Accumulation and remobilisation of ^{99}Tc in eastern Irish Sea sediments

Science commissioned by the Food Standards Agency

Environment Report RL 01/04
CEFAS Contract C1653
Food Standards Agency Project R01055

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Accumulation and remobilisation of ^{99}Tc in eastern Irish Sea

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2004

The work in this report was completed under contract to the Food Standards Agency

CEFAS Contract C1653
FSA Project R01055

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Executive summary

^{99}Tc is a long-lived ($t^{½}$ = 2.13 x 10^5 years) beta-emitting radionuclide and is becoming 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 treatment of a backlog of medium-level stored waste at Sellafield has resulted in enhanced ^{99}Tc discharges to the Irish Sea since 1994, and has been a subject of national and international controversy. Results from a previous FSA project (FSA, 2001) provided preliminary indications of ^{99}Tc accumulation in Irish Sea subtidal sediments. The aim of the present project was to confirm these data and to assess the implications for seafood contamination. This was achieved via a combination of an environmental survey and a programme of laboratory experiments. More specifically: i) A number of cores were collected throughout the Irish Sea in July 2002. These were sliced and analysed to produce ^{99}Tc depth profiles to substantiate the preliminary findings of accumulation in seabed sediments; ii) Simultaneously, large volume water samples were collected to assess levels in the water column. Selected samples were filtered to separate dissolved and particulate phases. Both fractions were analysed in order to derive ^{99}Tc K_d values. These are required to model present and future seafood contamination; iii) Laboratory experiments were carried out to assess the processes and mechanisms of ^{99}Tc remobilisation.

Sediment core data indicated ^{99}Tc released from Sellafield post-EARP has penetrated below 30 cm. The profiles varied between individual sampling locations and some were 'irregular'. This is suggested to be a result of variable mixing via bioturbation processes. Derived K_d values indicate the solid-solution partitioning behaviour of ^{99}Tc is complex. Those for suspended sediments were roughly an order of magnitude higher than the value

of 100 currently recommended by the IAEA for coastal sediments. The information obtained here will be used to update the WAT-ADO model for prospective dose assessment.

Results from the laboratory experiments indicated that there is little or no uptake of ^{99}Tc from seawater onto oxidising sediments low in organic matter. ^{99}Tc is redox reactive, i.e. it can exist in different chemical forms. Uptake only occurs onto anoxic sediments where it may be reduced from $^{99}Tc(VII)O_4^-$ (the stable form in oxic seawater) to insoluble Tc(IV) species. Desorption of ^{99}Tc from contaminated sediment into uncontaminated seawater was variable between different sediment types. Redissolution from oxidising sediment was rapid whereas ^{99}Tc associated with anoxic sediment remained bound metastably under oxic conditions.

The results have been used, together with information derived from a general review of the literature, to assess the implications for seafood contamination. There are three primary pathways for the accumulation of ^{99}Tc in items of seafood: i) direct uptake from surrounding seawater; ii) consumption of contaminated food items and iii) direct uptake from ingested sediment. Transfer from sediment into benthic organisms is low and the predominant pathway for ^{99}Tc accumulation by seafood is probably uptake from surrounding seawater. In the event that discharges from Sellafield should cease, the availability of ^{99}Tc in the subtidal sediments is likely to be governed by the rate and extent of redissolution processes. Although the mechanisms of ^{99}Tc uptake and release are entirely different to that of ^{137}Cs (^{137}Cs is not redox reactive), it is worth noting the K_d values are of similar magnitude. If the rate and extent of ^{99}Tc redissolution follows a similar pattern to that reported for ^{137}Cs then, the half-time for redissolution of ^{99}Tc bound to sedimentary material in the Irish Sea is likely to be in the order of several tens of years.

1. Introduction

^{99}Tc is a long-lived ($t^{½}$ = 2.13 x 10^5 years) beta-emitting radionuclide ($E_{\beta\,max}$ = 292 keV) and is becoming 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. Following the introduction of stricter discharge authorisations and new effluent treatment systems in the 1980s, sharp reductions occurred in releases of most radionuclides from Sellafield. The Enhanced Actinide Removal Plant (EARP) was commissioned by BNF almost ten years ago (1994). EARP was designed to further decrease alpha and beta activity from Sellafield effluents prior to discharge. The activity from latter day arisings has been substantially reduced, but operation of the EARP plant allowed the treatment of medium-level waste (which previously had been accumulating on site) to commence. Reprocessing this backlog has resulted in additional ^{99}Tc discharges to the Irish Sea since 1994, as it is not significantly removed during the EARP treatment process, and has been a subject of national and international controversy (Defra, 2002).

The additional 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). Another consequence, that was less readily anticipated, was accumulation of ^{99}Tc in the seabed sediment. Results from a previous FSA funded project (FSA, 2001), provided preliminary data indicating accumulation of ^{99}Tc in both surface sediment and sediment cores. One goal of this project was to substantiate these initial findings. This was achieved via an environmental survey involving the collection and analysis of sediment cores to produce ^{99}Tc depth profiles. Interpretation of the data was facilitated by the collection and analysis of samples from inter-tidal locations to assess the influence of grain-size.

Another goal was to improve modelling of future ^{99}Tc remobilisation from contaminated sediment and the consequences for seafood contamination. More specifically, one of the major factors influencing the distribution of artificial radionuclides in the marine environment is their affinity for sedimentary material. This association 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). For example, ^{137}Cs has a relatively low affinity for sedimentary material in the Irish Sea (K_d = 10^2-10^3, Kershaw et al., 1992) and consequently greater than 90% of the total activity discharged from Sellafield has been removed from this area with the general water circulation. In contrast, Pu radionuclides and ^{241}Am in the Irish Sea have comparatively high affinities for particulate material and, therefore, nearly all the activity discharged has been retained within the sediments of the Irish Sea basin (Kershaw et al., 1999). Parameterisation of radionuclide-sediment interactions, following discharge into the marine environment, form an important part of the WAT/ADO suite of prospective dose assessment models (Hunt, 1982; Round, 1998a,b). A study by Brownless et al. (2001) found that K_d is a particularly significant parameter in contributing to uncertainties in these models. This is further emphasised through the use of probabilistic models for marine dose assessment, where the large range in recommended K_d values can significantly alter predicted doses (Grzechnik, 2002).

Unfortunately, environmental measurements to assess the solid-solution partitioning of ^{99}Tc between seawater and suspended sediment in the Irish Sea are extremely sparse. On the aforementioned environmental survey large volume surface seawater samples were collected from the same sites as the sediment cores, to assess levels of ^{99}Tc in the water column. Selected samples were filtered to separate dissolved and particulate phases. Both fractions were analysed and the data used to derive K_d values. The resulting information enabled us to achieve our goal of providing more environmental K_d data to improve the accuracy of prospective dose assessments arising from changes to future Sellafield discharges.

The final objective of this project was to improve our knowledge of the rate and extent of processes controlling future remobilisation of ^{99}Tc from the seabed, in the event discharges from Sellafield should cease. Results from a separate study (Keith-Roach and Roos, 2004) indicate reducing environments may represent sinks for ^{99}Tc in the marine environment. We therefore carried out a programme of laboratory experiments using oxic and anoxic sediment to simulate potential release from contaminated sediment resuspended into uncontaminated seawater. It was anticipated the results would provide initial estimates of desorption rates, together with K_d values to compare with the environmental data.

2. Sampling and analysis

CEFAS was invited to take part in the IRSN (Institute for Radiological Protection and Nuclear Safety) DIAPLU (Diagenesis Plutonium) fieldwork programme in the Irish Sea between July 2nd to 21st 2002 (www.irsn.fr/va/09_int/09_int_3_lib/pdf/VA_IRSN_RA.pdf, IRSN 2003). This programme, performed as part of the European Commission REMOTRANS project, consisted of a number of collaborating organisations including IRSN (Cherbourg, France) and UCD (Dublin, Ireland). The CEFAS Whitehaven laboratory was used as a base for subtidal and land based fieldwork. Consequently, CEFAS was given a short window of opportunity aboard the French research vessel (Cotes la Manche), which had separately been chartered by IRSN for DIAPLU work in the Irish Sea. Inevitably there were operational constraints for the choice of sites, timing and methods of sampling, determined by other competing demands on the ship programme. Sediment cores and surficial samples were obtained by deploying a Reineck corer and a Day Grab, respectively. Large volume surface seawater samples (50 litres) were collected using the ship's pumped supply. Although the survey described in Section 3 afforded the project good coverage in terms of sites sampled, the coring equipment available did not allow deep (> 30 cm) sediment cores to be collected.

Additional surface sediment samples were collected in the vicinity of Whitehaven Harbour, in order to assess the influence of grain-size upon ^{99}Tc sorption behaviour. Sand was collected at low water in the Outer Harbour and separated into three separate grain-size fractions (>500 μm, 200-500 μm and 100-200 μm) by wet sieving through nylon mesh sieves, using local seawater. Other samples collected included i) material from a small patch of boulder clay exposed at low water in the Outer Harbour, ii) sand surrounding the boulder clay and iii) coarse grained sediment from the small beach immediately to the south of Whitehaven Harbour. These were not sieved and were analysed as whole samples.

Seawater samples were filtered (0.45 μm) to separate dissolved and particulate phases. To determine the concentrations of ^{99}Tc in seawater, rhenium carrier (10 mg), a chemical analogue of technetium, was added as a yield monitor. After thorough mixing, the determinand and monitor were pre-concentrated from seawater by anion exchange. Following subsequent 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. For solid samples, the yield recovery tracer was added to the dried sample, prior to chemical separations. The detection limit for seawater and sediment samples was ~0.06 mBq/l and ~0.3 Bq/kg, respectively. The combined uncertainty (1 standard deviation) on the data reported here was ~ 7%. Full details of the analytical procedures for ^{99}Tc are reported elsewhere (Harvey et al., 1991; 1992). For a few samples (surface sediments collected from Whitehaven Harbour) an additional characterisation was carried out, by counting γ emitting radionuclides on a high purity Ge detector.

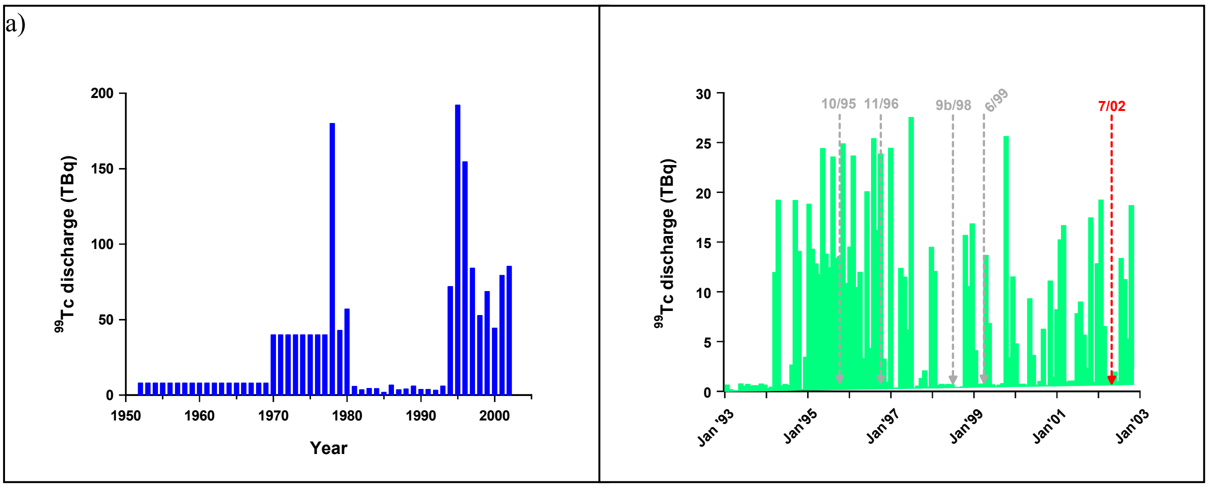
3. Results

3.1 Irish Sea survey data

3.1.1 Chronology of ^{99}Tc discharges into the Irish Sea

Since liquid discharges to sea began in 1952, a range of radionuclide determinations have 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 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 2002, based on published data (CEC, 1990; NRPB, 1995; BNFL, 1979-2003), are given in Fig 1a. ^{99}Tc discharges during the 1970s were significantly greater than those in the 1980s. Following the operation of EARP (in 1994) to remove other radionuclides, the discharge of ^{99}Tc returned to the previous higher levels. A more detailed chronology of the ^{99}Tc discharges (monthly), from January 1993 to January 2003 (BNFL, personnel communication) is provided in Fig. 1b, together with the timing of the survey cruises in the present study (Cotes la Manche 7/02) and previous projects. The monthly ^{99}Tc data show the extent, and pulsed nature, of elevated levels of discharge, first commencing in March 1994.

Figure 1. *Discharges of ^{99}Tc (TBq) from Sellafield, together with the timing of survey cruises. (a) Annual discharges of ^{99}Tc (1952-2002), (b) Monthly discharges of ^{99}Tc (January 1993 - January 2003). Survey timings indicated by dashed arrows. Sampling for present study carried out in July 2002 (Survey: Cotes la Manche 7/02).*



3.1.2 *Distribution of ^{99}Tc in surface sediment*

Distribution maps showing the activity of ^{99}Tc in surface sediment samples of the Irish Sea are presented in Figs. 2a-2d. Preliminary data from a previous project, indicating measurable levels of ^{99}Tc in surficial sediments (post-EARP), are provided in Fig. 2a (December 1995, Survey: Cir 10/95) and Fig. 2b (September 1998, Survey: Cory 9b/98). The results from the present study, shown in Fig. 2c, confirm these findings.

Figure 2. *^{99}Tc (Bq/kg dry weight) in Irish Sea surface sediments. a) December 1995 (Survey: Cir 10/95). These results were supported by Westlakes Scientific Consulting Ltd. (Cumbria, UK), b) September 1998 (Survey: Cory 9b/98), c) July 2002 (Survey: Cotes la Manche 7/02), d) July 2002 data superimposed on map of sediment composition.*

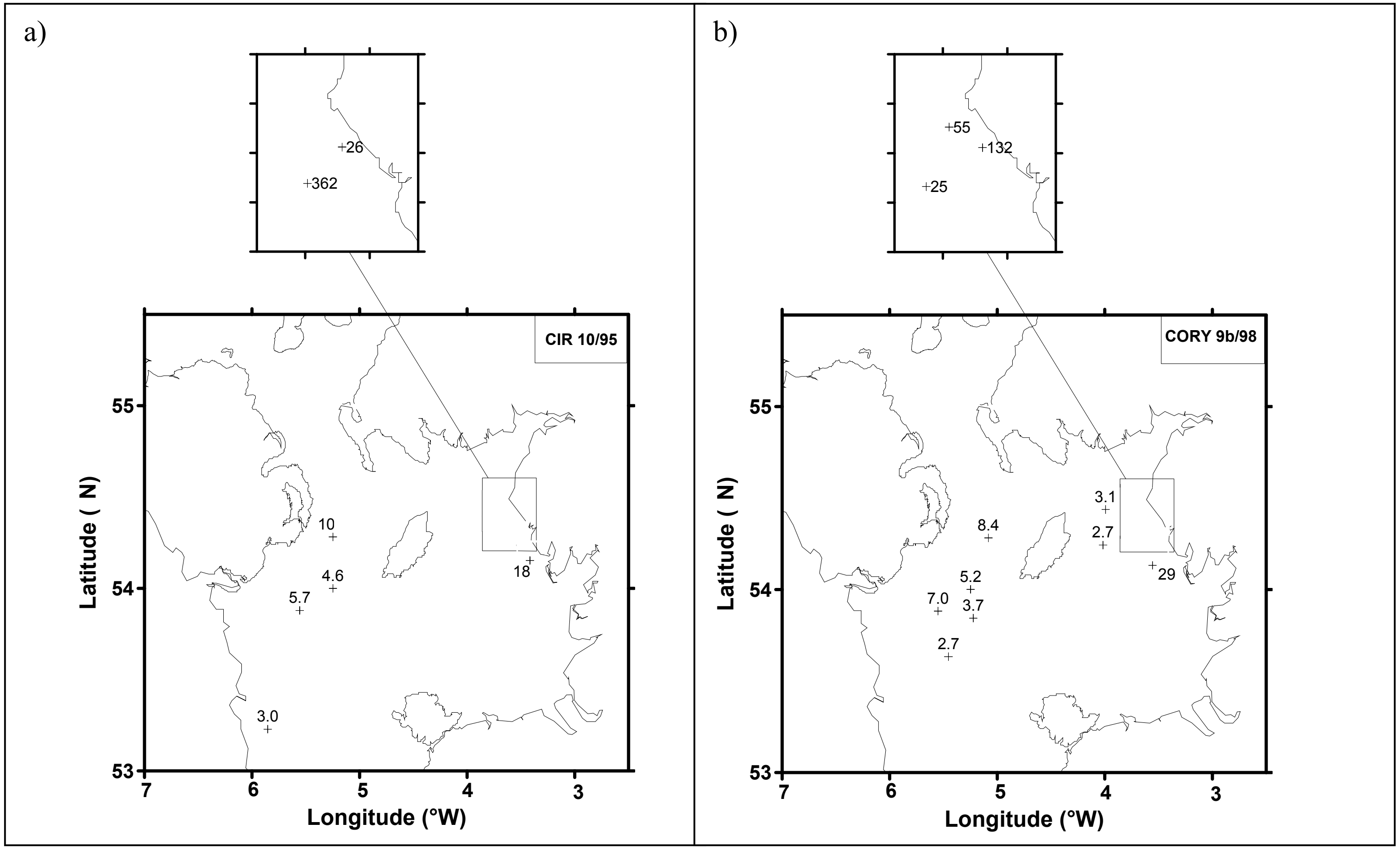
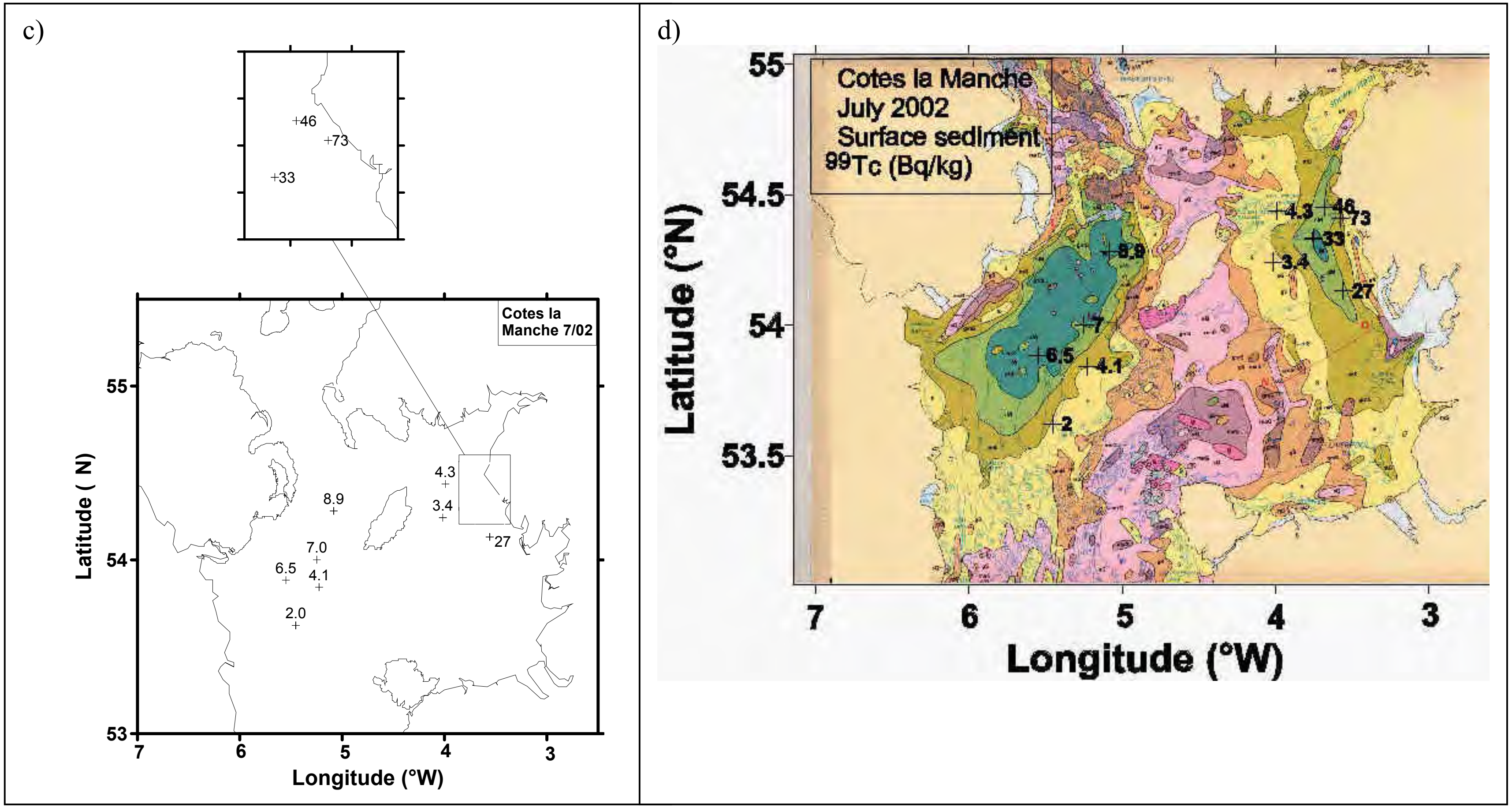


Figure 2. (continued)



The ^{99}Tc levels measured in surficial sediment samples in July 2002 (Survey: Cotes la Manche 7/02) were in the range 3-73 Bq/kg in the eastern Irish Sea and 2-9 Bq/kg in the western Irish Sea (Fig. 2c). These values are broadly comparable with those observed on previous surveys. Levels in the eastern Irish Sea were in the range 18-362 Bq/kg and 3-132 Bq/kg in December 1995 (Survey: Cir 10/95; Fig. 2a) and September 1998 (Survey: Cory 9b/98; Fig. 2b), respectively. In the western Irish Sea the range was 3-10 Bq/kg in December 1995 and 3-8 Bq/kg in September 1998.

The three most striking features of the data in Figs. 2a-2c are:

(i) The greatest concentrations (>20 Bq/kg) were observed at the sites closest to the Cumbrian coastline and within 30 km of the Sellafield pipeline;

(ii) Low concentrations (<4.3 Bq/kg) were observed at the two sites in the eastern Irish Sea sampled in September 1998 and July 2002, midway between the Cumbrian coastline and the Isle of Man. Levels were measurably greater at three of the five sites west of the Isle of Man, despite that concentrations in the water column were higher (by 3-4) fold in the eastern Irish Sea. The disparity coincides with differences in sediment composition between the two areas (Fig. 2d);

(iii) The similarity in levels at equivalent sampling sites between the three surveys (Table 1), albeit based on a limited amount of data and excluding two apparent outliers from the December 1995 survey along the Cumbrian coastline. This consistency contrasts sharply with the marked variation in concentrations of dissolved ^{99}Tc between individual surveys (see Fig. 6b).

Table 1. *Temporal variation in ^{99}Tc concentrations on surficial sediment, for samples collected from the Irish Sea between December 1995 and July 2002. Data taken from Figs. 2a-2c.*

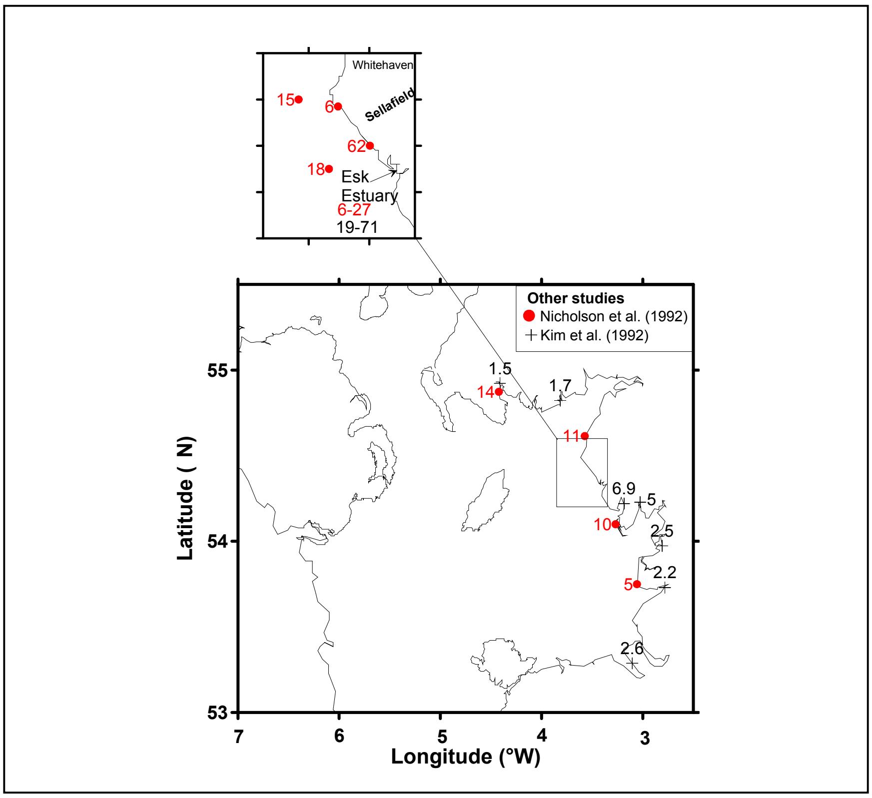
Sea Area	Latitude (N)	Longitude (W)	^{99}Tc on surficial sediment (Bq/kg, dry weight)		
			Dec. 1995	Sept. 1998	July 2002
Cumb. coast	54° 24.7’	3° 35.1’	26	132	73
Cumb. coast	54° 27.2’	3° 40.8’	_	55	46
Cumb. coast	54° 20.3’	3° 41.6’	362	25	33
Cumb. coast	54° 9.1’	3° 25.0’	18	29	27
East Irish Sea	54 ° 26.2’	3° 59.6’	_	3.1	4.3
East Irish Sea	54° 14.6’	4° 1.0’		2.7	3.4
West Irish Sea	54° 0.1’	5° 14.9’	4.6	5.2	7.0
West Irish Sea	53° 52.9’	5° 33.1’	5.7	7.0	6.5
West Irish Sea	53° 50.6’	5° 13.4’	_	3.7	4.1
West Irish Sea	53° 38.0’	5° 27.2’	_	2.7	2.0

Values shaded in grey are apparent outliers

The amount of field data reported in the literature, with which to compare the values in Table 1, is extremely sparse. In part, this is due to the difficulties in undertaking the analysis of ^{99}Tc (Holm, 1993). Furthermore, prior to the enhanced post-EARP discharges, other radionuclides with greater radiological significance than ^{99}Tc were studied as a matter of priority. Aside from the results presented here, ^{99}Tc Irish Sea sediment data appear to be restricted to two pre-EARP surveys carried out in the late 1980’s (Kim et al., 1992;

Nicholson et al., 1992). The information contained in these two reports has been collated and is provided in Fig. 3.

Figure 3. *Literature data for* ^{99}*Tc (Bq/kg, dry weight) in Irish Sea surface sediments sampled between 1984 and 1989, prior to commissioning of the Sellafield EARP plant.*



The literature data (Fig. 3) are almost entirely restricted to results for intertidal sediments. From a survey carried out in July 1988, levels in coastal sediments were reported to be in the range 1.5-6.9 Bq/kg (Kim et al., 1992). A considerably higher concentration (~71 Bq/kg) was observed in estuarine mud from the River Mite. A broadly similar range of values were reported by Nicholson et al. (1992) for a survey carried out in October 1989, albeit that their values for coastal sediments tended to be greater than those observed by Kim et al. (1992). They also observed an enhanced concentration (~ 3 fold) on silt material, compared with sand, in the Ravenglass estuary. It is, however, noticeable that the greatest concentration (62 Bq/kg) was observed closest to the point of discharge.

Results for offshore sediments are restricted to just two samples collected in 1984/1985 close to the Sellafield pipeline (within 15 km), over areas of sandy mud (Nicholson et al., 1992). Levels in both samples were very similar (15-18 Bq/kg) and are lower, by ~ 3 fold, compared with those observed at similar sites in July 2002.

3.1.3 Grain-size distribution

Additional surface sediment samples were collected from the vicinity of Whitehaven Harbour, to assess the influence of particle size upon ^{99}Tc sorption behaviour. Sediment in the Outer Harbour is predominantly sand with mean particle diameter predominantly (> 80 %) in the range 100-500 µm. The composition of the small patch of boulder clay, exposed at low tide, differs markedly from the surrounding sand (proportion of particles with mean diameter <100 µm is >90 % and <10 % for clay and sand, respectively). Sediment from the beach immediately to the south of the Harbour is considerably coarser (~99 % > 500 µm). Results for radionuclide concentrations in these samples, and on grain-size spilts, are given in Table 2.

Table 2. *Impact of grain-size upon ^{99}Tc concentrations on surficial sediment samples collected in the vicinity of Whitehaven Harbour in July 2002.*

Sample (1)	Radionuclide concentration (Bq/kg, dry weight)			
	^{99}Tc	^{40}K	^{137}Cs	^{241}Am
>500 µm sand	1.6	719	828	106
200-500 µm sand	11.6	473	296	296
100-200 µm sand	8.4	201	134	148
Boulder clay	5.6	890	2300	99
Sand surrounding clay (2)	5.2	543	269	173
Coarse beach sediment	<0.4	686	19	6.2

(1) All samples collected from Whitehaven Outer Harbour, with the exception of coarse beach sediment

(2) This sand sample collected ~100 m apart from material used for grain-size fractionation

Data for ^{99}Tc in individual grain-size fractions indicates the greatest concentration (11.6 Bq/kg) was observed in intermediate 200-500 µm material. The concentration in the finer 100-200 µm fraction (8.4 Bq/kg) was slightly less (by ~ 30 %), whilst that in the coarsest fraction (> 500 µm) was markedly lower (by ~ 7 fold). Levels in the fine grained boulder clay and the much coarser surrounding sand were remarkably similar. This limited body of data indicates grain-size is not a major factor in governing ^{99}Tc sorption behaviour. Finally, it is worth noting that levels in all samples were more than an order of magnitude less than the ^{99}Tc concentration observed on suspended particulate material (164 Bq/kg) from this location (see Table 4).

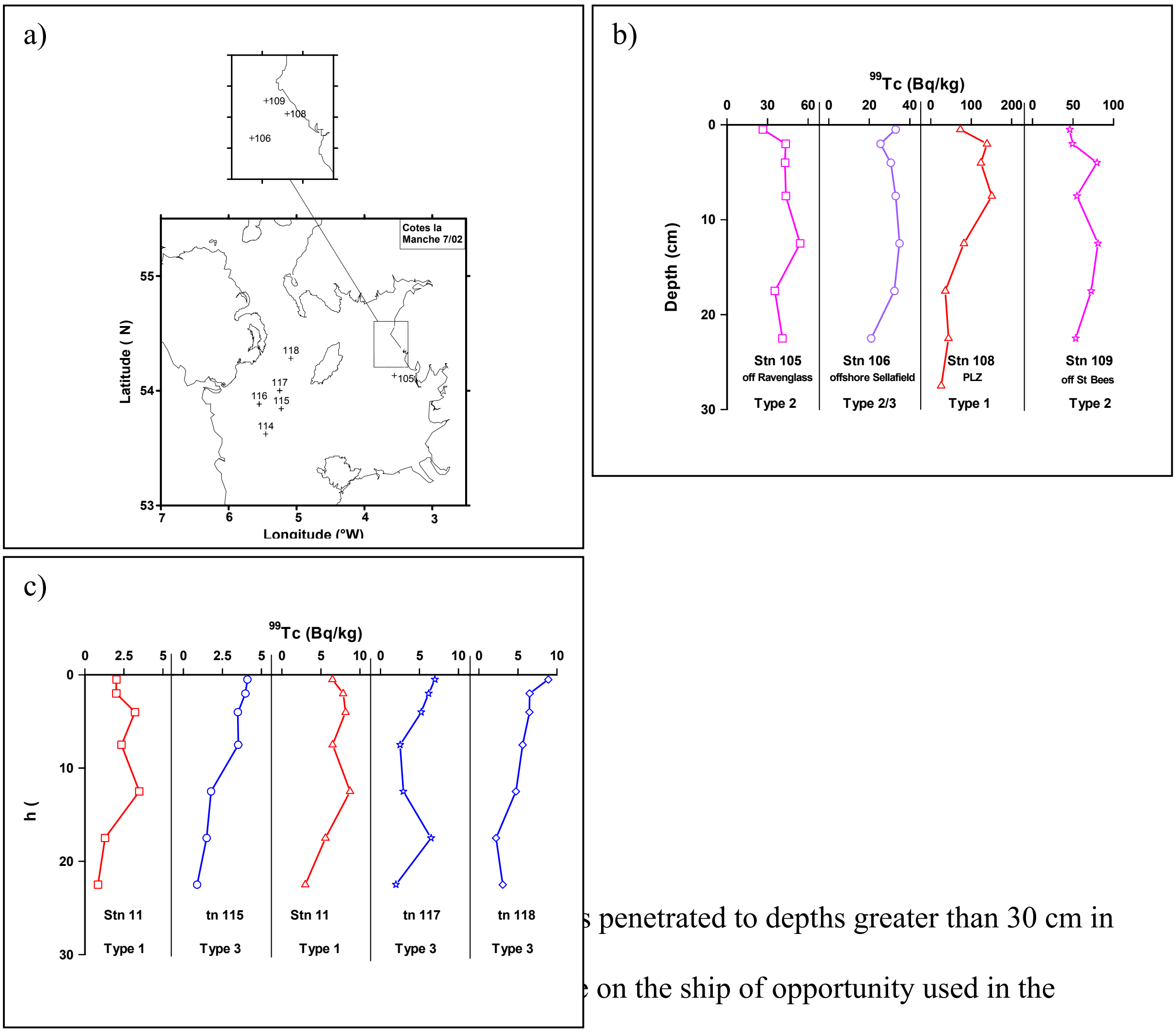
By comparison, concentration data for the other radionuclides indicate patterns of behaviour which are different to that observed for ^{99}Tc. ^{40}K and ^{137}Cs concentrations in the grain-size splits were greatest in the coarsest material and least in the finest (100-200 μm) fraction. Levels in boulder clay were measurably greater than that in the surrounding sand, most notably for ^{137}Cs. The ^{241}Am data indicate a bimodal distribution between the different grain-size fractions. The highest concentration (296 Bq/kg) was observed in the intermediate grain fraction (200-500 μm). Levels in the finer and coarser fractions were lower by ~2 and ~3 fold, respectively. Although the ^{241}Am grain-size distribution bears some resemblance to that observed for ^{99}Tc, the disparity between levels in individual fractions is significantly different. Finally, levels of ^{241}Am in boulder clay were measurably less than that in the surrounding sand. Overall these data illustrate that the uptake by sediment differs between individual radionuclides, presumably as a result of variation in their elemental chemical properties.

3.1.4 Sediment core profiles

Data for the ^{99}Tc depth distribution down sediment cores collected on our July 2002 survey (Cotes la Manche 7/02) are given in Figs. 4a – 4c. These data substantiate the preliminary findings from a previous project (FSA, 2001) of ^{99}Tc accumulation in subsurface Irish Sea sediments.

Figure 4. *Vertical distribution of ^{99}Tc (Bq/kg dry weight) down sediment cores from the Irish Sea in July 2002 (Survey: Cotes la Manche 7/02). a) location of sampling sites.*

Values are ship's station number, b) profiles in eastern Irish Sea, c) profiles in western Irish Sea.

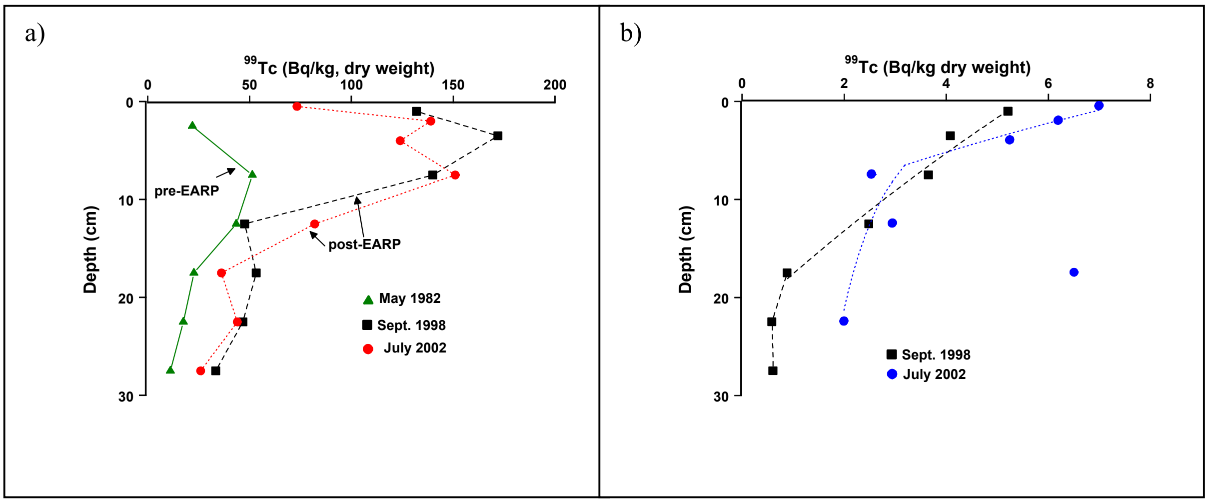


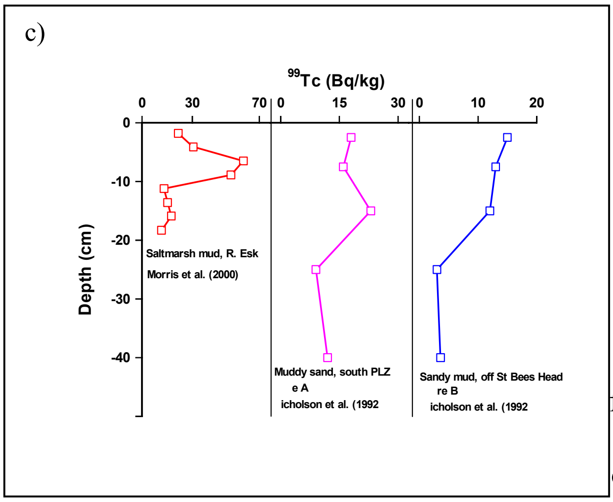
s penetrated to depths greater than 30 cm in on the ship of opportunity used in the present study did not allow deeper sampling of cores to determine the limit of ^{99}Tc penetration. Further observations are required, using an alternative coring device, to quantify ^{99}Tc contamination deeper in the seabed. The available data indicate significant variation between individual ^{99}Tc profiles. To facilitate interpretation they have been classified into three principal types. Type 1 profiles, exhibited a pronounced subsurface maximum. These were observed at Station 108 in the vicinity of the Sellafield pipeline and at Stations 114 and 116, the two most westerly sampling stations to the south-west of the Isle of Man. Concentrations in sub-surface sediment reached levels up to twice those observed in surficial sediment. Subsequently, below ~ 15 cm, there followed a marked decrease in levels down to about half those observed at the surface. Type 2 profiles also exhibited greater concentrations in subsurface sediment compared to those observed in surficial material. In contrast to the Type 1 profile, it was not possible, within the inevitable scatter in the data, to discern a subsequent decrease at the deeper levels. Type 2 profiles were observed at Stations 105 and 109 in the eastern Irish Sea close to the Cumbrian coastline. These would represent key sites to carry out further sampling in future work to determine the extent of ^{99}Tc penetration. Type 3 profiles exhibited a decrease in concentration with depth from the surface. These were observed at Stations 115, 117 and 118 in the western Irish Sea. By our simple classification system, the profile at Station 106 offshore from Sellafield in the eastern Irish Sea was intermediate between Type 2 and Type 3. It is somewhat surprising that it is the only one in the eastern sector that does not display an apparent near sub-surface maximum, but that the concentration is relatively uniform down the core.

Results for two selected sites are compared with the available historic CEFAS data (from surveys carried in May 1982 (Survey: Cir 5/82) and September 1998 (Survey: Cory 9b/98)) to assess the magnitude of temporal variability in ^{99}Tc core profiles (Figs. 5a and 5b). For completeness, the remaining data reported in the literature is collated in Fig. 5c.

Figure 5. *Comparison of ^{99}Tc sediment core profiles in July 2002 with historic data. a) off Sellafield pipeline. Results for May 1982 taken from Harvey and Kershaw (1984), b)*

western Irish Sea (Station 117), c) Literature data compiled from results in Nicholson et al. (1992) and Morris et al. (2000).





f the ^{99}Tc sediment concentrations off the ore varied markedly between the pre-EARP sample (May 1982) and those collected post-EARP in September 1998 and July 2002. Levels post-EARP were significantly greater (typically by ~ 3 fold) compared with those observed pre-EARP. The CEFAS pre-EARP results are corroborated by the data of Nicholson et al. (1992) who observed levels in the range 9 - 23 Bq kg throughout two cores collected within 15 km of the Sellafield pipeline in 1984/85 (Fig. 5c).

Subsurface maxima were apparent in all three cores collected off the Sellafield pipeline, albeit that the exact distribution was slightly variable (Fig. 5a). The pre-EARP data indicate that the greatest concentration occurred in the 5-15 cm section. The ^{99}Tc concentration in the surficial sediment (0-5 cm section) was ~½ that in the immediate underlying sediment between 5 cm and 15 cm. Below 15 cm there was a step change in ^{99}Tc concentrations (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. The dashed line in Fig. 5a illustrates that below a depth of 10 cm there was a step decrease in ^{99}Tc concentrations (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 sub-surface maxima appeared to be somewhat broader than that observed in September 1998, consistent with downward migration of contaminated sediment in the intervening period. It is also noticeable that the concentration on surficial sediment in July 2002 was ~½ that observed in September 1998, possibly as a result of redissolution processes.

In contrast to the behaviour observed in the eastern Irish Sea, the ^{99}Tc profile in the core obtained from the western Irish Sea (September 1998) exhibited an exponential decrease (by ~ 9 fold) in concentration with depth from 5.2 Bq/kg at the surface to ~0.6 Bq/kg at 30 cm (Fig. 7b). With the exception of a single anomalous value for the 15-20 cm section, a similar pattern of behaviour was observed for the core collected in July 2002, albeit with increases in levels of ~ 1.5 Bq/kg throughout.

Perhaps the most detailed information in the literature is provided by cores collected from salt marshes in the Solway Firth in 1986 (McCartney and Rajendran, 1999) and the Ravenglass Estuary in 1993 (Morris et al., 2000), where supplementary radionuclide data are reported. Results from the latter are shown in Fig. 5c. The ^{99}Tc distribution resembled that for ^{137}Cs with a broad sub-surface maximum (Morris et al., 2000). The ^{99}Tc distribution was interpreted as being reasonably consistent with the known and estimated ^{99}Tc releases from Sellafield, which, at this particular site, is seen when an element has a high particle affinity (e.g. Pu and Am). It was suggested that following rapid uptake by sedimentary material on release from Sellafield, the radiolabelled particles were transported tidally and incorporated into the salt marsh sediment as accretion occurs. Within the resolution of the core sections, it was not possible to detect evidence of post-depositional uptake or remobilisation over a period of 20 years. ^{99}Tc concentrations in the Solway Firth ranged from 1.6-19.3 Bq/kg (McCartney and Rajendran, 1999) and were, therefore, lower than those in the Ravenglass. The maximum concentration was observed at a depth of 30-35cm which, assuming a sediment accumulation rate of ~6.5 cm/annum (McCartney and Rajendran, 1999), corresponds to deposition around 1981. The deposition was suggested to be associated with the relatively large discharges from Sellafield in 1978, indicating sediment transport from Sellafield to the Solway Firth takes ~ 3 years. The decrease in ^{99}Tc levels in the sediment in the subsequent period up to 1986 (19.3 to 2-9 Bq/kg) were noted to be rather small compared with the very large reduction in discharges (180 to 4-6 TBq) over the same period. As for the other artificial radionuclides studied in this core, it was suggested that ^{99}Tc transport to the Solway Firth dominantly involves on-shore movement of contaminated marine sediment. The ^{99}Tc levels in the lower sections of the sediment core were generally much lower than the peak level corresponding with the 1978 releases, albeit that there was a secondary peak of 15.3 Bq/kg at 70-75 cm.

3.1.5 Distribution of ^{99}Tc in surface seawater

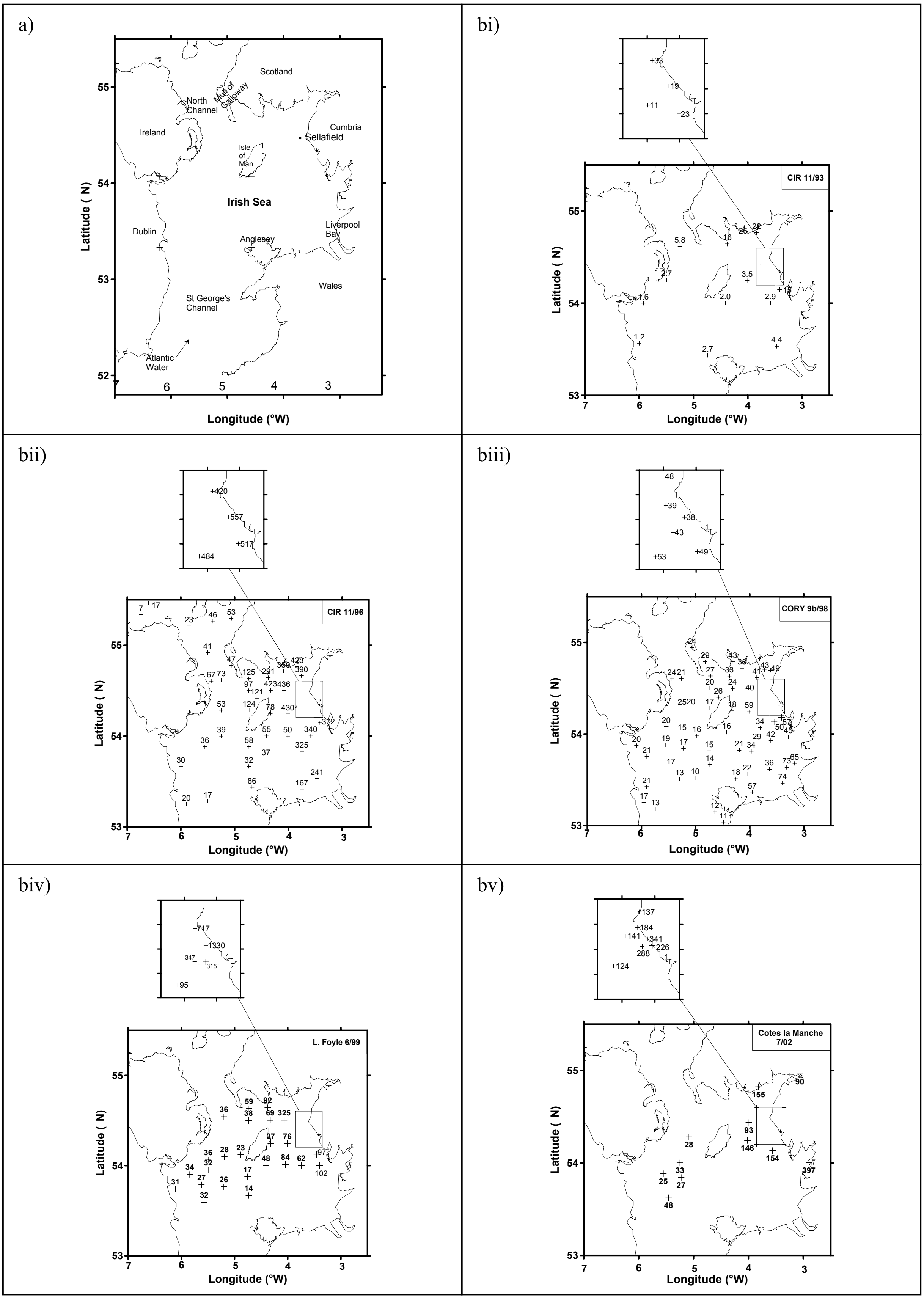
A location map for the Irish Sea is given in Fig. 6a. Distribution maps showing the activity of ^{99}Tc in the surface water samples of the Irish Sea are presented in Fig. 6b. In addition to data obtained in the present study, results are also shown for the December 1993 pre-EARP survey (Cir 11/93) and post-EARP surveys in December 1996 (Cir 11/96), September 1998 (Cory 9b/98) and June 1999 (L. Foyle 6/99). These data (up to June 1999) have been reported in the open literature, in papers subject to peer review (Leonard et al., 1997; McCubbin et al., 2002a; Leonard et al., 2004) and are valuable to compare and contrast with results from the present investigation. The average concentration close to the Sellafield pipeline in July 2002 was ~290 mBq/l. This is considerably less (by ~ 5 fold) than the maximum concentration of 1330 mBq/l observed in June 1999 (Lough Foyle 6/99), but more than order of magnitude greater than the pre-EARP value of ~20 mBq/l observed in December 1993 (Survey: Cir 11/93). It is worth noting that relatively low concentrations close to Sellafield (~40 mBq/l) were observed on the post-EARP survey carried out in September 1998 (Cory 9b/98), as a result of greatly reduced discharges for the six months preceding the September 1998 (Cor 9b/98) survey. Overall, these data provide some illustration of the response of the water body in the vicinity of Sellafield to fluctuations in the monthly ^{99}Tc discharges.

In the western Irish Sea and to the south of the Isle of Man, the average ^{99}Tc seawater concentration in July 2002 was ~33 mBq/l compared with values in the range 13-47 mBq/l for surveys between December 1996 and June 1999. The relatively small variation (~3 fold) indicates that, away from the immediate vicinity of Sellafield, the impact of the fluctuations in the discharge pattern was progressively less marked. The distinct peaks in the pattern of monthly discharges (Fig. 1b) are smoothed at locations distant from

Sellafield because: i) the complex hydrographic transport patterns in the Irish Sea mean individual ^{99}Tc pulses are dispersed to a variable degree before arriving at distant locations (McCubbin et al., 2002a) and ii) the residence half-time of water in the western Irish Sea is relatively long (~5½ months) (Jefferies et al., 1982).

To assess what effect continued ^{99}Tc discharges are likely to have on concentrations in the waters of the Irish Sea, the data in Figs. 1 and 6 have been used to derive Normalised Activity Concentrations for ^{99}Tc in seawater in the vicinity of Sellafield -that is the ^{99}Tc seawater concentration normalised to a unit rate of discharge (Table 3).

Figure 6. *Location and position maps of the ^{99}Tc distribution in the Irish Sea together with sampling positions and concentrations (mBq/l) in surface seawater. a) Location map. b) ^{99}Tc survey data.*



NACs are expressed in units of Bq/l per TBq/day discharge. NAC values for ^{137}Cs in seawater have been derived simplistically (Jefferies et al., 1982) by dividing seawater concentrations by the mean discharge rate in the month of sampling and the previous month. This method is appropriate under conditions where the discharges have remained fairly uniform compared with the time for environmental equilibrium to be achieved. However, discharges of ^{99}Tc were highly non-uniform. Consequently, an adaptation of the moving-average model used to assess timescales for the dilution and dispersion of transuranics in the Irish Sea (Hunt, 1985) has been applied to derive NAC values for ^{99}Tc:

$$C_{average} \sim [NAC] \text{ x 'Effective Discharge'} \qquad \text{(Eq. 1)}$$

where $C_{average}$ is the average ^{99}Tc seawater concentration derived from individual analyses of samples from stations in vicinity of Sellafield at any given time. The 'Effective Discharge' (TBq/day) was derived from monthly Sellafield discharge data (Fig. 1b) using the equation:

$$\text{'Effective Discharge'} = \{D_m + 2^{(-1)} D_{m-1} + ... + 2^{(-8)} D_{m-8}\} / \{1 + 2^{(-1)} + ... 2^{(-8)}\text{) x } (1/30.5) \qquad \text{(Eq. 2)}$$

where D_m = monthly discharge (TBq) at time of sampling and $D_{m-1}...D_{m-8}$ are discharges in the months preceding sampling. The factor (1/30.5) converts monthly discharge data to an average value for daily discharge. The factor $2^{(-n)}$, allowing for the effect of discharges n months preceding sampling, was selected from information that the residence half-time of water in the Cumbrian coastal region is ~1 month (Jefferies et al., 1982).

Table 3. *Normalised activity concentrations (NACs) for dissolved ^{99}Tc in the vicinity of Sellafield.*

Time of Survey	Name of survey	Average ^{99}Tc seawater concentration in Sellafield area (mBq/l)	‘Effective’ ^{99}Tc discharge (TBq/day)	NAC (Bq/l per TBq/day discharge)
December 1993	Cir 11/93	24	0.019	1.3
December 1996	Cir 11/96	509	0.199	2.6
June 1998	Lough Foyle 6/98	103	0.030	3.5
September 1998	Cor 9b/98	40	0.005	7.9
June 1999	Lough Foyle 6/99	677	0.232	2.9
July 2002	Cotes la Manche 7/02	224	0.070	3.2

(1) Sellafield area arbitrarily defined as being within 15 km of the point of discharge, comparable to the long-shore tidal excursion in the region

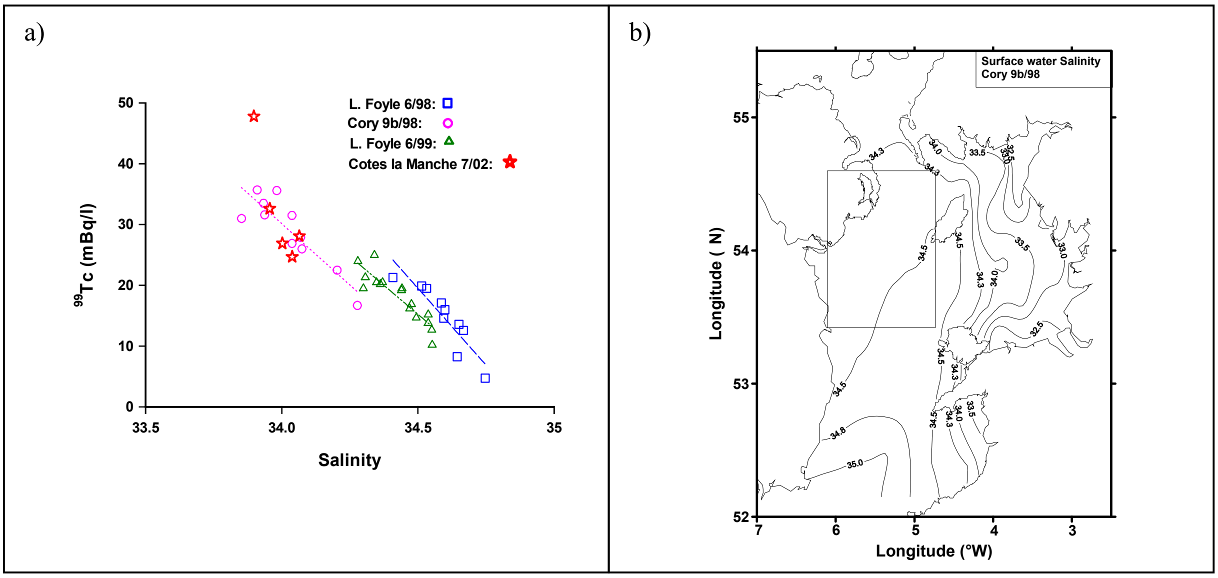
NAC values for ^{99}Tc, derived from the surveys carried out in December 1993, December 1996, June 1999 and July 2002, were in the order of 2-3 Bq/l per TBq/day discharge and of similar magnitude to that derived for ^{137}Cs in the Cumbrian coastal area (1.6 Bq/l per TBq/day discharge; Jefferies et al., 1982).

Data from recent observational and modelling studies (Brown and Gmitrowicz, 1995; Knight and Howarth, 1999; Young et al., 2000) indicate that considerable short-term (on timescales of days) variability occurs in Irish Sea water circulation patterns, largely driven by the prevailing meteorological conditions. For example, large wind stresses in February

1994 resulted in the equivalent of 34% of the volume of the Irish Sea exiting the North Channel in a single month (Knight and Howarth, 1999). Variability in the rate of dilution and dispersion of ^{99}Tc discharged into the Irish Sea is, therefore, to be expected and modelling the survey data in terms of a constant water residence time to derive NAC values is extremely simplistic. This is illustrated by the significantly greater NAC value for the survey carried out in September 1998 (Cor 9b/98). The most likely explanation is that there was an unusually large residual impact of the large ^{99}Tc discharges in the early months of 1998 (Fig. 1b) as a result of water flow patterns prior to sampling. Despite its limitations, the pragmatic and readily understood NAC approach provides a ballpark figure for assessing the impact of any future change in discharge practices upon seawater concentrations. The results may be extrapolated to predict levels in seafood using species specific equilibrium biological concentration factors (IAEA, 1985).

In addition to using the data in Fig. 6b to derive NAC values, a plot of dissolved ^{99}Tc versus salinity was made to establish the relationship between these two variables in the western Irish Sea away from the influence of varying discharges from Sellafield (Fig. 7).

Figure 7. *Correlation between salinity and dissolved ^{99}Tc in surface waters of the western Irish Sea. a) Survey data (Cotes la Manche 7/02). Results from Lough Foyle 6/98, 6/99 and Cory 9b/98 surveys also given for comparative purposes. Lines represent linear regression fits to seawater data. b) Box to indicate area of sampling stations used for salinity plot in Fig. 3a (Latitudes 53° 25'-54°36'N and 4°44'-6°6'W). Figure also shows typical salinity contour map (data taken from Cory 9b/98 survey).*



The data in Fig. 7a indicate that ^{99}Tc concentrations were inversely related to the water salinity. The slope of the linear regression lines for the three surveys preceding that undertaken for the present investigation were similar, within experimental error. The intercept on the x (salinity) axis was, however, slightly different for each survey, ranging from 34.76‰ in June 1999 (L. Foyle 6/99) up to 34.94‰ in September 1998 (Cory 9b/98). These data indicate a greater incursion of more saline water into the western Irish Sea in June and September 1998 compared to that observed in June 1999. With the exception of one outlying value, results from the present Cote la Manche 7/02 survey fit closely to the Lough Foyle 6/99 regression line. Overall, this pattern of behaviour indicates that differences in ^{99}Tc concentrations in the western Irish Sea are probably related to variable degrees of mixing between radionuclide-poor/saline-rich water entering the western Irish

Sea via St Georges channel (Fig 7b) or the North Channel with radionuclide-rich/saline-poor water emerging from the eastern Irish Sea.

3.1.6 ^{99}Tc K_d values

Partitioning of radionuclides between liquid and solid phases is often expressed in terms of K_d values whereby:

K_d = Concentration on sedimentary material /Concentration in dissolved phase.

The concentration on sedimentary material usually refers to suspended particulate material. Data for dissolved ^{99}Tc, and on particulate material suspended in the water column are given in Table 4. These results were used to calculate K_d values and they are also included in Table 4.

Table 4. *^{99}Tc K_d values, calculated from measurements of concentrations on suspended particulate material and the dissolved phase. Surface seawater samples collected from the Irish Sea in July 2002 (Survey: Cotes la Manche 7/02). Dissolved ^{99}Tc data taken from Fig. 6b.*

Ship's station number (1)	Location	Dissolved ^{99}Tc (mBq/kg)	^{99}Tc on suspended particles (Bq/kg)	K_d
108	Sellafield pipeline 1	288	546	1.9×10^3
112	Sellafield pipeline 2	264	87 (2)	3.3×10^2 (2)
117	Western Irish Sea	33	108	1.2×10^3
Shoreline sample	Whitehaven Harbour	137	164	1.9×10^3

(1) Station 108: 54° 24.65'N 3° 34.62' W

Station 112: 54° 23.99'N 3° 35.01' W

Station 117: 54° 0.06'N 5° 14.90'W

(2) Sample collected in middle of plankton bloom

^{99}Tc concentrations on suspended particles ranged from 87-546 Bq/kg. It is worth noting that whilst sampling was being carried out, a discrete phytoplankton bloom was present in the Irish Sea, as evident by well defined patches of red material at the seawater surface. Although most samples were collected away from the bloom, a sample of plankton material was collected close to the Sellafield pipeline (Station 112) using a portable surface pump, as opposed to the ship's supply which pumped water from ~ two metres beneath the surface. The results in Table 4 indicate that the concentration of dissolved ^{99}Tc in the two separate samples collected close to the Sellafield pipeline was remarkably similar. However, levels on suspended particulate material in these two samples varied considerably. The concentration in the sample largely composed of plankton material (87 Bq/kg) was less (by ~ 6 fold) compared with that on suspended particles collected away from the plankton bloom. The disparity provides an indication of the importance of particle composition towards uptake of ^{99}Tc in the marine environment, albeit that the two samples may represent extreme conditions. Associated K_d values ranged from 3.3×10^2 to 3.3×10^3. The lowest K_d value was derived for the sample collected from the plankton bloom.

3.2 Laboratory experiments

As mentioned in the introduction, laboratory experiments were carried out to compliment the information derived from environmental survey data, concerning the potential impact of remobilisation processes upon the fate of ^{99}Tc bound to sedimentary material in the Irish. At the outset it was recognised that, in order to facilitate the extrapolation of laboratory data to predict environmental behaviour, the experimental conditions should be as close as practical to those pertaining in Irish Sea coastal waters. The ideal experiments for this purpose would involve study of the rate and extent of release of ambient ^{99}Tc from 'contaminated' surficial Irish Sea sediment into 'uncontaminated' seawater, along the lines of those carried out to study remobilisation of $^{239+240}$Pu (McCubbin et al., 2002b). Unfortunately, preliminary calculations did not indicate this to be a practical proposition. Therefore, for purely logistical reasons, radiotracer sorption experiments were carried out to prepare sedimentary material labelled with ^{99}Tc for subsequent desorption experiments. The results from the sorption experiments are presented here as they provide useful ancillary information towards interpreting the desorption data.

3.2.1 ^{99}Tc sorption by sediment from seawater

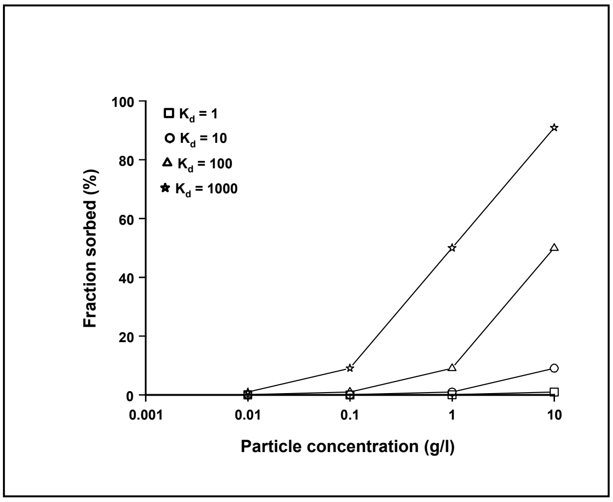
3.2.1.1 Calculations regarding experimental design

The uptake of radionuclides onto sedimentary material in laboratory experiments is dependent upon both the particle concentration and the partition coefficient K_d, Eq. 3 (McCubbin et al., 2002b).

$$\%_{sorption} = 100 \text{ x } \{1\text{-}1/[1 + (K_d \text{ x } P_c/10^3)]\} \qquad \text{(Eq. 3)}$$

where $\%_{sorption}$ is the extent of radiotracer uptake by sediment particles at steady-state and P_c is the experimental particle concentration in g/l. The concentration of suspended particulate material in the water column of the Irish Sea generally lies within the range 1-10 mg/l (i.e. 0.001-0.01 g/l; Kershaw et al., 1992), although significantly greater loadings may occur in shoreline waters. The IAEA recommends a mean K_d for Tc of 100 for both pelagic clays and coastal sediments with a minimum value of 10 and a maximum of 1000 (IAEA, 1985). Results from calculations to assess likely uptake by sediment as a function of K_d and particle concentration, under experimental conditions simulating offshore and shoreline waters, are given in Fig. 8.

Figure 8. *Variation in ^{99}Tc uptake by sedimentary material as a function of suspended particle concentration and K_d. Note logarithmic scale of x axis. Fraction sorbed calculated using Eq. 3.*



The results in Fig. 8 indicate that, using a particle concentration of 0.01 g/l, the percentage likely to bind to sediment is very small (<1 %), even using the maximum recommended K_d value. Extensive uptake (> 50 %) is only predicted to occur if particle concentrations are in excess of 1 g/l and K_d is in excess of 100. Particle loadings of > 0.1 g/l were, therefore, used in subsequent experiments, despite that these concentrations are considerably greater than those typically found in the water column of the Irish Sea.

3.2.1.2 Other considerations

Possible mechanisms by which ^{99}Tc remobilisation may occur include:

(i) loss from the seabed by diffusion or advective processes from interstitial waters to overlying waters;

(ii) desorption from surficial seabed sediment or suspended particulate material due to re-equilibration between solution and particulate phases (i.e. re-partitioning by the law of mass action, K_d);

(iii) reaction of sorbed Tc species to produce a less particle reactive form, followed by subsequent desorption of the latter more soluble form.

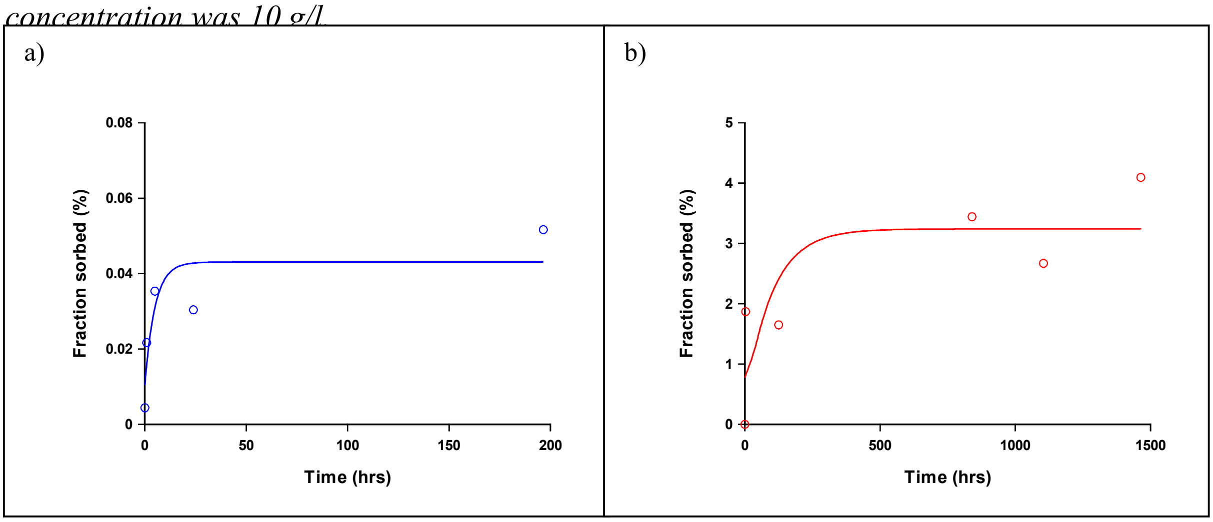
To inform the experimental design, a literature search was carried out to assess which processes appear to control the release of radionuclides other than ^{99}Tc from contaminated sediment in the Irish Sea. An extensive body of information is now available concerning the distribution of Pu radionuclides and ^{241}Am in the water column and sediments (Kershaw et al., 1999; Leonard et al., 1999). Latter day discharges of these nuclides are about two orders of magnitude less than in the period of peak discharges in the late 1970s. The elapsed time has allowed a significant proportion of the total Pu and Am activity in the sub-tidal sediments to be mixed to depths greater than 5 cm with traces of activity at depths greater than 71 cm (Woodhead and Pentreath, 1992). Migration through pore water by chemical diffusion or advection is considered to be exceedingly slow (e.g. a 10 % concentration front of $^{239+240}$Pu has been estimated to progress no more than 0.1 cm in 10 years by the diffusion mechanism; Nelson and Lovett, 1981). Therefore, dissolution of Pu radionuclides and ^{241}Am from surficial sediment surface or resuspended particles is likely to be a more important remobilisation mechanism.

Sediments in the Irish Sea have some capacity to be anoxic, although oxic conditions tend to be confined to the top ~5 cm (Malcolm et al., 1990). Assuming similar considerations for Pu radionuclides and ^{241}Am (as outline above), apply to ^{99}Tc, it was concluded that experimental effort in this study should initially be directed towards assessing remobilisation of ^{99}Tc under oxic conditions to simulate those found in surficial sediments of the Irish Sea.

3.2.1.3 ^{99}Tc uptake by oxic sediment

Several experiments were carried out in an attempt to label oxic marine sediment with ^{99}Tc, for use in subsequent experiments to study remobilisation behaviour, using particle concentrations in the range 0.1-10 g/l. Results for uptake with time are given in Fig. 9.

Figure 9. *Uptake of ^{99}Tc tracer from seawater onto oxic sediment with time. Curves represent lines of best fit to model of exponential growth to asymptotic plateau, to qualitatively assist trend identification. a) Sediment concentration was 0.1 g/l, b) Sediment concentration was 10 g/l.*



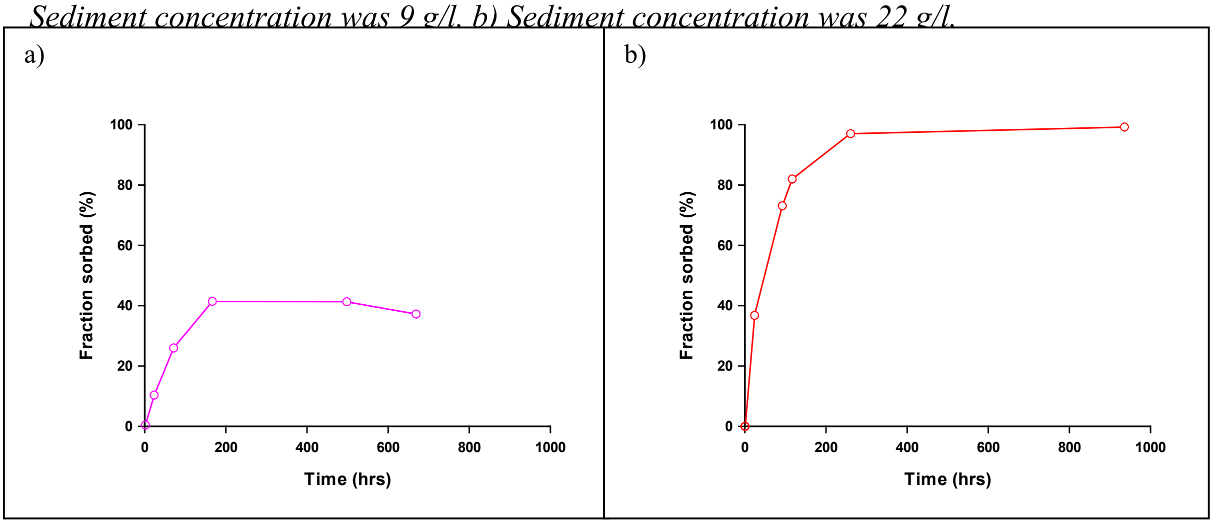
The data in Fig. 9a indicate that, using a sediment concentration of 0.1 g/l, uptake was extremely low (< 0.1 % uptake at the end of the experiment). The small amount of sorption that did occur was rapid (within 5 hours).

In an attempt to produce a source of labelled sediment containing sufficient ^{99}Tc to measure desorption behaviour, the experiment was repeated using a considerably greater sediment concentration (10 g/l). The results are provided in Fig. 9b. The extent of uptake measurably increased concomitant with particle concentration (sorption after ~ 1460 hours or 60 days was ~4 %), although the majority (> 95 %) of the ^{99}Tc tracer still remained in the dissolved phase. The notable data variability, as indicated by the range in sorption values over the period 840 hours (35 days) until the end of the experiment where estimates of uptake varied from 2.7 % - 4.1 %, is perhaps unsurprising given that the extent of sorption was small. The average amount of ^{99}Tc bound to sediment between 840 hours and 1464 hours was 3.4±0.7 % (i.e. the standard error associated with the average value was ~20 %). It is difficult to unequivocally identify temporal trends in the sorption behaviour as a result of data variability, although uptake after 840 hours (35 days) did appear to be greater (almost double) that after 125 hours (~ 5 days). Necessarily it is difficult to assess whether a steady-state distribution had been attained between solid and liquid phases at the end of the experiment. However, if it is assumed equilibrium had been attained then the extent of final uptake in both experiments corresponds to a K_d value of ~ 4.

3.2.1.4 ^{99}Tc uptake on anoxic sediment

It has been suggested elsewhere (Masson et al., 1981; Keith-Roach et al., 2003) that ^{99}Tc uptake by sediments can be variable, dependent upon biogeochemical properties. Further experiments were, therefore, carried out using freshly collected highly reducing (deep black colour) subsurface estuarine sediment. Sediment was collected on two separate occasions for this purpose, from the River Blyth estuary at Southwold. The results for uptake with time using each sediment sample are given in Figs. 10a and 10b.

Figure 10. *Uptake of ^{99}Tc tracer from seawater onto anoxic sediment with time. a) Sediment concentration was 9 g/l. b) Sediment concentration was 22 g/l.*



Comparison of the results in Figs. 10a/10b with those in Figs. 9a/9b indicate that uptake using freshly collected anoxic sediment was considerably greater than using oxic sediment.

The data in Fig. 10a indicate ~26 % sorption to sediment after ~72 hours (3 days) and moreover, that uptake occurred in an almost linear manner. Thereafter, the rate of sorption decreased reaching a plateau of ~ 41 % after ~ 167 hours (~ 7 days). This amount of uptake corresponds to an apparent K_d value of ~ 140. At end of experiment, a small but measurable decrease was observed in the fraction bound to sediment (down to ~ 37 % after ~ 660 hours or 28 days). It is worth noting that special precautions (i.e. the use of a nitrogen filled glovebox) are necessary to ensure anoxic sediment does not oxidise upon exposure to air (Malcolm et al., 1990). No attempt was made to prevent oxidation occurring in these experiments. As would be expected the sediment changed in colour from black to brown over the course of this experiment, indicating some change in redox potential had occurred with time. It is possible, therefore, that further uptake may have occurred had the experiments been carried out under consistent redox conditions.

The data in Fig. 10b indicate almost quantitative removal of ^{99}Tc from solution within ~261 hours (~11 days). Once again, to a first approximation, the initial uptake occurred in a linear manner. Normalised to a sediment concentration of 1 g/l, the initial rate of uptake in both experiments was similar (~0.03-0.04 % hr^{-1} g^{-1}).

3.2.2 ^{99}Tc redissolution from sediment into seawater

3.2.2.1 Redissolution from oxic sediment

Uptake onto oxic marine sediment was low (Fig. 9b) and significant uncertainty (standard error of ~ 20 %) was associated with the estimate for final extent of sorption. Nevertheless, an experiment was undertaken to provide an initial assessment of ^{99}Tc desorption behaviour. Results are shown in Fig. 11.

Figure 11. *Redissolution of ^{99}Tc tracer from 'contaminated' oxic sediment, into 'uncontaminated' seawater, with time. Error bars provide an indication of uncertainty associated with individual data points, as a result of uncertainty for initial ^{99}Tc sediment content.*

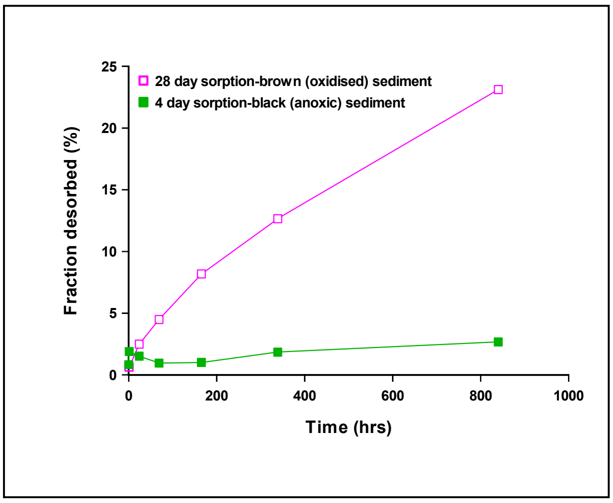
The results in Fig. 11 indicate that almost half the ^{99}Tc activity on the 'contaminated' sediment was eliminated within 48 hours upon exposure to 'uncontaminated' seawater. A small amount of redissolution did occur over a much longer time period and after 646 hours (~27 days), the extent of desorption had increased to ~60 %. As a result of the uncertainty associated with the initial ^{99}Tc content of the labelled sediment, estimates for the final amount of redissolution were variable (in the range 51-77 %).

3.2.2.2 Redissolution from anoxic sediment

Experiments were carried out to assess desorption of ^{99}Tc bound to sediment which was highly reducing at the time of collection. As mentioned previously, no attempt was made to reduce oxidation of reduced phases by carrying out experiments in a nitrogen filled glovebox. By the time the 'contaminated' sediment was resuspended in 'uncontaminated' seawater, it was almost certain that the surficial composition of the sediment particles was different to those at the time of collection as a result of oxidation reactions. It was not, however, possible to assess the impact of this experimental artefact.

Due to the extensive uptake which occurred within a short amount of time, when carrying out the sorption experiment using the greatest sediment concentration (Fig. 10b), it was possible to subsample an aliquot of labelled sediment after just 4 days. After only 4 days, the colour of the sediment remained black, indicating destruction of surface reduced phases was limited. Two separate experiments were, therefore, carried out to assess ^{99}Tc desorption from sediment which had been allowed to equilibrate with spiked seawater (in oxic conditions) for 4 days and 28 days (hence variable amounts of time for sediment oxidation). The results of both experiments are shown in Fig. 12.

Figure 12. Redissolution of ^{99}Tc tracer from 'contaminated' anoxic sediment, into 'uncontaminated' seawater, with time.



The data in Fig. 12 indicate that the initial desorption of ^{99}Tc activity from 'contaminated' sediment into 'uncontaminated' seawater was small (< 5 % after ~69 hours or 3 days) and considerably less than that observed using oxic sediment (Fig. 11). In addition, the results in Fig. 11 indicate a significant difference in the pattern of behaviour between anoxic sediment exposed to oxic conditions for variable amounts of time. Using the more reduced sediment (4 day uptake, black colour) rapid initial desorption (~ 2 % within 1 hour) was subsequently followed by resorption behaviour similar to that observed in the sorption experiment (Fig. 10b). In contrast, continual desorption was observed using the more oxidised sediment (28 day uptake, brown colour). These results indicate that both the sorption and desorption behaviour of ^{99}Tc from sediments in the Irish Sea is likely to be extremely sensitive to local changes in redox conditions.

4. Discussion

The results from the environmental survey and laboratory experiments are discussed separately in sections 4.1 and 4.2, respectively. The information obtained from this study, with respect to the implications for ^{99}Tc contamination of seafood, is discussed in section 4.3.

4.1 Survey data

4.1.1 ^{99}Tc concentration on surficial sediments

The results reported here confirm preliminary findings of measurable ^{99}Tc in surface sediments (FSA, 2001, Leonard et al., 2004). This is despite that ^{99}Tc is considered to be a conservative radionuclide. The range of concentrations (3-73 Bq/kg in the eastern Irish Sea and 2-9 Bq/kg in the western Irish Sea; July 2002) indicated variations of ~ 25 fold and 3 fold between sites in eastern and western sectors, respectively. Levels in surficial sediment were approximately an order of magnitude lower than those observed in the suspended particulate material from the same site.

Perhaps the most notable feature of the present dataset is the similarity in levels at equivalent sampling sites between surveys carried out between December 1995 and July 2002 (Table 1). This consistency contrasts sharply with the marked variation in concentrations of dissolved ^{99}Tc between individual surveys. The muted response of the seabed sediments, to fluctuations in the Sellafield discharges, compared with the water column, illustrates the fact that the concentration of Sellafield derived artificial radionuclides in the surface sediments of the Irish Sea tend to reflect the integrated discharge history of that radionuclide (MacKenzie et al., 1994). The incremental change in the ^{99}Tc seabed sediment concentrations is, therefore, dampened relative to variations in the discharges.

Another remarkable feature is that lower concentrations (<4.3 Bq/kg) were observed on sandy sediments in the middle of the eastern Irish Sea compared with muddy material west of the Isle of Man, despite that concentrations in the water column were higher (by 3-4 fold) in the eastern Irish Sea. In other words, the retention capacity of the sediments is variable between individual locations, being relatively low on the gravels/sands that are the predominant throughout much of the Irish Sea. In general terms, the highest concentrations of most radionuclides in bulk Irish Sea sediments are associated with fine-grained deposits. The lower levels observed in sands have usually been interpreted as reflecting the lesser surface area available (per unit mass) for sorption (Hetherington and Jefferies, 1974; McCartney et al., 1994). The information collated in this report (e.g. data for grain-size distribution given in Table 2) indicates that such an interpretation is oversimplistic (see subsequent discussion).

Results reported elsewhere (Keith-Roach et al., 2003) have demonstrated extremely large (three orders of magnitude variation) in the retention capacity of sediments at four European intertidal sites, chosen to represent extremes in geochemical characteristics. Differences in the solid phase speciation, as inferred from the Tessier sequential leaching scheme, occurred concomitant with variations in retention capacity. The highest uptake was observed at Mariager Fjord in Denmark. A sample of surface sediment obtained from this location in May 2001 contained ~30 Bq/kg which is of similar magnitude to that observed in the vicinity of the Sellafield pipeline. The high uptake at Mariager was suggested to be due to the fact that i) conditions in the bottom waters of the fjord are highly reducing and ii) the sediments have a high organic content (~18 %). Results from the Tessier sequential leaching scheme indicated the majority of ^{99}Tc was in the so-called oxidisable fraction (i.e. bound to organic matter or sulphides). The lowest uptake was observed at Needle's eye in the Solway Firth. Samples of sub-surface sediment (between 2-8 cm) obtained from this location in November 2001 contained ~5.4-7.1 Bq/kg which is of similar magnitude to that observed in the present study on subtidal sand in the eastern Irish Sea. Although the Solway sediments contained organic matter having a loss on ignition of 4-5 %, the majority of the ^{99}Tc was associated with the carbonate phase. The authors suggested that one reason for the low uptake might be that Tc(IV) carbonate species are largely soluble.

With respect to compositional differences in the subtidal sediments of the Irish Sea, a limited amount of information is available from a survey carried out in December 1995 (Leonard et al., 2004). Samples of surficial sediment were analysed for ^{99}Tc, ^{137}Cs, ^{241}Am, organic carbon and grain-size. The organic content was generally low (0.05-2.02%), although levels were somewhat higher on samples from the western Irish Sea mud patch (range ~1.4-2.0 %) compared those observed from the eastern Irish Sea (0.06-1.1 %). It was not possible to discern a clear correlation in ^{99}Tc retention with organic content or grain-size from this dataset. Given the relatively small range in organic content in these samples of subtidal sediments from the Irish Sea, compared with those from intertidal fjords of Denmark/UK estuaries, this is not perhaps surprising.

4.1.2 ^{99}Tc core profiles

Our data confirm preliminary findings of significant ^{99}Tc accumulation in the seabed. In all the cores examined as part of the present study, ^{99}Tc had penetrated to depths of > 30 cm. Comparison of the results with the limited amount of historic (pre-EARP) data indicates that most of the ^{99}Tc originates from the enhanced EARP discharges. Results from ^{14}C dating indicate net sedimentation in the north-eastern Irish Sea is extremely low (~0.1 mm/annum) (Kershaw et al., 1988). Penetration of ^{99}Tc below 5 cm in the sub-tidal Irish Sea sediments, resulting from Sellafield discharges over the last 50 years, cannot, therefore, be accounted for in terms of sediment accretion processes.

Alternative explanations were derived from literature concerning the behaviour of radionuclides other than ^{99}Tc. A rather larger body of information is available concerning the sediment profiles for Pu radionuclides and ^{241}Am, compared with ^{99}Tc, in the sub-tidal sediments of the Irish Sea (Kirby et al., 1983; Woodhead, 1988; Kershaw et al., 1992). Three principal types of $^{239+240}$ Pu, ^{241}Am and $^{239+240}$ Pu/^{238}Pu profiles occur, which have been interpreted in terms of progressively more efficient bioturbation (Kirby et al., 1983). As a result of their high particle affinity (K_d values > 10^5), the role of diagentic reactions in post-depositional migration is of minor importance. In sediment cores from heavily bioturbated zones, abrupt changes were observed in radionuclide concentrations and $^{239+240}$ Pu/^{238}Pu quotients with depth. The offshore muddy sands support dense populations of the thalassinidean crustacean *Callianassa subterranea*, in burrows. Softer muds are dominated topographically by mounds of the echiuran worm *Maxmuelleria lankesteri* and the Norway lobster *Nephrops norvegicus*. *Maxmuelleria lankesteri* is frequently found at depths of 30 to 40 cm whilst the *Callianassa subterranea* has been observed at depths down to 150 cm. Their burrows have been proposed to act as sinks for surface-derived radionuclides. Unfortunately, it is very difficult to quantify mixing by bioturbation other than on the basis of interpreting individual core profiles (Gurbutt and Kershaw, 1987). Similar considerations probably apply to the present ^{99}Tc sediment core data.

Information from studies at intertidal sites indicates the speciation of particle bound ^{99}Tc may vary concomitant with sediment composition (Keith-Roach et al., 2003). In turn, this could affect the susceptibility towards redissolution and post-depositional migration. Although ^{99}Tc profile in Ravenglass salt marsh sediment in the Ravenglass estuary (Keith-Roach et al., 2003) does not appear to be affected by post-depositional migration, in the absence of supporting information it is impossible to extrapolate these findings to the sub-tidal sediments of the Irish Sea. Further observations are required to i) quantify inventories at depth and ii) assess the solid phase speciation, along with geochemical parameters such as organic carbon and sulphide.

4.1.3 ^{99}Tc K_d values

Excluding a single low value, derived from the analysis of a water sample collected amidst a phytoplankton bloom, the average ^{99}Tc K_d observed in the present study was 2.1 x 10^3. This is of similar magnitude to that reported for ^{137}Cs in UK waters (Baxter et al., 1979; Kershaw et al., 1992) and is suggested to be the most appropriate value to use in the WAT-ADO model. Environmental observations, with which to compare the present ^{99}Tc data, are scarce and appear to be limited to measurements at a few sites in the Irish Sea (Harvey and Kershaw, 1984; Leonard et al., 2004). From a pre-EARP survey in May 1982, Harvey and Kershaw (1984) reported K_d values for two sites (250 and 1900) but no further details were given regarding sampling location. The same authors also carried out measurements upon a sediment core obtained close to the Sellafield pipeline. They reported K_d values ranging from 800 -1800, derived from the measurement of ^{99}Tc levels in individual core sections and interstitial water samples. More recently, post-EARP K_d values have been derived from measurements of ^{99}Tc in samples of surface seawater and suspended particulate material in December 1995 on the collaborative Cirolana 10/95 expedition (Westlakes Scientific Consulting Ltd., personal communication). These ranged from 320-4850 with a median value of 1650. The two lowest values were observed at sites along the Cumbrian coastline closest (within 30 km) of Sellafield. The measurements in the present study are, therefore, in broad agreement with earlier values. The currently recommended value of 100 for the K_d of ^{99}Tc in coastal sediments (IAEA, 1985) underestimates solid-solution partitioning behaviour in the Irish Sea by more than an order of magnitude. Finally, it is worth noting that the range of laboratory K_d values currently used in the WATP-ADOP model is 10^1 to 10^3. This range has an uncertainty of two orders of magnitude. The new, albeit limited, range of environmental K_d values varies by just one order of magnitude and will help to give improve predictions of prospective doses due to ^{99}Tc discharges into the Irish Sea. Further environmental measurements in UK waters would, however, be useful to define more robust values for upper and lower limits of ^{99}Tc K_d values in oxic seawater.

4.2 Laboratory experiments

4.2.1 Sorption behaviour

In an environment with high ionic strength and dissolved oxygen content such as the open sea, the predominant Tc species is the pertechnetate anion TcO_4^-. This Tc(VII) species, which is highly soluble and mobile in aquatic environments under oxidising conditions (Garland et al., 1983), can enter the food chain as a sulphate analogue (Wildung et al., 1979). The results in Figs. 9a and 9b indicate little, or no, Tc fixation on oxidising sediments. There are other reports that corroborate these results. For example, a distribution coefficient (K_d) of < 10 has been reported for sediments and mineral surfaces low in organic matter content (Fowler et al., 1983; Walton et al., 1986). In contrast, considerably greater uptake was observed on sub-surface anoxic sediment (Figs. 10a and 10b). Information in the literature indicates that Tc(IV) species are expected to be more strongly retained (Lieser and Bauscher, 1987) and K_d values as high as 1500 have been observed for reducing sediments high (7%) in organic matter, (Masson et al., 1981; Masson et al., 1989).

Results from laboratory experiments using monomineralic phases and pure bacteria cultures indicate that surface chemical reactions on specific minerals, and bacteria, could potentially play a role in ^{99}Tc uptake onto sediment from seawater. The results show 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.

Abiotic reduction involves electron transfer between Fe(II) containing minerals and Tc(VII). The most efficient mineral appears to be magnetite, particularly when it is anodically polarised. X-ray absorption spectroscopy techniques (XANES and EXAFS)) has been used to determine Tc oxidation states and to identify the local environment of Tc sorbed on mackinawite (tetragonal FeS) and "green rust". Mackinawite, the first sulphide phase formed following the onset of reducing conditions, is commonly found in anoxic horizons, and is believed to play an important role in controlling metal speciation in such systems (Lennie et al., 1995). Green rusts are mixed Fe(II)/Fe(III) hydroxides that contain interlayer anions such as carbonate or sulphate (Cuttler et al., 1990). The X-ray spectroscopy data indicate Tc(VII) is reduced to Tc(IV) following sorption on both surfaces. Tc bound to FeS appears to form a TcS_2-like phase, whereas its local environment on green rust resembled that in TcO_2 (Wharton et al., 2000).

Biotic precipitation of the pertechnetate anion, presumably resulting from its reduction to insoluble Tc(IV) oxide species, has been reported for a range of microbes. These include bacteria such as *Geobacter metallireducens*, *Geobacter sulfurreducens*, *Escherichia coli*, *Desulfovibrio desulfuricans*, *Shewanella putrefaciens*, and *Deinococcus radiodurans* (De Luca et al., 2001). Both the mechanism (hence rate and extent) of biotic reduction processes are (unsurprisingly) highly dependent upon the bacteria used and the growth conditions. Both indirect (chemical) and direct (enzymatic) reactions have been observed. Chemical processes have been clearly demonstrated in the case of the sulphate-reducing bacterium *D. desulfuricans* and in the case of the metal-reducing bacterium *G. sulfurreducens*. Cultures of *D. desulfuricans* supplied with sulphate and lactate as electron acceptor and donor, respectively, precipitated Tc extracellularly as an insoluble sulphide. In this case, the Tc sulphide resulted from the chemical reaction between H_2S, formed during reduction of sulphate, and TcO_4^-. Chemical reduction of TcO_4^- by Fe(II) has also been reported during reduction of Fe(III) by *G. sulfurreducens*. With respect to enzymatic reduction processes, the emerging body of evidence indicates that this involves hydrogenase, an enzyme which reversibly catalyses the splitting of molecular hydrogen into protons and electrons. Indeed, hydrogen is an effective electron donor for TcO_4^- reduction using *E. coli, D. desulfuricans*, and *S. putrefaciens*. Similarly, in the case of *G. sulfurreducens*, TcO_4^- reduction has an exclusive requirement for hydrogen as the electron donor, unlike the reduction of Fe(III), which can be coupled to the oxidation of different organic electron donors. It is interesting that, soluble Tc(IV) carbonates have been identified as reaction product using *S. putrefaciens* (Wildung et al., 2000) and these species could act to enhance post-depositional migration in anaerobic subsurface environments.

Extrapolation of information from laboratory experiments using pure cultures, to evaluate the impact of a mixed population of marine bacteria upon ^{99}Tc uptake by sediment in the sea, is not straightforward. In addition to the variable reduction behaviour of individual bacteria species, measurements of microbial activity in natural waters using tritium-labelled substrates indicate significant seasonal variability. The proportion of bacteria actively metabolising in waters of the Kiel Fjord (an eutrohic brackish water environment) have been reported to range from 10% during the winter up to 74% during the warmer seasons (Hoppe, 1979). In addition, the biomass of the total number of bacteria also decreased from summer to winter down to 8.3% (summer value = 100%) whereas the active bacterial biomass was reduced to 0.7%. Despite that caution is required in applying the laboratory data, it appears likely that, in the presence of reducing sediments, TcO_4^- is either reduced to insoluble tetravalent compounds such as hydrated TcO_2, coprecipitated with metallic sulphides in formation, or precipitated as Tc_2S_7.

4.2.2 Redissolution behaviour

Comparison of the data in Figs. 11 and 12 indicates that, when sediments contaminated with ^{99}Tc are returned to uncontaminated seawater, the desorption behaviour appears to be variable between different sediment types. Once again, although information in the literature is sparse, this observation is corroborated elsewhere (Germain et al., 1984). It has been reported that desorption from an oxidising carbonate sediment is rapid (less than 5 % remaining bound to the sediment after 24 hours whilst less than 1 % remained fixed in the sediment after 3 months). 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. A qualitatively similar observation has been reported for Tc bound to a well characterised monomineralic phase (as compared with heterogeneous poorly characterised natural materials). 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).

Supporting evidence that metallic sulphides other than Tc may be metastable under oxic conditions has been reported elsewhere. The rate of sulphide redissolution under oxic conditions appears to be variable between individual mineral phases (Boust et al. 1999). The technique used in this study was based upon classic acid extraction methodology, which gives rise to operationally defined phases (Cornwell and Morse, 1987). Acid-volatile sulphide (AVS) is the most labile fraction and is defined as the minerals that are soluble in cold acid, including amorphous iron monosulphide (FeS), mackinawite (FeS) and perhaps greigite (Fe_3S_4) (Casas and Crecelius, 1994). More severe treatments release sulphide from pyrite (FeS_2) and other compounds (e.g. organic sulphides). This fraction is termed chromium reduced sulphides (CRS). Upon resuspension of anoxic sediments in oxic seawater, only 50% of the initial CRS was destructed after a 40 hour long stirring experiment in aerated seawater, even though the AVS pool was totally solubilised within 24 hours (Boust et al., 1999).

Overall, there is an emerging body of evidence which implies that when Tc is reduced to insoluble TcS_2 in an anaerobic environment it may remain insoluble as Tc(IV) oxide even if the sediment is subsequently exposed to aerobic conditions (Wharton et al., 2000). The implication of this behaviour is that reducing sediments in the Irish Sea could form a temporary sink for ^{99}Tc, reducing the likelihood of rapid remobilisation from contaminated sub-surface material in the event discharges from Sellafield should cease.

4.2.3 Extrapolation of laboratory data towards ^{99}Tc behaviour in the Irish Sea

Almost all the ^{99}Tc discharged from Sellafield appears to be in "a truly dissolved form", as the TcO_4^- anion (Leonard et al., 1995). As particulate releases of Tc from Sellafield are not significant, the uptake mechanism of dissolved TcO_4^- onto sediment most probably occurs due to biogeochemical reduction. Diagenetic studies of the Irish Sea mud patch suggest that they 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). It may be reasonable to conclude that sediment ventilation by oxygenated seawater could be considerably greater in sandy material, compared with soft muds. Given that in the laboratory it has been shown that soluble TcO_4^- species can be reduced to insoluble Tc(IV) species and to precipitate onto certain iron minerals (Lloyd et al., 2000), it is conceivable that subsurface sediments may provide a site for reduction of pertechnetate, hence a sink. The fact that higher concentrations are observed on fine grained material is presumably a consequence of a difference in subsurface redox conditions, rather than a surface area effect.

Results from both the laboratory studies carried out as part of the present study, as well as other investigations, indicate that sorbed ^{99}Tc is retained on anoxic material upon exposure to oxic conditions. The mechanism of retention is, however, unidentified. Due to reworking of seabed sediments as a result of bioturbation, resuspension during storms and trawling activity, ^{99}Tc associated with subsurface may be resuspended into the water column and dispersed by general sediment transport processes (Burrows, 1986). Modelling of results for highly particulate reactive transuranic radionuclides indicates material remains available for resuspension for > 6 years following discharge (Hunt, 1985).

Remobilisation from contaminated sediment is now considered to be the predominant source term of ^{137}Cs (McCubbin et al., 2002a), Pu radionuclides and ^{241}Am in the Irish Sea (Leonard et al., 1999). The rate of dissolution of all these radionuclides from sediment into seawater is slow. The half-time for redissolution of ^{137}Cs and $^{239+240}$Pu bound to sedimentary material in the Irish Sea has been estimated to be in the order of several tens (Mitchell et al., 1999) and several hundreds of years (Leonard et al., 1999), respectively. The K_d values for ^{137}Cs and ^{99}Tc are of similar magnitude. It is tempting to conclude that the half-time for redissolution of ^{99}Tc might, therefore, be similar. Caution is, however, required in extrapolating data in this manner given that the mechanisms of uptake and release are entirely different (^{137}Cs is not redox reactive).

4.3 Implication towards accumulation of ^{99}Tc in seafood

There are three primary pathways for the accumulation of ^{99}Tc in items of seafood: i) uptake from surrounding seawater, ii) consumption of contaminated food items and iii) transfer from sediments.

With respect to the first pathway, although alternative mechanistic-based kinetic models have been suggested (LeFur et al., 1991), the concept of an equilibrium, biological concentration factor (CF) for marine biota which indicates the apparent bioaccumulation of radionuclides including ^{99}Tc from seawater has gained wide acceptance as a pragmatic measure despite the problems inherent in deriving and interpreting CF values (Lowman et al., 1971; IAEA, 1985). CF values are normally obtained from environmental observations (CF = biota concentration divided by aqueous phase concentration). The recommended generic CF value for Tc in marine crustacea is 1000 (IAEA, 1985). There is, however, a significant diversity in Tc bioaccumulation between individual marine organisms and the accumulation potential in evolutionarily more primitive homarid crustacea such as *Nephrops* and *Homarus* is generally greater than in the more advanced decapod crustacea such as *Cancer*. The equilibrium whole body CF for Tc in the European lobster, *Homarus gammerus* L. has been reported to be greater than 1500 compared with ~10 in the edible crab, *Cancer pagurus* L. and the common shrimp, *Crangon crangon* L., (Pentreath, 1981). Concentration factors in other marine organisms, as determined in laboratory experiments, are small (typically <10; Masson et al. 1989). The physiological and biochemical basis for the inter-species disparity in Tc accumulation is unclear.

The most important contributor with respect to dose arising from consumption of contaminated items of seafood from the Irish Sea is the Norway lobster (*Nephrops norvegicus*). It is fished in both the Sellafield offshore area and other areas of the Irish Sea (e.g. the mud patch of the western Irish Sea) and had a mean catch 8,136 tonnes over the period 1990 – 1994. CF values, as determined from environmental observations, were range 2.0-21 x 10^3 for wet muscle (i.e. edible) material (FSA, 2001). Results from laboratory experiments to study Tc bioaccumulation in Nephrops (Swift, 2001) are broadly comparable and indicate a steady state CF for accumulation from seawater to be about 2000 (wet weight). ^{99}Tc concentrations in other commonly consumed organisms such as the edible crab, and plaice were lower by one and two orders of magnitude, respectively, than those observed in the Norway lobster.

The other two pathways have been less well investigated. Sediment-dwelling fauna may absorb radionuclides from direct contact with sediment, from ingestion of contaminated prey, and from interstitial waters. Laboratory experiments indicate Tc accumulation in Nephrops from ingestion of labelled prey followed a biphasic model with one compartment containing about 94 % of the ingested activity and with a half-time of about 1 day. The second compartment contained about 6% of the ingested activity and with a half-time of about 56 days. Most (~43%) of the retained activity was found in the digestive gland (Swift, 2001). Further work is required to assess ^{99}Tc bioaccumulation by benthic organisms and demersal fish via transfer up the web of sediment dwelling microbes and meiofauna. The extremely limited amount of available data (Fowler et al., 1983; Germain et al., 1984) for accumulation of Tc from exposure to contaminated sediment indicate benthic organisms only slightly concentrate Tc via this pathway. Transfer factors reported for clams (Fowler et al., 1983) and annelid worms (Germain et al., 1984) are low (<0.6). It is worth noting, however, that the biological half-life of Tc in the clams was much longer (~120 days) than that reported for Nephrops.

Given that the predominant pathway for ^{99}Tc accumulation by seafood appears to be uptake from surrounding seawater, in the event that discharges from Sellafield should cease, the availability of ^{99}Tc in the subtidal sediments is likely to be governed by the rate and extent of redissolution processes.

5. Conclusions

Initial findings of ^{99}Tc accumulation in the bed sediments of the Irish Sea have been substantiated. ^{99}Tc released from Sellafield post-EARP (i.e. since 1994) has penetrated below 30 cm. Sediment core profiles are variable and some are ‘irregular’. This is suggested to be a result of variable mixing via bioturbation processes. Further investigations using an alternative coring device are required to determine the limit of penetration.

Our K_d values for suspended sediments were roughly an order of magnitude higher than the value of 100 currently recommended by the IAEA for coastal sediments. It is, however, apparent that the geochemistry of ^{99}Tc is complex and sensitive to site-specific factors. Additional measurements are required to establish more robust values for the range in UK waters, to use in the WATP-ADOP model, for prospective dose assessments.

Results from our programme of laboratory experiments indicate that uptake onto sediment occurs as a reduction of the highly soluble pertechnetate anion (TcO_4^-) to less soluble Tc(IV) species. Upon resuspension of anoxic sediments in oxic seawater, the ^{99}Tc remains metastably bound to particulate material.

In the event that discharges from Sellafield should cease, the availability of ^{99}Tc in the subtidal sediments to seafood is probably governed by the rate and extent of redissolution processes. Extrapolation of the available information to predict timescales for this to occur is difficult. However, it is worth noting that environmental K_d values for ^{137}Cs and ^{99}Tc are of similar magnitude. If the rate and extent of ^{99}Tc remobilisation follows a similar pattern to that observed for ^{137}Cs, then the half-time for redissolution of ^{99}Tc bound to sedimentary material in the Irish Sea is likely to be in the order of several tens of years.

6. Acknowledgements

The authors wish to thank Dr. D. Boust (IRSN) and the officers and crews of the COTES LA MANCHE for their support. We are grateful to our FSA coproject officer Dr. D. Cutts for his management and to British Nuclear Fuels plc for providing monthly discharge data. This work was funded by the UK Food Standards Agency (RO1055).

References

Baxter, M.S., McKinley, I.G., MacKenzie, A.B. and Jack, W. (1979). Windscale radiocaesium in the Clyde Sea area. Mar. Pollut. Bull., 10: 116-120.

BNF, (1979-2003). Annual report on radioactive discharges and monitoring of the environment, 1978-2002. British Nuclear Fuels, Risley, UK, 1979-2003.

Boust, D., Fischer, J.C., Ouddane, B., Petit, F. and Wartel, M. (1999). Le fer et le manganèse dans l'estuaire de la Seine:Réactivités et recyclages. Les fasicules de Seine Aval. Ed. IFREMER, Brest, France.

Brown, J. and Gmitrowicz, E.M. (1995). Observations of the transverse structure and dynamics of the low frequency flow through the North Channel of the Irish Sea. Cont. Shelf Res., 15: 1133-1156.

Brownless, G. P., Grzechnik, M. P., Round, G. D. and Pidcock, A. J. (2001). An uncertainty analysis for the marine environment, 2001. CEFAS Environmental Tech. Note RL 12/01, CEFAS, Lowestoft, UK.

Burrows, P.J. (1986). Contaminated sediments and circulation in the northern Irish Sea. J. Shoreline Management, 2: 85-91.

Casas, A. M. and Crecelius, E. A. (1994). Relationship between acid volatile sulfide and the toxicity of zinc, lead and copper in marine sediments. Environ. Toxicol.Chem. 13: 529-536.

CEC (1990). The radiological exposure of the population of the European Community from radioactivity in Northeastern European marine waters - project MARINA. Report by a group of experts convened by the Commission of the European Communities, Radiation Protection 47. Luxembourg, CEC, EUR 12483 EN.

Cornwell, J. C.. and Morse, J. W. (1987). Analysis and distribution of iron sulfide minerals in anoxic marine sediments. Mar. Chem. 22 : 55-69.

Cui, D., and T. E. Ericksen. (1996). Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. Environ. Sci. Technol. 30:2263-2269

Cuttler, A.H., Man, V., Cranshaw, T.E. and Longworth, G. (1990). A Mössbauer study of green rust precipitates: I. Preparations from sulphate solutions. Clay Min., 25: 289-301.

De Luca, G., de Philip, P., Dermoun, Z., Rousset, M. and Vermeglio, A. (2001). Reduction of technetium(VII) by *Desulfovibrio fructosovorans* is mediated by the nickel-iron hydrogenase. Appl. Environ. Microbiol. 67(10): 4583-4587.

Defra (2002). Decision of the Secretary of State for the Environment, Food and Rural Affairs and the Secretary of State for Health re the Environment Agency's proposed decision on the future regulation of techetium-99 discharges from the British Nuclear Fuels plc Sellafield site into the Irish Sea. www.defra.gov.uk. 24pp.

Farell, J., W. D. Bostick, R. J. Jarabek, and J. N. Fiedor. (1999). Electrosorption and reduction by anodically polarized magnetite. Environ. Sci. Technol. 33:1244-1249.

Fowler, S.W., Aston, S.R., Benayoun, G. and Parsi, P. (1983). Bioavailability of technetium from artificially labelled northeast Atlantic deep-sea sediments. Mar. Env. Res., 8: 87-100.

FSA (2001). Accumulation of ^{99}Tc in the Irish Sea. Food Standards Agency Project Report R01031.

Garland, T.R., Cataldo, D.A., McFadden, K.M., Schreckhise, R.G. and Wildung, R.E. (1983). Comparative behaviour of ^{99}Tc, ^{129}I, ^{127}I and ^{137}Cs in the environment adjacent to a fuel reprocessing facility. Health Physics, 44: 658-662.

Germain, P; Miramand, P and Masson, M. (1984). Experimental study of long-lived radionuclides transfers (americium, plutonium, technetium) between labelled sediments and Annelidae *(Nereis diversicolor, Arenicola marina*). Int. Symp. on the Behaviour of Long-Lived Radionuclides in the Marine Environment, pp. 327-340.

Gray, J., Jones, S.R. and Smith, A.D. (1995). Discharges to the environment from the Sellafield site, 1951-1992. J. Radiol. Prot., 15: 99-131.

Grzechnik, M.P., Round, G.D., Brownless, G.P. and Camplin, W.C. (2002). A probabilistic modelling suite for the marine environment. CEFAS Environmental Tech. Note RL 3/02, CEFAS, Lowestoft, UK.

Gurbutt, P.A. and Kershaw, P.J. (1987). Biological mixing of shelf sea sedimentswith implications for modelling. International Council for the Exploration of the Sea, Copenhagen, CM 1987/C:22 13 pp.

Harvey, B.R. (1981). Potential for post depositional migration of neptunium in Irish Sea Sediments. In: 'Impacts of Radionuclide Releases into the Marine Environment', IAEA-SM-248/104, pp. 93-103, IAEA, Vienna.

Harvey and Kershaw (1984). Physico-chemical interactions of long-lived radionuclides in coastal marine sediments and some comparisons with the deep sea environment. CEC Int. Symp. The Behaviour of Long-lived Radionuclides in the Marine Environment, 1983, La Spezia; 131-141.

Harvey, B.R., Ibbett, R.D., Williams, K.J. and Lovett, M.B. (1991). The determination of technetium-99 in environmental materials. Aquatic Environmental Protection: Analytical Methods, MAFF Directorate of Fisheries Research, Lowestoft (8), 1-22.

Harvey, B.R., Williams, K.J., Lovett, M.B. and Ibbett, R.D. (1992). Determination of technetium-99 in environmental materials with rhenium as a yield monitor. Journal of Radioanal. Nucl. Chem., 158: 417-436.

Hetherington, J.A. and Jefferies, D.F. (1974). The distribution of some fission product nuclides in sea and estuarine sediments. Neth. J. Sea Res., 8: 319-338.

Holm, E. (1993). Radioanalytical studies of Tc in the environment: progress and problems. Radiochim. Acta, 63: 57-62.

Hoppe, H.G. (1979). Microbial activity measurements by means of tritium-labelled substrates. In: Behaviour of tritium in the environment, IAEA-SM-232/5, pp. 205-218, IAEA, Vienna.

Hunt, G. J. (1982). IDLE – A computer program to estimate individual doses from liquid effluents. Sizewell enquiry series, MAFF Direct. Fish Res., Lowestoft, UK.

Hunt, G.J. (1985) Timescales for dilution and dispersion of transuranics in the Irish Sea near Sellafield. Sci. Tot. Environ., 46, pp 261-278

Hunt, G.J., Smith, B.D. and Camplin, W.C. (1998). Recent changes in liquid radioactive waste discharges from Sellafield to the Irish Sea: monitoring of the environmental consequences and radiological implications. Radiat, Prot. Dosim., 75: 149–153

IAEA(1985). Sediment K_d's and concentration factors for radionuclides in the marine environment, Tech. Rep. Ser. No. 247, IAEA, Vienna.

IRSN (2003). IRSN Activity Report 2002. Nuclear safety and radioprotection institute, ISSN 1637-6730, October 2003.

Jefferies, D.F., Steele, A.K. and Preston, A. (1982). Further studies on the distribution of ^{137}Cs in British coastal waters-1. Irish Sea. Deep-Sea Res., 29(6A): 713-738.

Keith-Roach. M.J., Morris, K. and Dahlgaard, H. (2003). An investigation into technetium binding in sediments. Mar. Chem., 81(3-4): 149-162.

Keith-Roach. M.J. and Roos, P. (2004). Redox-dependent behaviour of technetium-99 entering a permanently stratified anoxic fjord (Framvaren fjord, Norway). Est., Coast. Shelf Sci., in press.

Kershaw, P.J., Swift, D.J. and Denoon, D.C. (1988). Evidence of recent sedimentation in the eastern Irish Sea. Mar. Geol., 85: 1-14.

Kershaw, P. J., Pentreath, R. J., Woodhead, D. S. and Hunt, G. J. (1992). A review of radioactivity in the Irish Sea. Aquat. Environ. Monit. Report. MAFF Direct. Fish. Res., Lowestoft (32): 1-65.

Kershaw, P.J., Denoon, D.C. and Woodhead, D.S. (1999). Observations on the redistribution of plutonium and americium in the Irish Sea sediments, 1978 to 1996: concentrations and inventories. J. Environ. Radioact., 44(2-3): 191-221.

Kim, C. K., Morita, S., Seki, R., Takaku, Y., Ikeda ,N., and Assinder, D. J. (1992). Distribution and behaviour of ^{99}Tc, ^{237}Np, ^{239,240}Pu, and ^{241}Am in the coastal and estuarine sediments of the Irish Sea. J. Radioanal. Nucl. Chem., 156: 201-213.

Kirby, R, Parker, W.R., Pentreath, R.J. and Lovett, M.B. (1983). Sedimentation studies relevant to low-level radioactive effluent dispersal in the Irish Sea. Part 3. An evaluation of possible mechanisms for the incorporation of radionuclides into marine sediments. REP. INST. OCEANOGR. SCI., WORMLEY., no. 178, 66 pp.

Knight, P.J. and Howarth, M.J. (1999). The flow through the north channel of the Irish Sea. Cont. Shelf Res., 19: 693-716.

LeFur, J, Germain, P and Baron, Y, (1991). Modelling in situ mussel ruthenium-106 concentration dynamics due to fluctuating sea water radionuclide concentrations. Mar. Ecol. Prog. Ser., 75: 67–78.

Lennie, A.R., Redfern, S.A.T., Schofield, P.F. and Vaughan, D.J. (1995). Synthesis and Rietveld crystal structure refinement of mackinawite, tetragonal FeS. Min. Mag., 59: 677-683.

Leonard, K. S., McCubbin, D. and Lovett, M. B. (1995). Physico-chemical characterisation of radionuclides discharged from a nuclear establishment. Sci. Tot. Environ., 175: 9-24.

Leonard, K.S., McCubbin, D., Brown, J., Bonfield, R. and Brooks, T. (1997). Distribution of Technetium-99 in UK coastal waters. Mar. Pollut. Bull., 34(8) : 628-636.

Leonard, K.S., McCubbin D., Blowers P. and Taylor, B.R., (1999). Dissolved plutonium and americium in surface waters of the Irish Sea, 1973-1996. J. Environ. Radioact., 44: 129-158.

Leonard, K.S., McCubbin, D., McDonald, P., Service, M., Bonfield, R. and Conney, S. (2004). Accumulation of Technetium-99 in the Irish Sea?. Sci. Total Environ. (in press).

Lieser, K.H. and Bauscher, C. (1987). Technetium in the hydrosphere and in the geosphere – chemistry of technetium in natural waters and the influence of redox potential on the sorption of technetium. Radiochim. Acta, 42: 205-213.

Lloyd, J. R., V. A. Sole, C. V. Van Praagh, and D. R. Lovley. (2000). Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. Appl. Environ. Microbiol. 66: 3743-3749.

Lowman, F.G., Rice, T.R. and Richards, F.A. (1971). Accumulation and redistribution of radionuclides by marine organisms. In: Radioactivity in the marine environment, pp. 161-199. National Academy of Sciences, Washington D.C.

MacKenzie A.B., Scott R.D., Allan R.L, Ben Shaban Y.A. Cook G.T. and Pulford I.D. (1994). Sediment radionuclide profiles: implications for mechanisms of Sellafield waste dispersal in the Irish Sea. J. Environ. Radioact., 23: 39-69.

Malcolm, S. J., Kershaw, P. J., Lovett, M. B. and Harvey, B. R. (1990). The interstitial water chemistry of ^{239,240}Pu and ^{241}Am in the sediments of the Irish Sea. Geochim. Cosmochim. Acta, 54: 29-35.

Masson, M; Aprosi, G; Laniece, A; Gueguenia t, P and Belot, Y. (1981). Experimental Approaches to the Study of Technetium Transfers to Sediments and Benthic Marine

Species. Int. Symp. on the Impacts of Radionuclide Releases into the Marine Environment, Vienna (Austria), 6 Oct 1980. pp. 341-359

Masson, M., Patti, F., Colle, C., Roucoux, P., Grauby, A. and Saas, A. (1989). Synopsis of French experimental and in situ research on the terrestrial and marine behavior of Tc. Health Physics, 57 (2): 269-279.

McCartney M., Kershaw P.J., Woodhead D.S. and Denoon D.C. (1994). Artificial radionuclides in the surface sediments of the Irish Sea. Sci. Tot. Env., 141: 103-138.

McCartney, M and Rajendran, K. (1999). Historical Levels in the Irish Sea. In: Marine Pollution, Proceeding of International Symposium, Monaco, 5-9 October 1998, IAEA-SM-354/44, pp. 105-110.

McCubbin, D., Leonard, K.S., Brown, J., Kershaw, P.J., Bonfield, R.A. and Peak, T. (2002a). Further studies of the distribution of ^{99}Tc and ^{137}Cs in UK and European coastal waters. Cont. Shelf Res., 22/10: 1417-1445.

McCubbin, D., Leonard, K.S. and Emerson, H.S. (2002b). Influence of thermal and photochemical reactions upon the redox cycling of Pu between solid and solution phases in seawater. Mar. Chem., 80(1): 61-77.

Mitchell, P.I., Condren, O.M., Vintró, L.L. and McMahon, C.A. (1999). Trends in plutonium, americium and radiocaesium bioavailability in the western Irish Sea mud basin. J. Environ. Radioact., 44: 221-250.

Morris, K., Butterworth, J.C. and Livens, F.R. (2000). Evidence for the Remobilization of Sellafield Waste Radionuclides in an Intertidal Salt Marsh, West Cumbria, U.K., Estuar. Coast. Shelf Sci., 51(5): 613-625.

Nelson, D.M. and Lovett, M.B. (1981). Measurements of the oxidation state and concentration of plutonium in interstitial waters of the Irish Sea. In: Impacts of Radionuclide Releases into the Marine Environment, IAEA-SM-248/145, IAEA, Vienna, pp. 105-118.

Nicholson, S., Howorth, J.M., Sanders, T.W. and Blaine, L.M. (1992). Technetium-99 in the Irish Sea. Department of the Environment Report No. DOE/HMIP/RR/92.008.

NRPB (1995). Risks of leukaemia and other cancers in Seascale from all sources of ionising radiation, NRPB-276 (HMSO, London).

Pentreath, R.J. (1981). The biological availability to marine organisms of transuranium and other long-lived nuclides. In: Impacts of radionuclide releases into the marine environment, 241-272, Vienna, IAEA STI/PUB/565.

Round, G.D. (1998a). Individual doses from discharges of liquid effluents to the marine environment: Water concentration model-WAT. CEFAS Environmental Tech. Note RL 2/98, CEFAS, Lowestoft, UK.

Round, G.D. (1998b). Individual doses from discharges of liquid effluents to the aquatic environment: Dosimetric model-ADO. CEFAS Environmental Tech. Note RL 8/98, CEFAS, Lowestoft, UK.

Swift, D.J. (2001). The accumulation and retention of ^{95m}Tc by the Norway lobster, *Nephrops norvegicus* L. J. Environ. Radioact., 57(2): 139-149.

Walton, F.B., Paquette, J., Ross, J.P.M. and Lawrence, W.E. (1986). Tc(IV) and Tc(VII) interactions with iron oxyhydroxides. Nucl. Chem. Waste Manag., 6: 121-126.

Wharton, M.J., Atkins, B., Charnock, J.M., Livens, F.R., Pattrick, R.A.D. and Collison, D. (2000). An x-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS). Appl. Geochem., 15: 347-354.

Wildung, R. E., K. M. McFadden, and T. R. Garland. (1979). Technetium sources and behaviour in the environment. J. Environ. Qual., 8: 156-161.

Wildung ,R.E., Gorby, Y.A., Krupka, K.M., Hess, N.J., Li, S.W., Plymal,e A.E., McKinley, J.P. and Fredrickson, J.K. (2000). Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by *Shewanella putrefaciens*. Appl. Environ. Microbiol., 6: 2451-2460.

Woodhead, D.S. (1988). Mixing processes in near-shore marine sediments as inferred from the distributions of radionuclides discharged into the north-east Irish Sea from BNFL, Sellafield. In “Radionuclides: a tool for oceanography” (eds. J.C. Guary, P. Guéguéniat and R.J. Pentreath), Elsevier, London: 331-340.

Woodhead, D. S. and Pentreath, R. J. (1992). The dispersal of radionuclides in the sea. In: “The Treatment and Handling of Wastes”, Chapter 9. Edited by A.D. Bradshaw, Sir

Richard Southwood and Sir Frederick Warner, Chapman & Hall (London) for the Royal Society.

Young, E.F., Aldridge, J.N. and Brown, J. (2000). Development and validation of a three-dimensional curvilinear model for the study of fluxes through the North Channel of the Irish Sea. Cont. Shelf Res., 20: 997-1