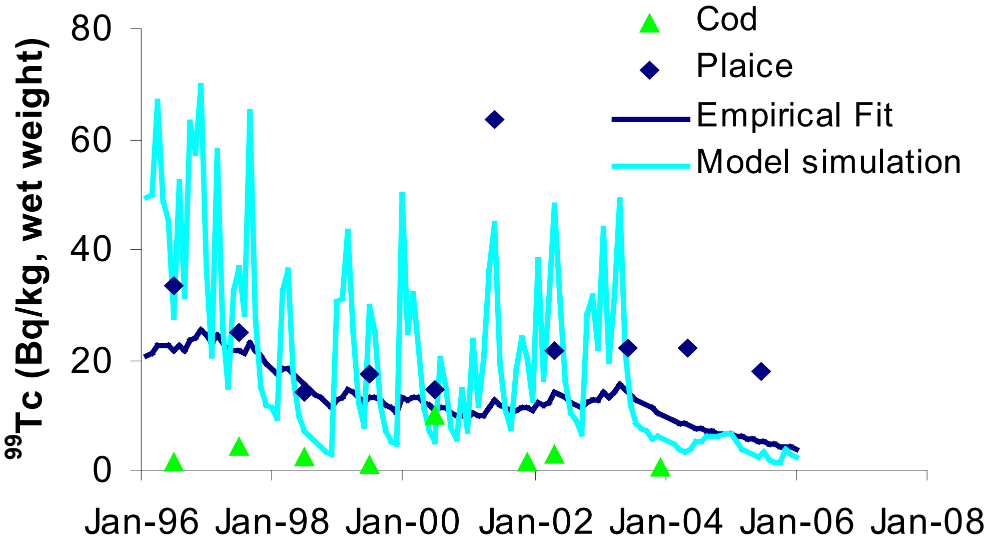
The results in Figure 20a show reasonable agreement between the available (very limited) survey data and both of the model simulations for values of ^{99}Tc in the water column of the Irish Sea. It is worth noting that, in contrast to the ^{137}Cs simulations (Figure 14d), output from both multi-compartmental simulation runs was broadly similar throughout the entire period considered here, indicating the influence of remobilisation upon the water column inventory was insignificant. The disparity in behaviour results from the fact that fluctuations in annual discharges of ^{99}Tc have been considerably less marked than the ^{137}Cs releases (Figure 3). The contribution due to remobilisation in 2004, taken as the difference between the two multi-compartmental model simulations (i.e. with K_d set to 2000 and 0, respectively), was ~5%.

3.3.7.2 Modelling ^{99}Tc seafood data and dose predictions

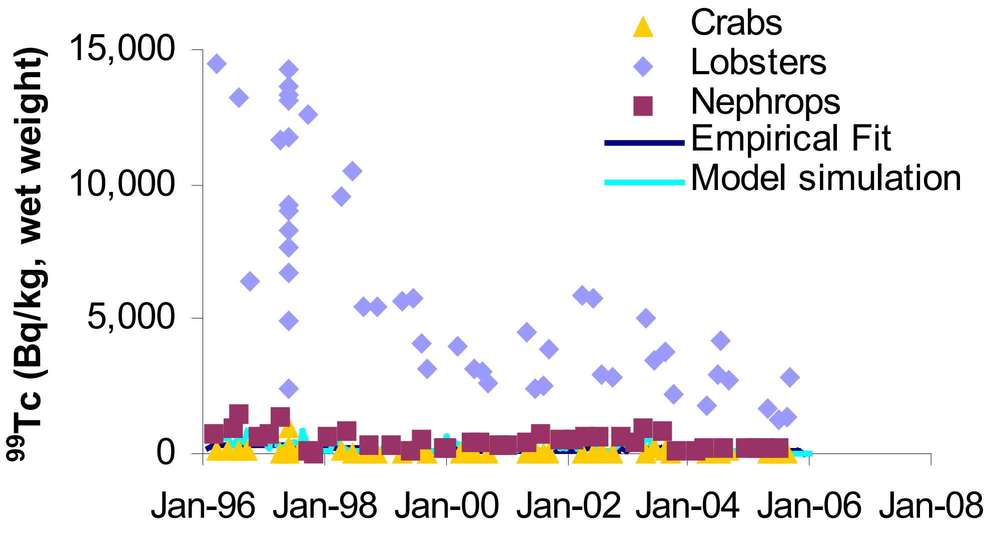
The results in Figure 20a indicate that both the multi-compartmental and semi-empirical models successfully simulate the limited survey data for the inventory of ^{99}Tc in the water column of the Irish Sea. In turn, the model outputs allow predictions of seawater concentrations to be estimated.,By applying the appropriate CF values (IAEA, 2004), it is possible to extrapolate further and to determine ^{99}Tc concentrations in seafood. Selected results from both models, showing predicted ^{99}Tc concentrations in fish, molluscs and crustaceans in the Cumbrian coastal box, are provided in Figure 21, for comparison with routine monitoring data.

Figure 21. *Comparison of predicted values and monitoring data for ^{99}Tc concentrations in seafood obtained from the Cumbrian coastal box (A1), a) Fish (CF = 80). Monitoring data are for fish caught within the Sellafield offshore area; b) Crustaceans (CF =1000). Crabs and lobster were caught in vicinity of Sellafield pipeline. Nephrops are Whitehaven commercial landing, c) Molluscs (CF = 500). Winkles and Mussels were obtained from St. Bees Seamill. Whelks are Whitehaven commercial landing, d) Predicted dose from seafood consumption due to presence ^{99}Tc (assuming consumption rates of 50 kg/a, 25 kg/a and 30 kg/a for fish, crustaceans and molluscs, respectively and a dose per unit intake of 6.4 x 10^{-10} Sv/Bq). Data for the Cumbrian critical group, derived from assessments undertaken in conjunction with the RIFE reports, are shown for comparison. Consumption rates were slightly variable from year to year. e) As Figure 21b, with logarithmic scale on y-axis to aid comparison of monitoring data with predicted values*

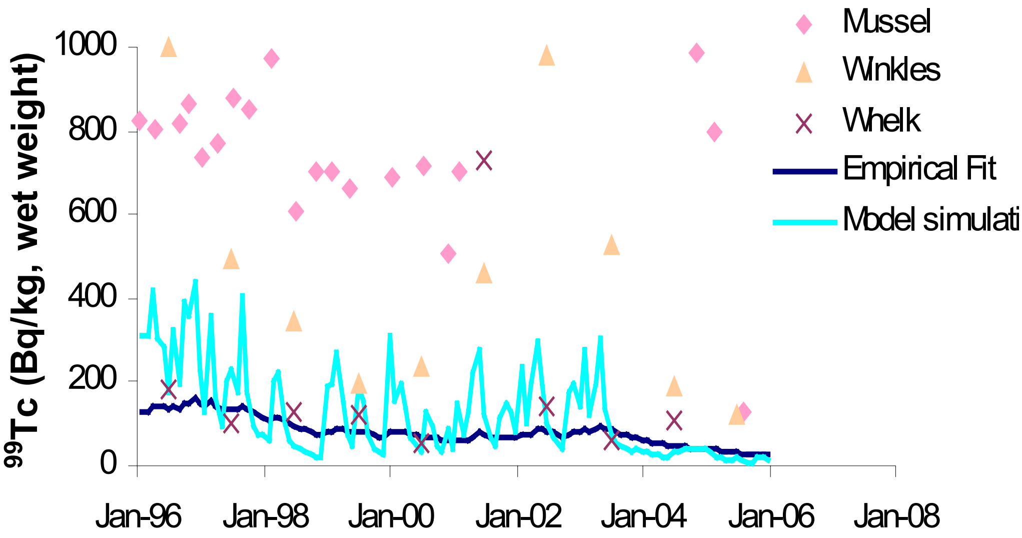
a) *Fish (CF = 80). Monitoring data are for fish caught within the Sellafield offshore area*



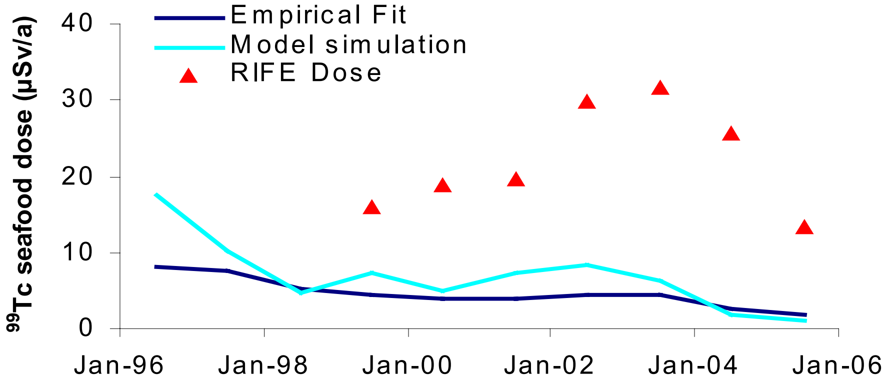
b) *Crustaceans (CF =1000). Crabs and lobster were caught in vicinity of Sellafield pipeline. Nephrops are Whitehaven commercial landing. See Figure 21e for*



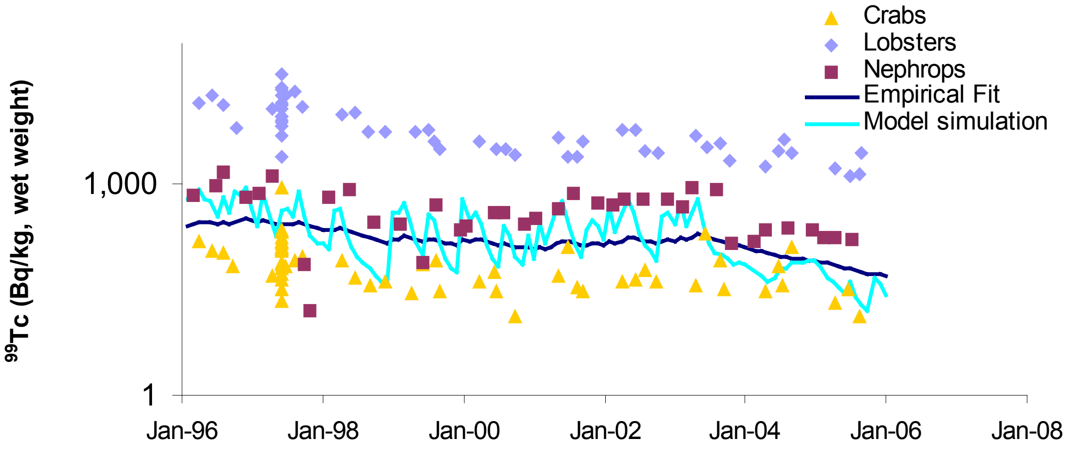
c) *Molluscs (CF = 500). Winkles and Mussels were obtained from St. Bees Seamill. Whelks are Whitehaven commercial landing*



d) *Predicted dose from seafood consumption due to presence ^{99}Tc (assuming consumption rates of 50 kg/a, 25 kg/a and 30 kg/a for fish, crustaceans and molluscs, respectively and a dose per unit intake of 6.4 x 10^{-10} Sv/Bq). Data for the Cumbrian critical group, derived from assessments undertaken in conjunction with the RIFE reports, are shown for comparison. Consumption rates were slightly variable from year to year*



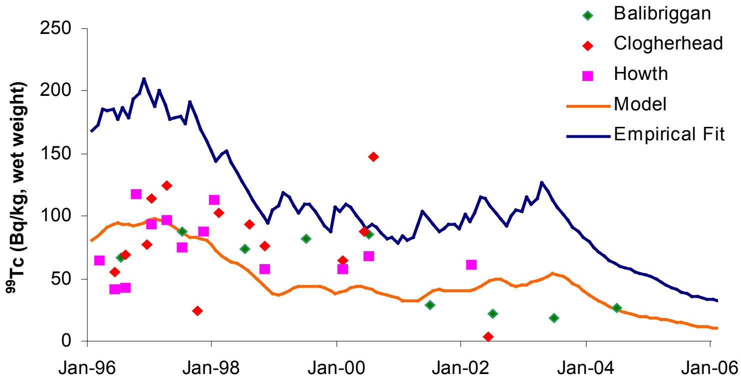
e) *As Figure 21b, with logarithmic scale on y-axis to aid comparison of monitoring data with predicted values*



The Cumbrian monitoring data in Figure 21 are significantly scattered between individual species of fish and shellfish (most notably crabs, lobsters and nephrops). Data from three long-term monitoring programmes (the UK, Ireland Norway) has recently been reworked in order to derive new CFs for several marine species-radionuclide pairs (Kershaw et al., 2005). Reported ^{99}Tc CF values for the three species of crustacean considered here range from ~200 in crabs up to 13,000 in lobsters. Allowing for the differential CF values between individual species, the data provided in Figure 21 indicates that the model predictions for all three items of seafood broadly follows the trend in the monitoring data. It is suggested that agreement between model predictions and monitoring data is sufficient for the purpose of dose calculations, where the uncertainties are inevitably compounded due to variable seafood consumption from year to year (Environment Agency et al., 2005). The predicted values for ^{99}Tc concentrations in seafood have been used to predict the dose arising from consumption of fish and shellfish, assuming constant consumption rates (Figure 21d). The predicted doses, due to ^{99}Tc seafood contamination, both show reduced values in 2005 (down from ~8 μSv/a in 1996 to ~2 μSv/a in 2005 and down from ~18 μSv/a in 1996 to ~1 μSv/a in 2005, using the empirical and multi-compartmental models, respectively). These values are less than those provided in recent RIFE reports – nevertheless, the disparity is overall remarkably small given the uncertainties associated with both the model output and the RIFE data. Finally, it is worth noting that the predicted doses due to ^{99}Tc seafood contamination are similar to those for ^{137}Cs. In turn, this indicates that the combined impact of the continuing low level ^{99}Tc Sellafield discharges and remobilisation is now broadly similar to the contribution from ^{137}Cs remobilisation on its own.

As mentioned previously, the western Irish Sea nephrops population occupies a much larger area of mud than in the east (Figure 9a), and provides the bulk of the commercial landings. The Radiological Protection Institute of Ireland (RPII) undertakes a wide-ranging programme of radioactivity monitoring in the Irish marine environment (http://www.rpii.ie/radiation/marine.html). This programme has been in place since the early 1980s and involves the routine sampling and testing of seafood and other materials, including nephrops. Selected results from both models (Figure 22), showing predicted ^{99}Tc concentrations in nephrops in the Irish Sea west (B2) box, are provided for comparison with routine monitoring data reported by the RPII for landings at Balibriggan, Clogerhead and Howth.

Figure 22. *Comparison of predicted values and monitoring data for ^{99}Tc concentrations in nephrops (CF = 3000) obtained from the Irish Sea West box (B2). Monitoring data are those reported by the RPII.*



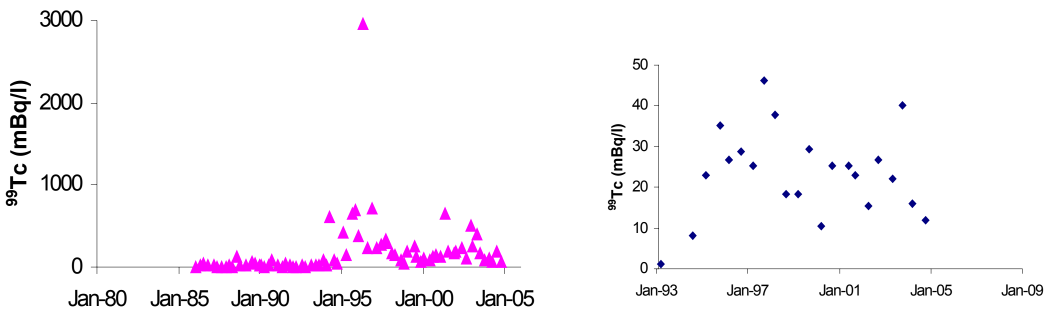
Once again, the data in Figure 22 indicate that output from both models provides a reasonable simulation of the available monitoring data, albeit that the empirical values tend to be overly conservative.

3.3.7.3 Shoreline seawater

The RIFE monitoring programme includes analyses of shoreline seawater, and assessment of some of the resulting data is useful for the purposes of the present study in order to corroborate interpretation of the offshore dataset. Although the number of seawater samples analysed for ^{99}Tc is limited, these results are useful to verify model predictions that the majority of ^{99}Tc found in the Irish Sea in 2005 is due to current discharges.

Routine measurements of ^{99}Tc in shoreline seawater are carried out by Cefas (as a contractor of the Food Standards Agency) at St Bees, ca 10 km to the north of Sellafield, and to the north of Larne representing seawater exiting the Irish Sea via the North Channel (Figure 23).

Figure 23. *Concentrations of ^{99}Tc in shoreline seawater samples from the Irish Sea. a) St Bees, b) North of Larne. These data are included here for completeness.*

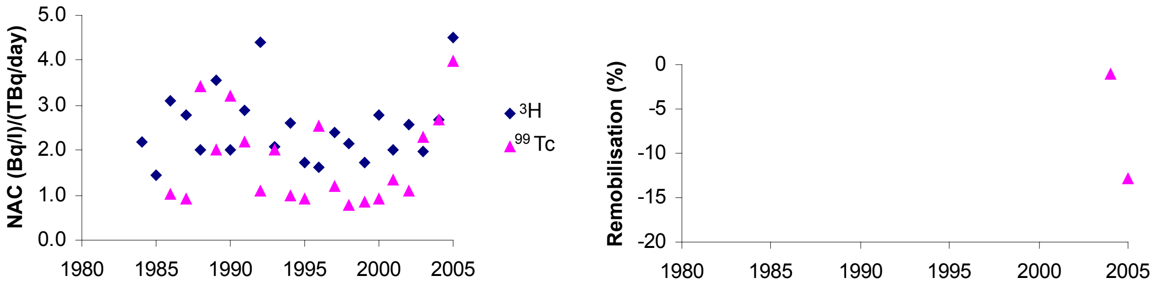

a)

b)

The period for which data are available varies between sites. Concentrations have varied widely (by ca three orders of magnitude) in response to, amongst other factors, differing discharges from Sellafield with time.

Comparison of the NAC values derived for ^{99}Tc and ^{3}H has been used to infer the proportion of dissolved ^{99}Tc in St Bees seawater due to remobilisation from seabed sediments in the Irish Sea (Figure 24).

Figure 24. *Normalised activity concentrations for radionuclides in seawater at St Bees close to Sellafield and associated estimates of contribution due to remobilisation. a) NAC values for ^{3}H and, ^{99}Tc, b) proportion of ^{99}Tc due to remobilisation (estimated as [NAC ^{99}Tc- NAC ^{3}H].[100/ NAC ^{99}Tc])*


a)

b)

NAC values for ^{3}H in St Bees seawater ranged from 1.4-4.5 Bq/l per TBq/day discharged with an average value of 2.5±0.8 Bq/l per TBq/day discharged (Figure 24a). The influence of remobilisation upon concentrations of dissolved ^{3}H is assumed to be almost zero for the reasons previously outlined in section 3.3.2.3. The average NAC value for ^{99}Tc (1.8±1.0, range 0.8-4.0 Bq/l per TBq/day discharged) was very similar to that observed for ^{3}H. The data in Figure 24b, derived from the difference between the ^{99}Tc and ^{3}H NAC values, indicate that the impact of remobilisation from the seabed on levels of dissolved ^{99}Tc in seawater close to Sellafield is not detectable, despite the recent decrease in ^{99}Tc discharges from 2004 onwards (Figure 3). Any ^{99}Tc remobilisation data derived prior to 2004 (in Figure 24b) are likely to be largely influenced by discharge rather than remobilisation of ^{99}Tc and therefore are not included in the figure. The post-2004 data, derived from environmental observations, substantiate the assessment derived from the model simulations. The minor impact is, in part, attributed to the fact that the reduction in ^{99}Tc discharges from Sellafield attained between 2003-2005 was proportionally less than that achieved for ^{137}Cs between 1983-1986. More specifically, the annual ^{99}Tc release in 2005 (~6.7 TBq) was ~0.4 % of the cumulative discharge (1693 TBq). Although the annual ^{137}Cs release in 2004 (5.9 TBq) was similar to the ^{99}Tc discharge, it was a much smaller fraction (~0.03 %) of the cumulative discharge (21,348 TBq).

3.3.7.4 Summary ^{99}Tc data

Reasonable agreement was obtained between the available (very limited) survey data and both model simulations for values of ^{99}Tc in the water column of the Irish Sea. The impact of ^{99}Tc remobilisation from sediments, contaminated by the legacy of enhanced discharges in the 1970s and between 1994-2004, upon levels in the water column is currently minimal. CF values for accumulation between individual species of shellfish are highly variable and complicate the comparison of environmental data and model simulations. Although predicted doses are slightly lower than those provided in recent RIFE reports, the disparity is relatively low (< 3 fold) given the errors associated with both sets of values.

4. Discussion

4.1 Future ^{99}Tc discharges from Sellafield

The contribution from remobilisation from contaminated sediment towards current levels of ^{99}Tc in seawater and seafood in the Irish Sea is minimal. The future contribution is dependent upon subsequent changes to the quantities of ^{99}Tc discharged from Sellafield. As mentioned previously, the dominant source of ^{99}Tc in the liquid effluent discharged to sea are the arisings associated with the reprocessing of spent Magnox reactor fuel routed through the EARP treatment plant. The uranium metal contained in Magnox spent fuel and its magnesium alloy cladding exist in a chemically reactive form. Once spent fuel from Magnox reactors has been wet stored, it is therefore necessary to reprocess the material due to corrosion effects to make the waste more suitable for safe storage and, possibly, eventual underground disposal. Although it has been suggested in some quarters that dry storing Magnox spent fuel could remove the need for reprocessing, the Radioactive Waste Management Advisory Committee (RWMAC, replaced in 2004 by the Committee on Radioactive Waste Management (CoRWM)) concluded that, at the present time, dry storage cannot be regarded as a practicable option for long-term management. It follows that reprocessing of spent Magnox fuel is likely to continue until the closure of the remaining Magnox power stations. Current predictions are that operations at the B205 Magnox reprocessing plant will cease in 2012 (www.nda.gov.uk). It therefore seems reasonable to presume that discharges of ^{99}Tc from Sellafield are likely to remain broadly similar to those in 2005 (i.e. ~7 TBq y^{-1}) in the near to medium term (i.e. up to 2012) (Parker, pers. comm.).

4.2 Future ^{99}Tc contamination of seafood

Given that ^{99}Tc discharges from Sellafield currently represent the major influence upon levels in fish and shellfish in the Irish Sea, it is likely that activity concentrations will remain broadly similar up to 2012. Levels in Nephrops are predicted to persist at ~100 Bq/kg (wet weight) and ~10 Bq/kg (wet weight) in the eastern and western Irish Sea, respectively.

5. Conclusions

The inventory of ^{99}Tc currently residing in the sub-tidal sediments of the Irish Sea is in the order of ca 37 TBq. An assessment of its availability to marine foodstuffs has been made using a multi-compartmental model to estimate the rate and extent of re-dissolution into the overlying seawater. The model was optimised and validated using our detailed long-term datasets for ^{137}Cs, given that remobilisation is known to provide the major contribution towards present levels in seawater and seafood. The ^{99}Tc seawater data, derived from model simulations, have subsequently been used to estimate levels in seafoods (and hence the dose to seafood consumers) using the concentration factor (CF) method. The impact of ^{99}Tc remobilisation from sediments upon levels in the water column is currently minimal. CF values for accumulation between individual species of shellfish are highly variable and complicate the comparison of environmental data and model simulations. Although predicted doses are slightly lower than those provided in recent RIFE reports, the disparity is relatively low (< 3 fold) given the errors associated with both sets of values. It seems reasonable to conclude that discharges from Sellafield (hence levels in fish and shellfish in the Irish Sea) are likely to remain broadly similar to those in 2005 in the near to medium term (up to 2012).

6. Acknowledgements

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