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Assessment of the relative importance of biological, physical and chemical processes on the transport and speciation of pollutants, particularly radionuclides, in the Irish Sea AE1129 Final Project report for DEFRA

Continental Shelf and Margins Programme

Commissioned Report CR/02/295

BRITISH GEOLOGICAL SURVEY

COMMISSIONED REPORT CR/02/295

Assessment of the relative importance of biological, physical and chemical processes on the transport and speciation of pollutants, particularly radionuclides, in the Irish Sea AE1129 Final Project report for DEFRA

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Executive summary (maximum 2 sides A4)

This study examined the relative influence of physical, chemical and biological processes on the transport and speciation of pollutants in the Irish Sea. The focus was on radionuclides discharged from Sellafield, but other contaminants were considered from a wide range of sources.

The results will help to underpin DEFRA policy by providing robust science to help understand the processes and influences that impact on the marine environment. DEFRA recognises that policy making needs to be developed on the basis of a proper understanding of pollutant distribution and behaviour in the marine environment. This assists the UK in meeting its obligations under international conventions such as OSPAR. The report is timely because a framework for nature conservation in the Irish Sea is being piloted as the next step in DEFRA's Review of Marine Nature Conservation.

The first stage of the work was a review of existing knowledge, presented as a report with new maps and backed by a database of recent references. This was followed by detailed studies of sediment cores from the NE Irish Sea from the area close to Sellafield. This included the mud patch and the inshore region with highest radionuclide levels. Intertidal cores were also collected, to greater depths than previously. These provided a contrast to the offshore cores, in a zone more accessible to man, and improved our knowledge of the inventory of radionuclides in this environmental compartment. The sediment studies were supplemented by modelling work that included 3-D hydrodynamic modelling and chemical modelling.

The study has shown that physical, chemical and biological factors are all important. Their relative importance varies from place to place and differs markedly when comparing intertidal and offshore environments. Further work is needed to move from a qualitative assessment of relative impact to a more quantitative approach. Some of the methodologies developed for this study offer this possibility, particularly with respect to biological processes. The behaviour of the offshore sediments is considered next and then compared to the intertidal sediments.

Typically, the offshore sediments are bioturbated near to the surface (commonly to depths of 10-20cm) but at greater depth show preserved physical sedimentary structures. Profiles of alpha, beta and gamma emitting radionuclides with depth are consistent with a time-integrated Sellafield discharge signature modified by mixing by burrowing organisms. This is supported by ratios of Pu isotopes that reflect progressively earlier discharges with depth. However, it is at odds with earlier work indicating very low sedimentation rates. The apparent discrepancy may be explained by the earlier focus on the mud patch (15-20km offshore) relative to a bias in this study in favour of the inshore zone (3-4 km offshore) adjacent to and north of Sellafield, where radionuclide contents are highest. Mesocosm work has shown that mud shrimps (*Callianassa, Upogebia*) are effective redistributors of radionuclides in the sediments, whereas other species studied appear to have relatively little impact. Experiments with another major Irish Sea bioturbator (*Maxmulleria*) were, unfortunately, not successful due to poor survival rates. Modelling techniques were used to estimate the degree of mixing produced by different species. Taken in conjunction with information on species density and geographical distribution, the impact of bioturbation could, in future, be estimated quantitatively. The principal influence on the distribution of the biotic communities appears to be the grain size of the sediments, along with the related parameter of water depth. This has been established using multivariate statistical methods applied to both the identified biota and sediment parameters.

Physical processes are more important offshore below the surface oxygenated zone. Sedimentary structures are apparent below the top 10-30cm and include the interpreted products of storms. The impact of storms was also examined by 3-D hydrodynamic modelling. In particular, three storms were studied where there were some direct observations of water movements that could be used to test the models. Modelling examined the relative impact of far-field (shelf-wide) effects and local wind forcing. Water movements in detail were controlled by the direction and duration of the storm, but showed the potential to move contaminated sediment into the estuaries of the eastern Irish Sea and more soluble phases over wider areas. Removal of oxygenated surface sediment could expose reduced sediments to aerated water and this could have implications for the release of redox sensitive contaminants. Bioturbation also has the potential to introduce local oxic conditions or recycle material from depth to the oxic near-surface environment.

Geochemical modelling has shown that Pu is partly soluble under oxygenated conditions, with up to 10% being available for removal in the aqueous phase. This fits well with the observed loss of Pu from the sediments over time. The much greater proportionate loss of Cs is well documented from both subtidal and intertidal sediments. Sequential extraction techniques suggest that much of the remaining Cs is relatively tightly bound in clays and therefore loss from the sediment may be expected to now be much reduced. Cs and U are more prevalent in the deeper sediments, perhaps also indicating their removal from near surface material. Pore water measurements, microbiological work and modelling all confirm the presence of a shallow (typically 10-15cm) oxygenated layer with increasingly reducing conditions below this. Sulphate-reducing bacteria are probably controlling sulphide production at depth, seen as dark colouration in the cores and microscopically as pyrite framboids within the sediments.

Bulk mineralogy does not appear to be a controlling factor in the uptake of radionuclides by the sediments – changes in the clay content or the available surface area are not well correlated with radionuclide levels. Grain size does, however, play a part. Radionuclides are distributed in the fine matrix of the sediments but are also associated with hot particles. Autoradiography has been used in combination with optical and backscatter scanning electron microscopy to investigate these particles. Contrary to previous studies, hot particles of possible spent nuclear fuel origin, or associated with iron minerals, have not been observed. Rather, the hot spots seen are organic gel-like particles with a high magnesium content or consist of mud pellets (possible faecal) or pellicles around shell fragments. It appears the latter may be associated with local reducing conditions, perhaps related to the breakdown of an organic coating. This is supported by the presence of pyrite. Shells lacking an organic coating (possibly older fragments) appear not to have the more radioactive rim. The difference in hot particle characteristics may reflect diagenetic breakdown of fuel particles, with the high Mg perhaps reflecting the Mg-alloy casing on Magnox fuel.

Multivariate statistics and sequential extraction techniques indicated that the most extractable U was in carbonates. Th was mostly non-extractable, but the more available Th was held in Fe oxides. A new method of sequential extraction suggests that a potential redistribution of elements occurs between phases in traditional Tessier type schemes. This can lead to erroneous conclusions regarding solid phase speciation. As and V show possible redox effects, being associated with relatively labile forms in near-surface sediments and bound in Fe-oxyhydroxides or carbonates under deeper more reducing conditions.

The intertidal sediments appear to be dominated by physical sedimentary processes. Although burrowing is evident on the surface, the cores are characterised by well-developed laminations that are little affected by bioturbation. It seems that the migration of tidal channels across the estuary is responsible for the extensive reworking of the sediments and may obliterate the smaller scale mixing by bioturbation. The estuaries, with their tidal dominance, are filling with sediment from seawards with little landward input from rivers. They therefore remain a sink for particle-associated contaminants, although they have clearly released significant amounts of more mobile Cs since Sellafield discharges were reduced.

Deeper coring of the intertidal sediments has, in places, reached uncontaminated sediment at depths of less than 1m. In many places, further from the shore, radionuclides are still present down to at least 2.5m. Further deeper coring is required to finally define the volume of contaminated sediment, but inventory estimates for ^{137}Cs, ^{241}Am and plutonium isotopes in the Solway Firth and Morecambe Bay can now be revised upwards by factors of at least 4.5 and 3.5 respectively. Using the known depth of contaminated sediment (where the base is reached) and radionuclide profiles showing a pronounced subsurface peak, sedimentation rates can be estimated. They range from <1 to 6 cmy^{-1}, consistent with the range observed on Solway salt marshes and in the Esk Estuary.

In general, heavy metal contamination is not a problem in the sediments studied. The highest values of a range of metals (Ni, Cu, Cr, Pb, Zn) are seen in a sample off the coast between Whitehaven and Workington. Relatively high levels of Cd are seen within all the Solway Firth cores, consistent with the seaward source of the sediments and the previously observed higher Cd levels off Whitehaven that have been linked to phosphate processing.

Analysis of PAHs in the offshore and intertidal sediments showed typical ranges for marine sediments. The patterns of relative proportions of different PAHs were characteristic of assemblages derived from high temperature fossil fuel combustion (pyrolitic). Petrogenic (petroleum-derived) patterns were only seen in one offshore sample, from near Whitehaven, and may relate to fuel spillages associated with the port. PAH contents were lower in the intertidal cores, consistent with the lower TOC levels and coarser grain size. However, there was also an appreciable petrogenic contribution. This may result from spillages from small craft operating in the shallow waters.

A number of recommendations for future work are made as a result of the study and are outlined at the end of this report.

Scientific report (maximum 20 sides A4)

1. Background

Sellafield discharges are the most significant source of radioactive pollutants in the Irish Sea, with lesser components arising from the operation of other nuclear plants, such as Springfields, and the past processing of phosphate ore at Whitehaven. Other contaminants known to be present are heavy metals, hydrocarbon compounds and endocrine disrupters. Heavy metal contamination in the Irish Sea arises chiefly from mining activity, industrial waste and sewage sludge disposal. Of particular note as contaminants in the sediments are Cd and Ag off the Cumbrian coast, Hg in Liverpool Bay and Cu and Zn in Dulas Bay (Anglesey).

Discharges from Sellafield have declined markedly since the late 1970s and early 1980s, although changes in reprocessing practices have led to a recent increase in some radionuclides, most notably ^{99}Tc. Because of the lower levels discharged, the reservoir of radionuclides held within the Irish Sea sediments, particularly those from the mud patch and nearshore zone off Sellafield, is now of greater importance as a source of longer-lived radionuclides such as ^{137}Cs and the transuranides. Indeed there is a body of evidence strongly suggesting that ^{137}Cs is desorbing significantly from the sediments, both in subtidal and intertidal areas[1, 2].

Whilst the project examined the entire Irish Sea system, the focus was on processes in the Sellafield mud patch, inshore areas of sediment with higher radionuclide contents and in intertidal areas where there is most direct interaction between members of the public and contaminated sediments and biota. The mud patch has been extensively studied, particularly to try to establish sedimentation rates (which appear to be very low[3]) and to assess the impact of bioturbation, which studies indicate to be significant over depths of 10s of cm[3, 4]. There has been little work done on the impact of storms in resuspending fine-grained sediment[3], permitting its transport within and outside the mud patch and inshore areas. Recent studies in other parts of the world[5] indicate that particulates re-suspended during storms are extremely effective at scavenging radionuclides from the lower half of the water column. The project addressed the specific impact of storms in the NE Irish Sea by work on 3-D numerical modelling and careful examination of sediment cores (e.g. for signs of storm lag horizons). The cores provided material for targeted in-depth laboratory studies which examined in detail, at the local scale, the relative importance of different processes by an integrated range of non-destructive and destructive tests.

The storm-driven circulation of the Irish Sea, and the associated increase in bed stress and sediment movement, are produced not only by wind events over the Irish Sea but by shelf wide storms[6]. Consequently, it is necessary to have both three dimensional models covering the whole shelf and higher resolution limited area models of the eastern Irish Sea (which can take account of bed forms and types) of the form developed at the Proudman Oceanographic Laboratory (POL).

Scavenging of radionuclides occurs by both sorption and co-precipitation processes. Sorption is particularly important and can be inversely correlated with grain size[7]. Hence, the higher proportion of finer material present in the sediment profile, the higher the concentration of radionuclides sorbed. In addition, the redistribution of silt particles is a major mechanism for radionuclide transport from Sellafield in the Irish Sea[8]. Early diagenetic processes within the unconsolidated sediment profile can also affect the radionuclide inventory. In particular, sorption or co-precipitation of radionuclides with authigenic phases (such as Fe, Mn-oxyhydroxides), or the reduction of soluble species (e.g. U^{6+}) to insoluble species (e.g. U^{4+}) during sulphide reduction in the upper few cms of sediment, can effectively retard or immobilise radionuclides.

In order to understand the relative importance of physical, biological and chemical processes it is necessary to identify the key processes occurring at the sediment-water interface and within the top layers of the sediments. This can be achieved by a detailed characterisation of the existing and potential hosts for radionuclides within the benthic environment. Several studies have examined the fate of radionuclides in the marine environment at the gross scale to determine patterns of radionuclide movement, particularly in coastal and estuarine areas. Although inferred as potential mechanisms, few of these studies attempted to identify the specific processes that occur within the sediment pores, which will ultimately control the transport behaviour of radionuclides and their interaction with the ecosystem. Potential release mechanisms could include desorption and dissolution of host phases during sediment reworking or changes in porewater chemistry. The results of the detailed studies at the sample scale need to be placed in the larger scale context of the Irish Sea system to further evaluate their relative impact.

A recent BGS study for MAFF[2] highlighted areas of uncertainty with regard to the distribution, remobilisation and inventories of radionuclides in intertidal sediments. The most significant of these was the focus of a part of this study.

One of the major scientific issues that was addressed was the importance of biological processes on the fate of pollutants, particularly radionuclides. This required more detailed information on biological communities in the Irish Sea and, in particular, their relationship with environmental (sediment) parameters. There was also a need to demonstrate the effects of different biota on mixing consequences for radionuclide profiles. Macrobiological sampling was undertaken on box-cores from the NE Irish Sea and biota identified and counted. Patterns in community distributions were matched with grain size characteristics, radionuclides, stable elements and other environmental factors using multivariate statistics.

The mesocosm facilities at the MBA's Plymouth Laboratory were used to study the mixing behaviour and assimilation of sediment-bound radionuclides. Such an approach has recently proved valuable in a study of metal bioavailability in Dogger Bank sediments (DETR funded[9]).

2. Scientific Objectives

The objectives of the project, as set out in the original proposal with some modification in the course of the project were:

1. Review of existing knowledge of the importance of physical, biological and chemical processes on the speciation and transport of pollutants in the Irish Sea, with the emphasis on radionuclides. This was summarised in a report accompanied by the compilation of a bibliography of recent published source material and tabulation of important data sets. Possible associations between radionuclides and other contaminants and their movement and fate were investigated. Compilation of relevant thermodynamic/chemical speciation data formed a small part of the review.

2. Appraisal of the large volume of data held by BGS on sea floor bedforms and sediment types, including Hydrographic Office (HO) data, with physical oceanographic data and models to re-evaluate sediment distributions, predict sedimentation patterns and separate areas of sediment accretion from zones of relict sediment or erosion. (N.B. The HO data were not reviewed in detail because they were too extensive and there were unresolved questions of royalty payments to HO).

3. Evaluation of the relative importance of each of the three groups of processes, based on current knowledge, and identification of significant gaps in knowledge formed part of the report. This was used to refine and focus the field and laboratory studies carried out during the project and define recommendations for possible future research.

4. Revision of the proposals for field and laboratory studies and agreement of a detailed programme of work with MAFF

5. Examination of existing data for the sediments in the NE Irish Sea to identify 'typical' sites for the collection of sediment cores for detailed study. Collection of material for laboratory investigation. Macrobiological survey of the NE Irish Sea cores and analysis of community distributions in terms of environmental variables.

6. Examination of the sedimentary record in the intertidal zone to reduce uncertainties in the radionuclide inventory.

7. Laboratory studies on collected samples to investigate in detail the distribution of radionuclides (and other contaminants), the relative importance of different hosts, their stability with respect to radionuclide remobilisation during reworking (whether physical or biological) and diagenesis, and mechanisms controlling partition between different solid and aqueous phases, including:
Core logging
Macro- and micro-biology
Chemistry
Mineralogy and petrology
Gamma and alpha spectrometry

8. Calculation of revised intertidal radionuclide inventories based on the depth of contaminated sediment, calculated areas of each environment and profiles of radionuclides with depth.

9. Assessment of temporal changes in radionuclides in intertidal sediments by comparison of new sample studies and new work on archived samples collected up to 20 years previously (and earlier published studies). This allowed evaluation of the relative importance of different processes over longer timescales.

10. Assessment of the bioavailability of radionuclides in subtidal sediments from the Sellafield mud-patch.

11. Mesocosm studies to assess the kinetics of radionuclide remobilisation by bioturbating organisms introduced into subtidal sediments from the NE Irish Sea, including the Sellafield mud-patch and the surrounding areas.

12. Development of conceptual and computer models of sediment transport and associated pollutant transfer. Determination, using existing three dimensional models of the shelf and Irish Sea, under which wind and wave conditions significant sediment, and associated pollutant, movement can occur in the eastern Irish Sea. The importance of wave-current interaction and reduction of bed stress due to self stratification upon the mobilisation of sediment, and appropriate formulations of turbulence to use in these models to correctly account for the above processes and hence predict sediment movement.

13. Synthesis of results and final evaluation of the relative importance of different processes on pollutant speciation and transport in the Irish Sea. Recommendations for further research.

3. Primary Milestones

The major milestones for the project, as specified in the proposal were as follows (the initial part of the number is the objective number, followed by the primary milestone number for that objective):

No.	Milestone
01/01	Review report(s) (also primary milestone for objective 3) and revised programme of detailed investigations (objective 4)
02/01	Sediment distribution, sedimentation type (accretion, erosion, relict), sediment transport maps
05/01	Completion of offshore sampling (Sellafield mud patch) (also part of objective 10)
06/01	Completion of intertidal survey work
07/01	Reports on laboratory studies on samples
08/01	Reports on revised intertidal radionuclide inventories and temporal changes in radionuclide inventories (also objective 9)
10/01	Completion of surveys of intertidal biological material (N.B this aspect of the study was dropped due to access problems arising from the outbreak of Foot and Mouth Disease)
11/01	Complete implementation of mesocosm studies
12/01	Setting up numerical models and simulation of a storm.
12/02	Completion of further storm simulations and a sensitivity study of wave effects and self stratification.
13/01	Final project report(s)

4. Methods

The first stage of the project was a review of current knowledge that was presented as a BGS Technical Report[10]. Included in the report were new compilation maps of sea bed sediments and sedimentation type/regime. As part of the review process an extensive reference list was drawn together in the form of a library using Endnote software. This list has been added to throughout the lifetime of the project and now includes almost 1400 recent references. The Endnote library and an exported text version (Word document) are available along with a range of other data files.

Following on from the review, field sampling was carried out in two areas: the offshore zone, largely on the mud patch off Sellafield and adjoining areas, and the intertidal zone. The intertidal sampling was concentrated on the two largest expanses of tidal flats in the NE Irish Sea, those of the Solway Firth and Morecambe Bay (including the adjacent Duddon Estuary). In addition to a programme of laboratory work on the samples, a variety of modelling was undertaken. This included chemical, biological and hydrodynamic modelling.

The offshore sampling was carried out using a box corer. This recovered large, relatively undisturbed, sediment samples. Subsamples were taken from the box cores immediately following collection; three 6cm diameter plastic tubes were pushed into the sediment to obtain samples for BGS investigations. A larger (11cm diameter) pipe was used for macrobiological study at the MBA laboratory in Plymouth. The smaller subcores were sealed in aluminised layflat tubing, filled with inert nitrogen gas and stored at 5°C to try to preserve them in their seabed condition. The larger subsamples were stored in a tank of aerated seawater to maintain the integrity of the core. After subsampling, the residue of sediment in the box was sieved to recover the > 0.5mm fraction for identification and counting of the macrofauna. For analysis of this biological data, non-parametric multivariate techniques were employed using *PRIMER* (Plymouth Routines In Multivariate Ecological Research). The overall reason for investigating benthic faunal communities, in this study, was to see how the occurrence of different communities was related to sediment properties, such as grain size and composition.

A wide range of techniques was applied to the cores. Firstly, continuous gamma spectrometric logging was carried out. This non-destructive technique provides information on the distribution of gamma-emitting radionuclides with depth. The cores were then cut longitudinally, photographed and X-rayed and sedimentological descriptions were made. One half core was air dried and covered with alpha and beta sensitive autoradiographic materials. These provide a detailed surface distribution of alpha and beta emitting radionuclides. The mineralogy of the core surfaces was examined rapidly using a portable infrared mineral analyser (PIMA). The gamma profiles, autoradiographs and associated initial data were then used to select a subset of cores for more detailed investigation. Small blocks of core were resin-impregnated and prepared as polished thin sections. The thin sections were then covered with autoradiographic films to enable the sources of alpha and beta tracks to be examined precisely. This was done using both optical and backscattered electron microscopy (BSEM). Grains responsible for high alpha and beta track densities were investigated using energy dispersive X-ray analysis (EDXA).

Background information on the surface area and particle size distribution of the offshore sediments was obtained to investigate whether they were significant influences on the radionuclide distribution. The surface area of the sediments was determined by the 2-ethoxyethanol (or EGME) method, which gives a measure of the available surface area.

The matching parts of the other half core were sampled, split and the radionuclides analysed by gamma spectrometry and alpha spectrometry, major and trace inorganic elements by X-ray fluorescence, organic components (most notably PAHs) by HPLC and fluorescence detection, TOC by high temperature oxidation following carbonate dissolution and particle size by sieving and X-ray Sedigraph. The bulk and clay fraction mineralogy were studied using X-ray diffraction. Subsamples were taken for microbiological analysis, including an assessment of sulphur cycle organisms.

The larger box core subsamples were seeded with different burrowing infauna in mesocosm experiments at the MBA Laboratory, Plymouth. After a period of 10 months the cores were gamma logged, allowing the impact of the fauna on radionuclide distribution to be assessed. Some cores were also sectioned in order to measure down-core concentrations of ^{241}Am and ^{137}Cs. Burrows were tested by autoradiography and some burrowers were recovered for assessment of radionuclide uptake. Selected cores were examined for pore water chemistry, Eh, pH and sulphur species bacteria. The results were examined in conjunction with chemical speciation modelling carried out using the PHREEQC code. Sequential extraction geochemistry was carried out on a pair of samples from one of the offshore cores.

Intertidal coring was intended primarily to attempt to address the depth extent of contaminated sediment with a view to improving radionuclide inventories. Initially a range of methods of sampling, plus core logging, or in situ borehole logging was considered. Eventually a preferred method using a small 3m vibrocorer was chosen. This was used to sample across the Solway Firth, in the Duddon Estuary and Morecambe Bay. The cores obtained were treated in a very similar way to those collected offshore, with a range of detailed studies being applied to a subset of cores.

Hydrodynamic modelling was undertaken at POL using a range of scales of model.

5. Results

5.1 Offshore Samples

5.1.1 Sedimentology

The sea floor off Sellafield is covered by mud and fine-grained sand with broken shell debris. A broad belt of mud-rich sediments extends in the nearshore zone around Cumbria from south of Walney Island to Workington, and then across the outer Solway Firth to the coast of Dumfries and Galloway. The recent sea bed sediments are of variable thickness from less than 1 to 40 m thick. Extensive trawl scours occur, locally exposing the underlying Quaternary sediments[11].

Bioturbation of the sediments is evident in all the cores. The use of X-radiography has allowed identification of *Palaeophycus*-type clay lined burrows and *Teichichnus*-type burrow traces with internal layered sediment fills (spreiten). *Palaeophycus* is a combined feeding/crawling trace which, although not diagnostic of a particular water depth, is commonly found in lower shoreface sediments. *Teichichnus* burrows are produced by infaunal deposit feeding animals, probably worms, and are often found in muddy, subtidal environments, typically from the middle to outer shelf. Thin slender (1-2 mm wide) vertical or inclined tubes, typical of shallow water oxygenated environments, are also abundant in the cores. Bivalve feeding tubes and escape burrows, formed by an organism moving rapidly to the sediment surface following sudden burial by sediment, also appear to be present.

Bi-directional wave ripple lamination is commonly observed in coarse silts to fine sands within the cores. Symmetrical and slightly asymmetrical ripple forms often show internal structure that is form-discordant confirming their wave origin.

Shell-rich fine sands, comprising a chaotic mixture of reworked whole valves and shell hash within muddy sediments, are a conspicuous feature of the offshore cores. Whole *Turritella communis* shells, or single valves of bivalves, are most common with varying amounts of shell hash. Sometimes the beds are bioturbated, with the burrow traces extending into overlying beds. The shell lags are often overlain by sands showing indications of rapid deposition, such as the inclusion of wisp-like mudflakes or parallel lamination. These beds are interpreted as the products of rapid deposition from storm-induced currents, and infer transport of sediment away from the coast. The shell beds show no obvious grading or fabric, which is often observed in proximal storm beds. Scoured surfaces are also commonly recorded from storm-affected shelf seas, and mud-filled scours within silt were observed in one core, but the shell beds do not appear to have scoured bases in the cores studied.

During intense storms, especially when they coincide with high tides, sediment is eroded in the nearshore region and transported out across the shelf by the storm-enhanced ebb current, or a storm-wave density current. The deposition of sand is often preceded by slight erosion of the shelf mud. The presence of a shell layer often marks the base of a storm sand layer. With decreasing wave energy, suspended sand settles to form parallel laminated and subsequently wave rippled sand. In the last phase of deposition, from the waning energy flow, a mud blanket is deposited on top of the sands. Normal shelf mud deposition then follows, and organisms may re-colonise the substrate leading to bioturbation especially of the upper layers of the storm beds. Escape burrows are an uncommon but distinct feature of storm beds. More commonly, burrow traces often stop at a particular surface, which can mark the recolonisation by animals of a new substrate after rapid sediment deposition.

Comparisons can be made with the storm layers in the German Bay, North Sea[12]. The offshore Sellafield examples could be called "proximal" storm sands due to their close proximity to the shoreface source areas. Proximal storm beds include a mixed fauna comprising winnowed parautochthonous bivalves together with allochthonous shell debris introduced from tidal channels or tidal flats. This fits well with the presence of intertidal *Cerastoderma edule* shells mixed with subtidal species, most notably of *Turritella communis.* However, the shells could be eroded from earlier Holocene intertidal sediments, now offshore. This could only be resolved by dating specific occurrences. The grain size of the storm layers mostly falls in the fine sand to silt range which is sufficiently fine for transport in suspension under storm currents in the German Bay.

Turitella communis, appears to be less common in the Irish Sea today than at other times over the last few thousand years[13]. Vibrocores have shown that the muddy sediments off Cumbria, which extend to a depth of several metres, locally contain layers of shell debris up to 0.5-1.0 m in thickness with abundant shells of *Turitella communis* Risso[11]. Other common bivalve species recorded in the Irish Sea include *Abra alba* (Wood), *A. prismatica* (Montagu), *Corbula gibba* (Olivi), *Cultellus pellucidus* (Pennant), *Dosinia exoleta* (Linnaeus), *Spisula elliptica* (Brown) and *Venus (Chamelea) striatula* (da Costa). *Like Turitella communis*, *Corbula gibba* is rarely found living today. The significance of the shell debris (or 'fossilised') faunal assemblages found in the cores is twofold:

i) the probability that many shells have been reworked from scoured earlier Holocene intertidal and subtidal sediments, evidence of which is provided by carbon age dating[3]

ii) the mixture of intertidal and subtidal species may be partly explained by storm reworking of nearshore sediments and their subsequent deposition further offshore, but the abundance of older Holocene forms complicates interpretation.

5.1.2 Radionuclide profiles

In general, the depth profiles of gamma-emitting radionuclides fall into a small number of types. Typically, muddy samples with higher ^{137}Cs contents, particularly those near Sellafield, are characterised by relatively low near surface ^{137}Cs values that rise with depth to a peak and then fall off towards the base of the core. The most pronounced peaks are seen in the highest activity samples that occur inshore, from just south of the outfall to just north of Whitehaven. The Cs contents reach their maximum values at a depth of between 15 and 35cm, with 20-30cm being most common. Offshore, the sediments from the 'mud patch' also show a Cs peak with depth, but it is more subdued, with lower maximum Cs levels that appear to be slightly deeper, at 30-40cm. At greater distance from Sellafield, and where the sediments are sandier, the cores show little variation in Cs content with depth and lower Cs contents.

The group of most active cores all have an extensively burrowed surface zone 10-20cm deep, with no apparent sedimentary lamination and lower Cs levels. This probably corresponds to an intensely bioturbated oxygenated surface horizon. Burrows are still common below this horizon, but sedimentary laminations are preserved, indicating that bioturbation is less intense. Layers rich in fragments of bivalves and turritellids, or scattered complete or fragmented shells, occur frequently. The Cs content increases markedly in this zone to peak values and then declines sharply to the base of the cores.

Similar patterns are seen in the autoradiography, with greater relative track intensities below 10-20 cm and generally similar depths for peak relative intensity. The gamma depth profiles are consistent with models that incorporate both an element of sediment accumulation and one of mixing through bioturbation or physical processes[14]. They thus have the form of a modified Sellafield discharge history, where the integrated pattern of releases is smoothed by mixing, but the late 1970s maximum is apparently preserved.

There may be problems, however, with such an interpretation. Available evidence[3] suggests that sedimentation rates in the NE Irish Sea are extremely low (~0.1 mm y^{-1}) and not consistent with implied rates of more than 1cm per year from the subsurface ^{137}Cs maxima. Several authors[3] have stressed the importance of bioturbation in mixing radionuclides within the sediment. It is felt to be responsible for the great variety of radionuclide profiles observed in cores. However, our profiles, from both gamma logging and autoradiography, appear to fall into a relatively small number of types.

Much of the previous work in the NE Irish Sea has focused on the mud patch and concentrated on the area of greatest fine sediment content, some 15-20 km offshore. The present work also investigated this area, but in addition focused on the area of highest radionuclide contents in the surface sediments, which lies only 3-4 km from the shore[3]. This may explain why we have seen more evidence of primary depositional sedimentary structures than observed by earlier studies. ^{238}Pu/^{239,240}Pu ratios have varied in Sellafield discharges over time. Data for the core samples are consistent with variable degrees of mixing of Pu discharged at different times. One core showed relatively little change in the ratio with depth, indicating a high degree of mixing. More commonly, the data show progressively earlier discharged material with depth. Taken overall, the available evidence would appear to support a depositional regime for the inshore, most active sediments, modified by bioturbation. The mesocosm studies, taken in conjunction with faunal community distribution (section 5.1.9) offer the possibility of quantifying the degree of mixing by burrowing fauna.

The low ^{137}Cs contents in the near surface sediments are consistent with observations of the decline of ^{137}Cs levels over time from the surface offshore sediments[1]. A similar (though smaller scale) reduction of actinide levels has also been observed[15]. The evidence supports loss of Cs (and actinides) from the surficial sediments into the water and its wider dispersion.

5.1.3 Mineralogy and Petrology

The offshore sediment cores all have very similar mineral assemblages. They are dominated by major quartz, with subordinate amounts of calcite, plagioclase feldspar (determined by XRD as albite), orthoclase (potassium feldspar), chlorite, mica and pyrite. Kaolinite was also tentatively identified in most of the samples. The only observed variation in bulk sediment mineralogy was in the relative proportions of these minerals, and the tentative identification of trace amount of dolomite and/or amphibole in a few cases. The minor amounts of halite identified in virtually all of the samples represents halite precipitated from residual porewater (seawater) during drying of the cores, and is an artefact of the sample preparation.

The clay mineralogy of the offshore sediments shows little variation, and the same assemblage of clay minerals is found in virtually all the samples. This is consistent with screening results from PIMA analyses. The clay mineralogy of the sediments comprises chlorite, illite and kaolinite. No evidence of smectite or other expandable (swelling) clay minerals were detected in any of the offshore samples. The clay mineralogy is consistent with the results of earlier studies of offshore sediments in the Irish Sea[10]. The offshore sediment mineralogy differs significantly from that of the estuarine, intertidal and alluvial sediments of west Cumbria and Lancashire, which contain mixed-layer clays - particularly illite-smectite. The clay mineral assemblage resembles closely the mineralogy of the Quaternary glacial deposits of the Isle of Man. Therefore, it seems likely that most of the offshore sediment is derived from the reworking of older glacial sediments (East Irish Sea Drift) on the seabed.

The EGME surface area reflects the amount of clay minerals present. No systematic relationship was observed between sediment radioactivity, recorded by gamma logging or alpha and beta autoradiography, and either the EGME surface area or clay content of the individual sediment profiles. It should be noted however, that a large proportion of this clay material is present as pelleted mud - probably faecal pellets. It was disaggregated during grain size analysis. Therefore, in reality, much of this clay represents originally sand-grade sediment and not material primarily transported or deposited as mud.

The petrography of the samples reveals a consistent suite of predominantly fine-grained sediment. This ranges in particle size from clay-fine sand, i.e muddy sands and sandy muds in the Folk[16] classification. The sediments are extensively bioturbated, poorly consolidated wackes (muddy matrix-supported sands). Diagenetic overprinting comprises minor pyritisation and rare calcium carbonate cement formation (calcite or aragonite) associated with detrital clay.

The framework components of the sediments are dominated by monocrystalline quartz, with minor amounts (typically <5%) of polycrystalline quartz, potassium feldspar, plagioclase feldspar, lithic material (reworked igneous, metamorphic and sedimentary rock fragments), chert and heavy minerals. The grains are largely angular to subangular. Calcareous bioclastic debris is present in variable amounts (<5 to c.10%), and comprises an assemblage of foraminifera, ?ostracods, molluscan debris, echinoderm fragments, and some unidentified bioclastic fragments. Minor amounts of phosphatic debris (apatite- or collophane-replaced bioclasts) are also present. Altered detrital Ti-Fe oxides, magnetite, ilmenite, and fragments of hematite are present as minor to trace components. Other trace detrital minerals include zircon, rutile, and rare monazite and xenotime.

The ductile detrital components are dominated by a combination of ‘matrix’ clay and mudclasts. The matrix clay lines, fills and locally bridges pores, has a granular appearance and is highly birefringent in transmitted light, and shown by BSEM-EDXA to be of an illitic composition. Some areas of the mud matrix appear to be relict clasts (pseudomatrix). Discrete mudclasts are well rounded and may contain appreciable amounts of silt-grade (and finer) granular material, and may have concentric clay-rich outer margins. The origin of these clasts is ambiguous, however, the well-rounded (pellet-like) morphology and internal fabrics of some these grains is strongly suggestive of a possible faecal origin. Alternatively, they may represent clay-filled burrows. However, this seems unlikely given the fact that ‘tubes’ of similar material have not been observed in thin section.

Organic matter occurs in all samples, and is most typically seen associated with detrital clay. However, organic matter is also present within body cavities of bioclasts and as distinct detrital grains. Detailed BSEM work indicates that this material is partially pyritised, and framboidal pyrite has been observed in close association. Coarse fragments of coal are present in some samples. These often contain very fine-grained disseminations of pyrite, or concentrations of pyrite along fine laminae. Rare glauconite pellets are noted in most samples. Minor muscovite mica is also evident in some samples.

Diagenetic overprinting is minor, with pyrite noted in most of the samples. It is commonly associated with detrital clay, and more rarely within the body cavities of bioclastic debris. The pyrite forms spherules and framboids, which replace detrital organic matter and line interstitial porosity. Framboids of pyrite, and thin films of minute (sub-micron) pyrite crystals, rest on or coat the surfaces of calcitic shell fragments. These appear to be associated with possible organic films on the surface of the shelly detritus. Authigenic pyrite was found throughout the sediment profiles. The formation of authigenic pyrite within the intergranular porosity, as well as within isolated internal cavities of bioclasts, indicates that the sediment porewaters are generally reducing.

In addition to pyrite authigenesis, a glauconite-like clay mineral has formed diagenetically within these sediments. It is uniquely associated with altered calcareous shell fragments. The surfaces and margins of many of the shell fragments contain numerous micro channels and cavities. These are typically 10-20 µm in diameter and up to 200 µm long, and probably represent the borings of microorganisms such as fungi or algae. Detailed BSEM-EDXA observations reveal that they are lined by a very fine-grained illitic clay mineral. However, it also contains iron as a major component of its chemistry, which would indicate that it is either ferroan illite or glauconite-like clay. Because it has not been possible to confirm its mineralogy precisely, it is referred to hereafter as 'glaucony' (by convention) since glauconite is strictly defined. The presence of glaucony suggests low sedimentation rates and thus supports the conclusions of previous studies[3]. The glaucony typically forms microglobular masses, which line or partially fill the cavities produced by boring microorganisms. The 'globules' vary from 1-10 µm diameter, and may sometimes have a cellular appearance. Framboidal and fine-grained pyrite is also present in many of these cavities. However, the pyrite usually rests on top of the glaucony, suggesting that it has a slightly later paragenesis. Some of the samples contain minor amounts of authigenic calcite associated with the detrital clay. The calcite occurs as tiny rhomb-like crystals or diffuse patches of cement growing displacively within, or replacing, the clay matrix. Traces of authigenic calcite have also developed as overgrowths on some calcareous shell fragments. The pyrite and glaucony authigenesis is closely associated with enhanced α and β radioactivity within the rims of altered shell fragments. Possible authigenic apatite was noted in two samples. It occurs as thin overgrowth rims on the surfaces of detrital apatites.

Dissolution of unstable calcareous shell debris is a major diagenetic feature in all of the offshore sediments. Many of the shell fragments are corroded and have been partially removed by dissolution. Dissolution affects a wide variety of types of bioclastic material including; the bi-laminated-fibrous fragments of molluscan shells, foram tests, and echinoid fragments. Other calcareous fragments are unaffected by dissolution, and can often be found adjacent to altered shell fragments.

5.1.4 Autoradiography

Autoradiography demonstrated that there are several different mineralogical sources and controls on the distribution of radioactivity in the offshore sediments. These different sources vary in the amount of radioactivity that they host and in their distribution in the sediment profile. Sediment profiles with enhanced levels of radioactivity have alpha and beta radioactivity concentrated mainly in the fine-grained muddy matrix material. Areas of matrix enhancement show diffuse alpha tracks throughout the fine-grained 'mud' component, accompanied by higher concentration radioactive 'hot-spots' associated with very small and very radioactive organic grains. Detailed petrographical analysis suggests that these particles are gel-like or amorphous, and are very magnesium-rich. They differ from previously reported hot particles of obvious effluent origin[3]. This may reflect diagenetic breakdown; particles with a well-defined shape were observed previously only in surface sediment and water and appeared to be dissolving at depth[17]. The high Mg content could reflect the original Mg-alloy casing of Magnox fuel. The observations suggest that a significant proportion of the radionuclide contamination is associated with clay minerals and disseminated organic matter. Previous reports have not used BSEM, but link the particles to BNFL effluent on the basis of U isotope ratios and the presence of Pu and Np[3, 17].

Shell detritus also appears to contribute significantly to the radioactivity of the sediment. This association does not appear to have been observed previously. The most radioactive shell debris is generally found in the part of the profile exhibiting enhanced radioactivity. High concentrations of radioactivity are localised in the altered and corroded margins of shell fragments, where they have been bored by microrganisms. The radioactivity is very closely associated with authigenic fine-grained pyrite and glaucony - which have precipitated within the borings and on the altered shell surfaces. A variety of shell types have more radioactive rims, but similar shells may not have concentrations of radioactivity. The evidence suggests that the age of the shells may be the critical factor; modern shells with associated organic matter creating local microbially-driven reducing conditions on burial, with the precipitation of sulphides and redox-sensitive radionuclides. Older Holocene shells, lacking organic matter, would not promote such reactions. Corroded shells might be expected to be composed of relatively unstable aragonite or high-Mg calcite. However, there is no evidence for preferential association of 'hot spots' with certain types of shell fragment.

The influence of burrowing organisms on alpha distribution is seen in burrows, which are infilled by relatively alpha-rich muddy matrix material, contrasting with less alpha-rich sediment in the surrounding core. This suggests that burrowing organisms can have an important effect on the redistribution of radionuclides in the sediment profile. Observations from whole-core autoradiographs suggest that the larger burrowing organisms are most important, and that they may introduce radioactivity into lower activity near surface sediments from underlying more contaminated sediment horizons. Smaller, slender burrows have less influence on the distribution of radioactivity.

5.1.5 Inorganic geochemistry

Interpretation of the geochemical data, in conjunction with particle size, radionuclide content and other parameters involved the use of correlation coefficients, scatterplots, regression analysis and multivariate statistical analysis. This was applied to both offshore and intertidal datasets.

In general the offshore Irish Sea samples have a much higher mud content than the intertidal Solway Firth sediments. For both datasets, mean and median values for most elements are very close, indicating near normal distributions of concentrations. Standard deviations are generally small, the notable exceptions being for ^{137}Cs and ^{241}Am, particularly in the Irish Sea dataset. The grain size differences between the datasets are reflected in the overall higher metal values found in the Irish Sea samples, in line with the commonly observed association between high metal values and fine particulates. Silica is, of course, higher in the sandy Solway samples, whilst Ba, Cs, Ge, Mo and U maintain similar levels in both datasets.

The data generated by the project were treated both as a single entity and separately as offshore and Solway subsets. Correlation coefficients for the 63 samples of the combined dataset show that most elements are strongly associated with the mud content of the sediments. Only TOC, Cs, Ge, Mo, Ba, U, ^{40}K, ^{137}Cs and ^{241}Am fail to show this relationship. Overall, the radionuclides are relatively weakly correlated with other elements and each other, whereas the heavy metals generally show strong positive correlations with each other and with Al_2O_3, which is associated with the clay mineral content of mud, and Fe_2O_3, representing oxide coatings on fine particulates that 'scavenge' trace metals. These grain-size related factors apparently have a much stronger influence on the distribution of metals than complexing by organic compounds, as represented by TOC. Although ^{137}Cs and ^{241}Am do not show strong correlation with the mud content, the large differences in their levels between the sandy Solway samples and the more muddy Irish Sea samples, along with significant positive correlation coefficients with Al_2O_3, shows that they are preferentially concentrated in the finer grained sediments.

When the Irish Sea dataset is considered alone, correlations with grain size and related factors are still clear, but less strong than for the combined dataset, reflecting the generally smaller spread in values for almost all elements. Offshore and intertidal sediments are considered together in terms of heavy metal contamination. Samples which depart from a normal regression trend when heavy metals are plotted against Al_2O_3 and Fe_2O_3 can be considered to be contaminated[18]. In general, metal contamination does not present a problem, the highest values (in ppm) of 24 Ni, 25 Cu, 101 Cr, 54 Pb and 113 Zn all occur in a core from off the coast between Whitehaven and Workington. The only other contamination of any significance is in Cd. None of the samples from the Irish Sea are enriched in Cd, but all the cores from the Solway Firth have more than 3 ppm Cd at some part of their depth profile.

Multivariate data analysis identified 7 distinct physico-chemical units within the Irish Sea chemistry data. Three units were associated with the fine sediment fraction (Fine Silt and Clay Fraction - Pearson correlation coefficient 0.89); a Clay Fraction – predominantly made up of Si and Al, an Fe/Al oxide fraction –predominantly Al and Fe with a high proportion of organic C and a Silt/Fine Sand Fraction – predominantly Si (>85%).

Four units were associated with the coarse sediment fraction (Coarse Silt and Sand - Pearson correlation coefficient 0.95): Sand 1 – This material is probably a relatively coarse sand (>85% Si), Sand 2 – probably another relatively coarse sand which has slightly less Si(c. 80%) and slightly higher Ca (c. 8% compared to ca.2% in Sand 1) content than Sand 1, Carbonate 1 – is predominantly made up from Si (c. 40%), Ca (c. 20%) and organic carbon (c. 18%). This is probably sand coated with appreciable shell content and; Carbonate 2 – this is probably also sand with shell fragments. It has a higher proportion of Si than Carbonate 1 (c. 55%) but a lower organic carbon content (c. 8%). Most of the mass of the sediment samples is found in the two sand components that make up the coarse fraction and the clay component of the fine fraction of the samples.

Uranium is mostly associated with a coarse sand fraction and the clay component with smaller amount associated with the carbonate phases. When compared to the CISMeD[19] sequential extraction test data there is good agreement between the two independent methods and both showing that the easily extractable U is associated with carbonates. Thorium is mostly associated with the clay component with a smaller amount being with sand, silt and Al/Fe oxide components. There is good agreement between the two methods for both core samples showing that most of the Th is in a non-extractable form and that the extractable Th is mainly associated with Fe oxides.

Cs is mainly associated with the Clay and Coarse Sand fractions with smaller amounts in the oxide and carbonate phases. The agreement for Cs between the CISMeD test and total element modelling is not quite as good as for U and Th since the total sediment data model suggests that there is more Cs in extractable forms as carbonates and Fe oxides than found by the CISMED test but both methods show that most of the Cs is in a non-extractable form.

5.1.6 Sequential extraction

The solid phase distribution of trace metals, including those that account for potential radioactivity (Cs, Th and U), within an offshore Irish Sea sediment core were examined by sequential extraction techniques. The methods used were a traditional Tessier sequential extraction scheme[20] and a new methodology called Chemometric Identification of Substrates and Metal Distributions (CISMeD)[19]. Two samples from one relatively high radioactivity core were used for this study; one from the oxygenated surface sediments and one from a more reducing environment where peak radionuclide levels were observed.

There is generally an increase in the trace and major element concentrations in the deeper sample (median value 14%), which is balanced by a decrease in the Si content of 5%. This suggests that the deeper sample has a higher proportion of secondary minerals than the shallower sample. The elements As, S, Cs and U show the greatest increase with enhancements of c. 50% or greater.

For the total concentration extracted from the CISMeD sequential extraction, there is a more pronounced increase in the deeper sample (median value 24%) for all elements (apart from P which decreases by c.40%) and in particular the elements As, Ni, S and U are enhanced by 95, 123, 123 and 215% respectively. It is possible that the large increase in U in the more reactive fraction accessed by the sequential leaching process is responsible for the increased autoradiography intensity in the deeper sample.

Comparing the total element compositions with studies of similar samples shows that Mn, Ni, and U values are within the range of values found for these samples but the Cr and V values are significantly enhanced. V is possibly derived from oil spillages and Cr, in the past, has been discharged from the Albright and Wilson phosphoric acid plant at Whitehaven. The CISMeD test identifies nine separate extractable components in the two sediments:

(i) Pore-water residual salts

(ii) Exchangeable fraction

(iii) Carbonate 1 - Both samples> 94% Ca.

(iv) Carbonate 2 – A Higher proportion of magnesium than in the Carbonate 1 fraction. (the shallow sample is ca. 56% Ca and 18% Mg and the deeper sample ca. 87% Ca and 9% Mg)

(v) Carbonate 3 – Predominantly calcium, and has appreciable quantities of iron (ca 9% in the shallow sample and ca 13% in the deeper sample). This is probably a mixture of calcium and iron carbonates.

(vi) Organic - Probably an organic/humic acid like material. In the shallow sample this component consists of 57% P by weight and the deeper sample is predominantly Na (c. 35%), K(c.33%) and P (c. 23%).

(vii) Iron-oxyhydroxides – This phase is made up predominantly of Fe (>41% in each sample) and is probably fine-grained iron oxy-hydroxides.

(viii) Iron-oxide –It contains a higher proportion of Fe (c. 70% in the shallow sample and 64% in the deeper sample) and is probably a crystalline iron oxide.

(ix) Clay –It consists predominantly of Fe, Al, Si and K although the deeper sample contains appreciable amounts of S as well (c.19%). The evidence points to this material being an aluminosilicate, probably a clay material.

The three elements that are most likely to show a 'Sellafield' signature (Cs, Th and U) show very different behaviour in their CISMeD extractable fractions. Cs (>70% for both samples) is predominantly associated with the clay fraction with only minor amounts in carbonate and iron oxide forms. Thorium is predominantly bound up in iron oxides (>62% for both samples) with smaller amounts in the clay fraction (>21% for both samples) and minor amounts in carbonate fractions. Uranium, however, is predominantly associated with carbonates (c. 99% in the shallow sample and 78% in the deeper sample). In the deeper sample there are small but appreciable amounts in the more labile fractions (pore-water, exchangeable and organic) and associated with Fe-oxyhydroxides compared to the shallower sample. This is consistent with α autoradiography which also shows an association with carbonate (shells) and organic grains and shell coatings.

Arsenic and vanadium show possible redox effects in the two cores. In the shallow, more oxidising, sample a larger proportion of each element is associated with the more labile forms (pore-water, exchangeable and organic) and for the deeper reducing core the distribution shifts to more of the metal being bound up as either Fe-oxyhydroxides or as carbonates. For the elements Cu, Pb, and Zn the CISMeD test places most of the labile metal (i.e. that not in the residual phase) in the carbonate phase, but the Tessier method shows the metals are more evenly distributed amongst the carbonate, Fe/Mn oxide and the sulphide/organic phases. Recent studies, using a sequential extraction scheme similar to the Tessier method,[21] have shown that Pb, liberated from extraction from the carbonate phase, is redistributed into subsequent phases giving an erroneous solid phase speciation. The evidence presented in this study suggests the CISMeD test, in which the extractant does not remain in contact with the sample for long periods of time, is producing results which are more representative of the true sediment properties than the Tessier method. Solid phase speciation for Hg and Sn in the sediments, using the Tessier method, show that most of the Hg and Sn are associated with the Fe/Mn oxide designated fraction. However, because of the potential for redistribution of metal during a Tessier extraction, the results should be regarded with some caution.

A number of previous studies have examined the phase associations of Cs, Th and U in samples from the around the Cumbrian coast and in the Irish Sea. It was found that 80-98% of Cs in Solway salt marsh sediments is non-extractable[22] compared to 95% of the total Cs in a marine reference sediment[23]. This compares well with the findings of this work (Extractable Cs c. 3-4%). The CISMeD extraction scheme suggests that extractable Cs is associated with a fine-grained clay fraction. This is supported by many other studies.

Previous work has shown that the contaminant radionuclides are dominantly associated with clays and silts in the NE Irish Sea whilst a significant part of the actinide content occurs as coatings on two iron minerals, magnetite and haematite; there is also a significant diffuse distribution associated with hydrated iron oxides attached to quartz grains[24]. This agrees well with the CISMeD results that indicate that both hydrated iron oxides and crystalline iron oxides exist in the sediment under study and that Th, and to a lesser extent U, associates with both of these phases. In a sequential extraction study of non-Irish sea sediment, Th[23] is found mostly associated with the organic/sulphide phase (c. 20%) and the residual phase (c. 80%) but this result may suffer from the problems of redistribution of metals between phases that occur in Tessier-style schemes

Using Tessier-style extraction schemes on reference marine sediments, previous work[25] showed that the extraction profile of ^{238}U was similar to that of the refractory elements Al, Ti, and K. It was also shown that 25% of the total U in the sample was associated with the organic/sulphide fraction and that 54% was in a non-extractable form[23]. In another investigation, which focused on the operational speciation of U in 8 inter-tidal sediments from the Cumbrian coast around Whitehaven, most of the U was found in the organic/sulphide fraction[26]. In the CISMeD test, from the present study, most of the U is found in the exchangeable (carbonate fraction) and the residual fraction. There is a clear suggestion that the Tessier style extraction scheme could be underestimating the amount of U in more labile fractions (i.e. carbonates) because of problems associated with metal redistribution during the extraction.

Further work on a wider range of samples using the new CISMeD test is required if solid phase distributions, representative of the true *in-situ* conditions, are to be determined for elements such as U,Th and Cs

5.1.7 Pore water chemistry, microbiology and geochemical modelling

This study has shown that redox processes (at least some of which are biologically driven, particularly S and Fe cycling) appear to control the chemistry of important elements within the sediment of the Irish Sea. Observations concerning the distribution of Fe, would agree with ferric iron reduction producing soluble ferrous iron. Ferrous iron is thought likely to precipitate as iron-sulphides. This is consistent with the blackening observed with depth in the core and pyrite observed in petrographic work. These iron-sulphides are likely to be unstable phases and may undergo dissolution (probably aided by sulphide oxidising bacteria) that is consistent with a rise in Fe concentration. It has also been noted that, initially, 99% of all Pu entering into the Irish Sea is tied up within the sediment[27]. However, over a longer timescale, 7% enters the oceans and is free for circulation, of which 6% must be mobilised from the sediment. Geochemical modelling has suggested that within the first few cm of the sediment, 90% of Pu is locked up as the insoluble phase $Pu(OH)_4$, but 10% is available as PuO_2^+, thus providing a mobile source for re-entry to the aqueous phase. Furthermore, it was noted that the redox profile may be changed through the burrowing of invertebrates which may expose deep sediment to oxygenated water, and release those elements bound to the solid phase by a low Eh regime. Also, dramatic events like storm disturbance may remove surface sediment. That sediment removed will be oxygenated and redox changes incurred can be predicted to release bound elements. The new sediment surface will also be exposed to oxygenated water, and the oxic conditions may further release more bound elements.

5.1.8 Organic geochemistry

The analysis of 26 marine sediment samples from the offshore and intertidal sampling was accomplished using high performance liquid chromatography (HPLC) and fluorescence detection. The analytical technique permitted the quantification of fifteen PAHs, *i.e.* all the commonly encountered suite of sixteen PAHs specified by the USEPA with the exception of one member that could not be detected because of its non-fluorescent nature.

For the Cumbrian offshore coastal samples the range of total PAH concentrations was 274-4856 µg/kg. Such ranges are fairly typical of marine sediment PAH concentration levels[28].

The PAH distribution patterns revealed that the relative proportions of PAH were similar in all the samples regardless of sampling location and total concentration. They correspond with global patterns typical of PAH assemblages resulting from high temperature combustion of fossil fuels[28]. Such PAH generation is referred to as being *pyrolitic* in origin, distinguishing it from the *petrogenic* (petroleum-derived) PAHs that arise, for example, from fossil fuel spillages. Unlike petrogenic PAH that is dominated by low molecular weight PAHs, pyrolitic PAH is marked by a predominance of the high molecular weight PAHs fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd) pyrene and benzo(ghi)perylene, together with some prominence for the low molecular weight PAH phenanthrene, the most stable of the three-ringed members. It was observed for the offshore sediments that these nine pyrolitic PAHs were the dominant species, in all except one core taken close to Whitehaven and its harbour. It was concluded that the pyrolitic PAH output from local coal-burning industry was probably the main contributor to the relatively high levels of PAH in the offshore samples. The typical pyrolitic PAH signature was modified by a small petrogenic input, assumed to have resulted from incomplete fuel combustion and/or leakage attending shipping activities in Whitehaven harbour.

For two offshore cores where depth profiles were available, the surficial sediment had the lowest total PAH concentration in both cases. Assuming that sediment from the surface is more recent than underlying sediment, this may reflect the decline of coal-burning industry in the Cumbrian coastal region. However, because the surficial sediment is more oxic than deeper sediments, aerobic biodegradation of PAH, a more favourable process than anerobic biodegradation, may be responsible for the diminished surface concentrations.

Some correlation was found between the total organic matter content (TOC) and the total PAH concentration in all the sediments. Given the primarily pyrolitic nature of the PAHs, it is probable that the PAH is bound to soot particles, generated during fossil fuel combustion, and that these formed a somewhat variable proportion of the total organic phase of the sediments leading to a loose though perceptible correlation. The TOC in the offshore Cumbrian sediments had a higher PAH loading than did that in the intertidal Solway Firth sediments. This implies larger concentrations of combustion particles, containing PAH, associated with the TOC of the former, presumably because the Cumbrian coastal region was more industrialised compared to the Solway.

The findings were supported by an alternative form of PAH pattern analysis that employs ratios for certain isomeric pairs of PAHs called molecular indices. The molecular indices revealed the same sort of conclusions that the ranking of abundance had produced, *i.e.* that the offshore Cumbrian sediments contained greater proportions of pyrolitic PAHs, whereas the intertidal Solway Firth sediments had increased contributions of petrogenic PAHs.

5.1.9 Macrobiology

Macrofauna from cores from more than 30 sites in the NE Irish Sea, were identified and quantified. An array of environmental data was also collected including grainsize, organic matter and metal contents, maximum γ-activity and water depth. This data was analysed through multivariate techniques - principal component analysis (PCA) and multi-dimensional scaling (MDS)[29] - to reflect the similarity between sediments at each site and to interpret the main underlying causes of differences between the sediment samples (e.g. grain size, metals and organic content). When grain size distribution in the sampling area is mapped, the overall pattern of sediment distribution in the survey area appears to be primarily oriented parallel to the coastline, approximately north-south, in the direction of residual tidal currents. Fine ‘muddy’ sediments occur in the deepest areas, surrounded by extensive areas of sand, with a relatively narrow band of finer silty sand inshore, north of the Esk estuary.

For analysis of biological data, non-parametric multivariate techniques were again employed[29, 30]. Three groupings were identified based on similarities in assemblages. The first consisted of only one site typical of the gravely or shelly sediments found on sandbanks of the central Irish Sea. In the second grouping the most abundant species were the brittle star *Amphiura filiformis*, the tube building polychaete *Pectinaria koreni*, and the small bivalve *Mysella bidentata*. The latter is often found in association with *Amphiura*, or inhabiting burrows of sipunculids such as *Golfingia procera*, which was also found at these sites. Larger fauna included the burrowing mud-shrimp *Callianassa subterranea*; the heart urchin, *Echinocardium cordatum* and active, burrowing polychaetes *Nephtys* spp. Other notable though less common fauna in this group included the polychaete *Notomastus* and the amphipod *Ampelisca*. Group 3 comprised the remaining nine sites in the median central/southern region of the survey area. Only five species accounted for over 90% of the similarity within this group, the most abundant being the small bivalve *Mya truncata* and polychaetes *Nephtys* spp. Other large, though less abundant species included the mud-shrimps *Callianassa subterranea* and *Jaxea nocturna*, together with the echiuran, *Maxmuelleria lankesteri*. Thus, on the basis of behaviour and size, several species capable of major sediment disturbance feature strongly in the associated communities of the NE Irish Sea.

The final stage in this analysis of field data was to determine the link between environmental variables and the biological communities. This showed that the single environmental variable giving the best correlation (0.560) to biota was the percentage sand fraction of the sediment. For the best 2-variable combination, addition of the overlying water depth improved the degree of rank correlation (to 0.645). Further small increases in rank correlation were apparent upon sequential addition of other environmental variables, including: % silt, 1M-HCl-extractable Ni concentrations (log transformed) and % clay (taking the correlation to 0.658). The combination of the five environmental variables provides the ‘best explanation’ of the biological data. Clearly, grain size distribution appears to be a major determinant of species occurrence together with overlying water depth. As indicated above these factors co-varied, resulting in two major faunal groupings; one set of communities associated with the coarser sandy sediments in shallower regions, another with fine-grained muddy sediments in the median southern section of the survey area (‘Sellafield mud-patch’).

A methodology was developed to measure the impact of bioturbation on radonuclide profiles in the sediments. Offshore sub-cores from Irish Sea sites were maintained intact, in laboratory mesocosms. The majority were seeded with either *Callianassa subterranea* or *Upogebia deltaura* to examine the bioturbatory effects of these major excavators. A small number of cores were seeded with fauna representing different types of bioturbating organism: mobile epifauna (*Turritella communis*), deposit feeding clam (*Mya truncata*) and burrowing echinoderm (*Cucumaria elongata*). Effects of the activities of these organisms on the initial gross vertical distribution of the radionuclides was examined by repeat γ-logging of intact cores. Cores were also sectioned to measure ^{137}Cs and ^{241}Am to confirm profiles obtained by γ-logging.

Following 10 months incubation in the mescosm, the pattern of ^{137}Cs activity in unseeded Irish Sea cores did not change significantly. Counts before and after the incubation period are virtually identical suggesting little redistribution or loss of activity from the sediment. Seeding the sediment cores with *Callianassa subterranea*, resulted in marked changes to the pattern of ^{137}Cs activity. Thus, the peak activity levels, at depth often ~35cm, became more homogenised throughout the core as a result of the excavating activities of these shrimps. There is a corresponding increase in ^{137}Cs counts in the upper 10-15 cm indicating transfer of material towards the surface. The effects of *Callianassa* on remobilisation also extend to the bottom of the cores used in the mesocosm experiment (max 50cm).

Seeding the sediment cores with another species of mud shrimp *Upogebia deltaura* resulted in changes of ^{137}Cs activity, which were similar to those in *Callianassa*, though usually less marked. Peak activity levels at depth were often reduced as a result of the activities of these shrimps, but the increase in ^{137}Cs counts in the upper layers, due to transfer of material towards the surface, is less apparent. These differences may reflect behavioural distinctions between the two thalassinid shrimps. The homogenising effect on sediment profiles of *Turritella*, *Mya* and *Cucumaria* is much less intense, in line with their behavioural and feeding habits.

Simple models were used to quantify the effect of the excavating activity of *C. subterranea* on contaminants buried in sediments. The dispersion coefficients of ^{137}Cs are increased by almost two orders of magnitude from 0.4 to 35 cm^2 y^{-1}. Several *Upogebia* and *Callianassa* were counted for ^{137}Cs and ^{241}Am at the end of the experiments. Concentrations in both species were relatively low and were not magnified with respect to surrounding sediments.

5.2 Intertidal samples

5.2.1 Sedimentology

The Solway estuary is a strong sink for sediment. It has been gradually filling with sediment for centuries and continues to do so. Much of the sediment is reworked Pleistocene material derived from the Irish Sea. The rivers Eden and Esk contribute little sedimentary material to the estuary, except some clay at times of flood. The sediments within the estuary are predominantly sand. Mud layers intercalate with the sands on the higher intertidal flats, especially in sheltered embayments where rivers enter the estuary. Patches of gravel occur locally along the margins of the estuary.

Sedimentation in the firth is controlled by the flood-dominant tidal currents and the funnel shape of the inner Solway Firth, which heightens the tidal range to 8.4 m, allowing large amounts of sediment to be held in suspension. The intertidal sediments of the inner Firth are known to be very mobile due to tidal reworking with frequent shifts of the tidal channels[2].

The very fine to fine-grained nature of the sand fraction, which may contain significant amounts of coarse silt, characterises all the cores taken from the inner and outer estuary. Mica flakes and carbonaceous material commonly occur in the sands. Grain size variations are difficult to delimit within the estuary, with sands being the dominant sediment type. Mud drapes and silty-mud partings occur within the intertidal and supratidal sequences along both the English and Scottish shores of the estuary. A greater proportion of mud is present in the sediments along the northern shore, particularly in the intertidal areas offshore from Caerlaverock nature reserve and just east of the River Annan. On the southern side of the firth, patches of mud occur within Moricambe Bay. But reworking of sediment during high tides means that there are frequent changes in the distribution of the finer, muddy sediments deposited from suspension. It is also likely that gravel lags may be periodically hidden and subsequently exposed along the firth margins due to the shifting sediments. Much of this gravel material may not be a natural occurrence.

Fine, even, horizontal lamination is a very common feature observed in the cores. Units of parallel lamination are intercalated with beds of wave ripples, but horizontal lamination predominates. Sands deposited by the migration of small dune bedforms are indicated by truncated units of tangential cross-bedding seen in two cores. Gravel lags occurs at the base of two cores and may represent the floors of tidal creeks.

Whole or broken valves of shells commonly occur within the cores. A few shells remain articulated and may well be in their life position. But predominantly the shells are transported, disarticulated valves that may be scattered through the sediment randomly, or grouped in thin shell lags. Their state of preservation, distribution and orientation within the cores records the processes involved in the extensive reworking of sediments within the estuary system. Most of the shells are intertidal bivalves, with *Cerastoderma edule*. being most commonly represented. Very finely fragmented shell hash derived from bird predation on the intertidal flats of the Solway Firth occurs scattered throughout the cores, but also forms a shell hash matrix within some beds containing whole valves.

Field observations indicate the presence of a burrowing fauna on the intertidal flats of the Solway Firth. However, clear evidence of burrowing organisms is relatively uncommon in the cores. Structures interpreted with some confidence as fine worm tubes or burrow mottling are confined to the top 30 cm of the cores. The overall paucity of preserved bioturbation structures is, in all likelihood, caused by two factors:

(i) the uniform grain size and lack of clay material to distinguish burrow fills and burrow linings from the host sediment
(ii) the frequent reworking of the sediments on the tidal flats which obliterates most burrow traces and leaves a sedimentary record of parallel lamination and ripple cross-lamination.

Thin bands or clusters of carbonaceous particles occur within several cores. The clusters of carbonaceous particles with mica might, in some instances, represent burrow fills. The likely source of the carbonaceous material is the former coal mining, and iron and steel works, along the west Cumbrian coastal strip.

5.2.2 Radionuclides

Previous studies produced estimated intertidal inventories of radionuclides in the NE Irish Sea[2] to a depth of 50cm. In order to examine the radionuclide contents of the sediments to greater depth, new sampling methods were investigated, culminating in the use of a small (3m) vibrocorer. This provided cores 2-3 times longer than those obtained previously by hand coring. Over 50 cores were obtained from the Solway Firth and Morecambe Bay, although the final phase of sampling was delayed seriously by the outbreak of Foot and Mouth Disease. All the cores were logged on the BGS gamma core logger. The cutting shoe samples, representing the base of each core, were analysed by low background HpGe gamma spectrometry. This was primarily to assess the ^{137}Cs content and thus establish whether contamination was present at depth.

The logger results showed much greater variation than had been seen in previous shorter intertidal sediment cores. Interestingly, no detectable Cs was seen in the basal samples from 7 Solway cores and 12 from Morecambe Bay. The data suggest that the thickness of sediment contaminated by the Sellafield discharges is quite variable in detail, with significant differences between the Solway and Morecambe Bay. In certain relatively nearshore settings less than a metre of contaminated sediment is present, particularly in Morecambe Bay. Further from the shore, there are good indications of 2m or more of sediment containing Cs, especially in the Solway Firth. We do not yet have sufficient evidence to define the depth of the contaminated zone in any degree of detail. However, the evidence does support our earlier suggestion[2] that, in areas of active tidal channel migration, there is likely to be several metres of sediment mixing, taking Cs and other radionuclides at least to those sorts of maximum depths. In Morecambe Bay the total thickness of recent sand is between about 4 and 14 m[31]. There is no comparable information for the Solway Firth, but one can anticipate similar values.

A wide range of profile types was seen in the cores. They range from cores where there is little variation with depth, through profiles that show significant, if variable, changes with depth to cores that display a marked peak of Cs activity. This peak may occur at almost any depth down to the base of the longest cores. The profiles reflect the complex interplay of depositional, erosional and mixing processes in the estuary[2]. The sedimentology of the cores suggests that physical reworking of the intertidal sediments is more important than bioturbation. Cores with little change in Cs content with depth are indicative of the efficiency of that mixing. For half of the cores from the Solway Firth there is no apparent relationship between sedimentary structures and elevated ^{137}Cs values. This is either because K and Cs values are fairly uniform down the core, or because Cs peaks cannot be matched with any obvious sediment feature. However, higher Cs values do seem to correspond to zones of carbonaceous particles with mica flakes, and/or shells or shell hash in several of the cores. Radioactive particles can be associated with coatings around shells (localised reducing conditions) and mud clasts. Organic membranes on the host shells can form localised sites of reduction following death and shallow burial of the organism[32]. This is well documented by the early diagenetic crystallisation of pyrite within algal or fungal borings in shells as well as around the outer surfaces of the valves.

Cores with a single well defined peak (not linked to a change in sediment type) and evidence for sediment accretion, and cores where the base of the contaminated sediment is defined, may be used, in principle, to provide estimates of net sedimentation rates. The method assumes no significant post-depositional movement of radionuclides vertically, through bioturbation, diffusion or porewater advection. Since physical reworking of the intertidal sediments appears to be more important than bioturbation, and statistical analysis of geochemical data indicates that most of the Cs is strongly bound to solid phases, the assumptions may be justified.

Although they should be viewed with caution, the Solway data indicate a range of values between 1 and at least 6 cm y^{-1}. These values are consistent with rates derived from *in situ* gamma spectrometry on Caerlaverock salt marsh in the Solway[33], which ranged from about 0.2 cm y^{-1} on the inner marsh to 1 cm y^{-1} adjacent to the tidal flats. Figures from Morecambe Bay and the Duddon Estuary are similar ranging from 1.8 to over 5.1 cm y^{-1}.

5.2.3 Radionuclide inventories in Solway and Morecambe Bay

Previous inventories were based on large numbers of surface gamma measurements, collected either during hovercraft surveys or on foot. These measurements can now be linked to the deeper core profile data obtained for this study, rather than the shallow cores collected previously. The relationship between surface observations and the complete core profiles has been examined for the Solway and Morecambe Bay cores. ^{137}Cs data for the complete profile has been compared to the near surface data represented by data points for the top 10cm.

In most cases, the top 10cm has lower levels of ^{137}Cs than the complete core, or the part of the core with detectable ^{137}Cs, where the base of the contaminated sediment is seen. Three Morecambe Bay cores and one from the Solway have higher surface levels of ^{137}Cs than the average for the core. The ratio ^{137}Cs top10cm/^{137}Cs whole core averages 0.75 for the Solway samples (range 0.41-1.09) and 0.80 for Morecambe Bay (range 0.22-1.28).

Inventories can be revised in the light of the information from the new cores. The mean depth of known contaminated sediment can be calculated from the cores. This is taken as the base of contaminated sediment, in cases where Cs-free sediment is found at depth, or the base of the core where Cs is still present. The figure, therefore, represents a minimum value and will be an underestimate of the true depth of contaminated sediment. Cores from the Solway and Morecambe Bay give similar mean depths of known contaminated sediment of 1.3 and 1.1 m respectively, before allowance for compaction during coring. Assuming an average compaction rate of 30%, gives uncompacted depths of 1.7 and 1.4m.

Thus the known contaminated sediment depth is extended by a factor of about 3, from the previous mean figure of around 50cm (i.e. 3.4 in the case of the Solway and 2.8 for Morecambe Bay). Given that the surface ^{137}Cs content of the sediment under represents the Cs levels throughout the cores, as given by the ratio of values for the top 10cm compared to the complete core, this increases the overall estimate of the known ^{137}Cs inventory in the tidal flat sediments by a factor of 4.5 for the Solway and 3.5 for Morecambe Bay. Thus the estimated inventory of ^{137}Cs of 10.5 TBq for the top 50cm of Solway Firth sediments increases to at least 47 TBq, whilst that for Morecambe Bay (including the Duddon and Ribble Estuaries) goes from 11 to at least 39 TBq. Given the relationships between ^{137}Cs and Am and Pu isotopes, established from earlier work[2], the estimated inventories of these radionuclides, in the Solway, would increase to 21TBq for ^{241}Am, 14TBq for ^{239,240}Pu and 2TBq for ^{238}Pu. For Morecambe Bay, the figures become 26TBq for ^{241}Am, 18TBq for ^{239,240}Pu and 3TBq for ^{238}Pu.

5.2.4 Mineralogy and Petrology

The X-ray diffraction and petrographical analyses of the intertidal cores from the Solway Firth reveal a set of predominantly very fine-grained sands, with no significant variations in mineralogy observed either between or within the cores.

Autoradiography indicates that the sediments are characterised by variable levels of background "matrix" alpha activity, with localised point sources of moderate to high alpha-activity.

The source of the matrix alpha activity, and the cause of variations in its intensity have not been identified. Indeed, most samples are essentially undifferentiable on the basis of the available mineralogical (XRD) and petrographical information. Autoradiography of the polished sections from the offshore cores indicates that the majority of the "matrix" alpha signal could be related to the distribution of detrital clay and clay-pellets.

The alpha-emitting point sources are considered to largely natural and represented by detrital zircons and apatite, which have been identified petrographically. Petrography also indicates the presence of rare monazites and garnets which are also likely to act as point sources of alpha-emissions from natural U and Th.

The core gamma logs indicate locally pronounced variations in intensity of gamma response. Mineralogical investigations (XRD) and petrography have failed to provide an explanation for these variations, with samples from high core-gamma and low core-gamma response being undifferentiable.

The sediments have been subject to minor diagenetic modification. Within the majority of samples, pellicles of detrital grains retain an illitic composition. However, some pellicles are oxidised and haematite and Ti-oxide replacements are present. In the more clay-rich and organic-rich sediments pyrite framboids are well developed. In one case these framboids are specifically associated with replaced organic material. In addition, minor pyrite is also seen replacing organic material within the body cavities of some bioclasts. The occurence and distribution of pyrite are consistent with the development of reducing conditions within less permeable, clay-rich parts of the sediment during the decay of organic material. Bioclastic debris is typically uncorroded, which, coupled with the presence of rare authigenic calcite overgrowths on detrital calcite grains, indicate relatively low activities of carbonate and bicarbonate within the pore fluids. However, minor corrosion of calcium carbonate bioclasts was observed.

5.2.5 Inorganic geochemistry

The Solway samples are dominantly sandy, compared to the more muddy offshore sediments. They therefore have lower metal values, but higher SiO_2, whilst Ba, Cs, Ge, Mo and U are at similar levels in both datasets.

For the Solway dataset, correlations with grain size and related factors are weaker than for the offshore sediments. The small range of values for most elements, is a critical factor and some of the strongest correlations probably relate to heavy mineral associations (Ti, Cr, Zr, Hf, Y, Nb, La, Ce, Th).

Three Solway datasets from sampling made in 1980, 1995 and 1999/2000 (this project) were available for comparison, but this was made difficult by the use of different sampling stations, ranges of determinands, and analytical methods. However some general conclusions can be drawn. The 1980 samples were the most muddy overall, ranging from sandy muds, through muddy sands to pure sands. The 1995 and 2000 samples were predominantly pure sands with some muddy sands. This grain size difference is reflected in enhanced Al, TOC (as loss on ignition at 450°C), Pb, Zn and ^{137}Cs in the 1980 dataset when compared with the two later ones. However, the pattern of variation is not simple, Zr and ^{241}Am values are highest overall in the 1995 data, whilst Cr, Ce, ^{137}Cs, ^{208}Tl, and ^{214}Bi are all higher in the 1995 results than in the 2000 data. The range of variation in the 1995 data is very high and does not appear to be directly related to grain size. The average ^{137}Cs concentration falls by almost 50% from 1980 to 1995 and by almost 60% from 1995 to 2000. Conversely, ^{40}K is some 15% higher in 2000 than in 1995.

Grain size appears to be a controlling factor in the distribution of metals in the 1980 Solway samples, with Ni, Cu, Pb and Zn all correlating strongly with Al, whilst a heavy mineral association is suggested by high correlation coefficients between Ti, Zr, Y and Rb. In contrast to the 2000 dataset, TOC is highly correlated (0.88 v 0.10) with Al and less highly (0.58 v 0.01) with mud content. In the 1995 data similar strong correlations between Ti, Fe, Cr, Zr, Ce, Th, ^{208}Tl and ^{214}Bi again indicate that these elements are held in a heavy mineral fraction, but there are no data for Ni, Cu, Pb, Zn or TOC.

Some of the 1999-2000 cores penetrated to depths below the level where ^{137}Cs occurs. In order to examine relationships in the three datasets, samples with concentrations of ^{137}Cs below the detection limit were eliminated from the 1999-2000 dataset and highly anomalous samples, probably related to heavy mineral concentrations, removed from the 1980 (3) and 1995 (1) datasets before correlation coefficients were recalculated. The metals Ni, Cu, Pb and Zn are all strongly associated with Al and TOC in the 1980 data and slightly less strongly with Fe. Iron is not strongly correlated with Al in the 1980 or 1999-2000 data, but has a coefficient of 0.86 with Al in the 1995 results. Although Ni and Zn still correlate strongly (>0.5) with Al in the 1999-2000 dataset, Cu and Pb do not. Correlation with TOC is also lower for Zn, and to a lesser extent Ni. However, all four metals correlate more strongly with Fe. This leads to the tentative conclusion that the differences in metal-Al and metal-Fe correlations between the1980 and 1999-2000 datasets might be related to early diagenetic effects in the cores. Metals were initially being adsorbed on clay mineral surfaces, but with time and burial, co-precipitation with Fe-oxides became more important. In the1980 dataset the correlation coefficients between ^{137}Cs and Al_2O_3 and TOC were 0.85 and 0.89 respectively and for ^{241}Am 0.65 and 0.74. In 1999-2000, the respective figures for ^{137}Cs fell to 0.57 and 0.54, whilst for ^{241}Am they fell to 0.53 and 0.05. Conversely, the correlation coefficient for ^{241}Am and Fe_2O_3 rose from 0.56 in the1980 data to 0.74 in 1999-2000. For ^{137}Cs, the figure stayed constant at 0.57. A similar explanation to that proposed above for metal-Al and metal Fe relationships might apply to ^{241}Am, but the situation is less clear for ^{137}Cs, which shows a decreasing strength of correlation with both ^{241}Am and Al from 1980 (0.80 and 0.85), through 1995 (0.75 and 0.79) to 1999-2000 (0.52 and 0.57). Correlation between mud content and ^{137}Cs also decreases through the 3 datasets (0.85 to 0.58 to 0.29), whilst that between mud and ^{241}Am remains almost constant (0.74, 0.75, 0.72). Organic carbon still seems to be an important factor in controlling ^{137}Cs distribution in the 1999-2000 samples (correlation coefficient 0.54), but the carbon has no significant association with either the mud content or Al as a clay mineral proxy (-0.01 and 0.05) despite being strongly correlated with both in the 1980 data (0.87 and 0.89).

All the cores from the Solway Firth have more than 3 ppm Cd at some part of their depth profile. The highest values of 29-51 ppm occur between 90 and 115 cm depth in a core from the north shore of the Firth. Although no definitive values exist for the assessment of levels of contamination in marine sediments, the OSPAR Environmental Assessment and Monitoring Committee have produced tables of metal/Al ratios for areas they consider to be relatively uncontaminated[34.] The highest upper quartile value tabled for Cd/Al is 6.6 with 9 out of 11 values being below 0.07. The two highest Solway samples have Cd/Al ratios of 10.7 and 19.7 and would, on this basis, be considered heavily contaminated. Higher Cd levels were observed off Whitehaven in earlier studies[10] and may relate to phosphate processing. The presence of elevated Cd in the Solway is consistent with the net influx of sediments from seaward into the firth.

5.2.6 Microbiology

The population of bacteria seems to show correlation with the high resolution gamma logging results and mineralogical content of some of the cores. In three cases total bacterial numbers are higher at or close to peak ^{137}Cs levels. In other cores there does not appear to be any obvious correlation with the gamma log data.

The apparent linkage between ^{137}Cs and microbial numbers is interesting particularly as the sediment contains clay minerals . Previous work[35] on the influence of microbes on the sorption of ^{137}Cs onto calcium montmorillonite (Fullers Earth) showed that active sulphate-reducing bacteria (SRB) can influence the retardation of this radionuclide onto Fullers Earth under anaerobic conditions. The effects are complex but in general, active SRB change the sorption characteristics of ^{137}Cs in unpredictable ways - sometimes increasing retardation, sometimes decreasing it and possibly 'out-competing' the nuclide for sorption sites. This complexity appears to be seen in the cores from the Solway Firth. However, as total counts only were undertaken it is not possible to ascertain which section of the microbial population (or indeed, the whole population) is implicated in the higher gamma counts at certain depths in the sediments. If SRB are preventing sorption then the nuclide is liable to migrate to other areas within the sediment where sorption can occur or be mobilised into the water column. If they are enhancing sorption then any change in their growing conditions (e.g. by bioturbation) could alter the sorption characteristics possibly mobilising the nuclide.

5.2.7 Organic geochemistry

For the Solway Firth samples total PAH concentration was found to range from 12 μg/kg to 1512 μg/kg, appreciably lower than values for the offshore sediments but well within the normal range for marine sediments. As for the offshore sediments the PAH distribution patterns were similar and dominated by PAHs of pyrolitic origin.

However, unlike the offshore Cumbrian coastal sediments, the Solway Firth intertidal sediments displayed an appreciable presence of low molecular weight PAHs in addition to the nine pyrolitic members. Naphthalene, acenaphthene and fluorene were frequently present in significant quantity. Their presence suggests a proportionally greater petrogenic contribution to the total PAHs than for the offshore samples, a conclusion supported by the use of PAH molecular indices. This may stem from a locally flourishing leisure and tourist industry and the consequent likelihood of leakage and incomplete combustion of fuel from small boats.

The only intertidal core for which a depth profile was obtained exhibited low total PAHs concentration down to 100 cms, but a comparatively high level of total PAHs concentration between 175-190 cms. This perhaps reflects the history of PAH deposition, *i.e.* the reduced use of the Solway Firth by modern commercial shipping because of its comparative shallowness.

Some correlation was found between the total organic matter content (TOC) and the total PAH concentration in all the sediments. However, this was stronger for the offshore samples than the intertidal Solway Firth sediments. This may reflect the proximity to coal burning industry and the association of fine soot particles with the finer grained offshore sediments. It could also be affected by the presence of coarse carbonaceous particles in the Solway; these would contribute to the TOC values but would not be associated with fine grained soot.

5.3 Hydrodynamic modelling

A range of three dimensional hydrodynamic models covering the continental shelf, west coast of Britain, and eastern Irish Sea were set up by POL and used to examine the spatial variability of currents during three major storm events when measurements were available to check the flows into the Irish Sea[36, 37].

The first storm period during November 1977 was initially characterised by strong winds from the south-west changing to winds from the west giving rise to a major surge at Liverpool. This was followed a few days later by a period of strong winds from the north-west which drove water through the North Channel of the Irish Sea and into Liverpool Bay. At this time current measurements were being made in Liverpool Bay, giving an opportunity to check the accuracy of the computed currents. The model appeared to accurately reproduce the major features of the flow in the region for the majority of the time, particularly at times of outflow from Liverpool Bay. During one inflow event the model gave an inflow in the region of Anglesey whereas observations suggested it was farther north. A recent detailed investigation of this suggested that the exact position of the inflow into Liverpool Bay at this time was a delicate balance of flows through the North Channel and St George's Channel and local wind-induced currents. Obtaining sufficient 'far field' flow information and detailed wind forcing with sufficient accuracy to be able to reproduce the detail of such storm-induced currents is particularly important. The spatial variability of the flow and intensity of currents in the region of the 'mud patch' and hence the erosion of the sea bed and sediment movement is critically dependent upon the accuracy of the model in determining currents in the region. This in turn depends upon accurate meteorological data both over the shelf and eastern Irish Sea. Wave effects are also crucial in determining the initiation of sediment movement.

The second storm event to be simulated occurred during the 3-5 February 1994 when there was a major flow to the north in the North Channel of the Irish Sea, (namely a major outflow). Although there were no observations in the eastern Irish Sea, there were ADCP and HF Radar measurements across the North Channel which were used to check that the model was reproducing this outflow. In the eastern Irish Sea there were very strong currents producing a flow towards the north. This storm event was very interesting in that it represented a major outflow of Irish Sea water through the North Channel.

The third surge event that has been simulated[37] corresponded to a major inflow to the Irish Sea through the North Channel, during the period 13 to 15 March 1994 and 24 to 25 March 1994. Although no eastern Irish Sea current measurements were available for model validation there was an ADCP deployment in the North Channel that could be used to check the accuracy of the computed flow into the Irish Sea.

The majority of the flow to the south through the North Channel continued to the south. At times this flow produced an inflow to the eastern Irish Sea in the region to the north of the Isle of Man, with a subsequent transport to the south in the eastern Irish Sea. At other times this flow pattern was reversed depending upon wind events over the shelf region, although the flow to the south was maintained in the deep regions of the Irish Sea.

These storm calculations show significant spatial and temporal variability in the magnitude and direction of flow within the eastern Irish Sea and further analysis of their impact upon bed stress and sediment transport is required.

Following the model validation described above, calculations have been performed to understand the role of ‘far field’ (shelf wide flows) and local (eastern Irish Sea) wind-induced flows upon currents in the region of the mud-patch. Far field effects were investigated by injecting currents through the northern and southern boundaries of a west coast model. They showed that although the major flow took place in the deep water of the western Irish Sea, some of the current reached the shallower mud-patch region and could move material suspended during a storm from this region and deposit it in eastern Irish Sea estuaries.

Calculations with local wind forcing, showed that winds from the south acting over the eastern Irish Sea could also transport sediment from the region of the mud-patch into the estuaries, with a dominant transport pathway to the west in the region to the north of the Isle of Man.

6. Conclusions

Physical, chemical and biological processes are all important in the speciation and transport of contaminants in the Irish Sea. They can interact in a complex way. This study has shown that the relative importance of each type of process varies significantly between intertidal and subtidal environments and from place to place within those environments. Further work is needed to quantify relative effects and some of the methods developed here have potential in that respect, for example for bioturbation.

The offshore sediments appear to reflect a balance between physical sedimentation, biological mixing and chemical effects, with redox processes being of significance. The intertidal sediments appear to be dominated by physical processes, with chemical and biological effects playing a relatively minor role.

The influence of storms on the Sellafield mud patch is a potentially important mechanism for the transport of contaminants into the estuaries of the NE Irish Sea. The direction of movement of sediment can vary significantly depending on the interaction of far-field and local conditions. This may give rise to longer distance transport of contaminants, through the North Channel or southwards. Storms also have the potential to expose anoxic sediments to oxygenated conditions, allowing the potential for mobilisation of Pu and other redox sensitive contaminants. Evidence of the importance of storm activity comes from the sediments themselves as well as from 3-D hydrodynamic modelling.

Physical reworking of sediments is very important in the estuaries around the E Irish Sea. Tidal asymmetry is such that the net movement of sediments is from the offshore area into estuaries such as the Solway and Morecambe Bay. Lateral migration of tidal channels and banks appears to be a dominant force here, due to the extreme tidal range. Bioturbation is of secondary importance except in the more cohesive finer grained sediments. Depths of contamination appear to be highly variable, reflecting the dynamic environment and interplay of erosional and depositional processes. They can range from <1m near high water mark to >2.5m further offshore. Radionuclide depth profiles have been used to estimate sedimentation rates. These fall in the range <1-6 cm y^{-1}, consistent with published values for the Solway salt marshes and the Esk Estuary. Physical processes become more important in the subtidal sediments below the surface oxygenated zone, with sedimentary structures being commonly seen on X-radiographs.

Chemical processes control the speciation of radionuclides and other contaminants, but act in concert with biological and physical processes. For example physical grain size plays a part in sorption by increasing available surface area, whilst the composition of particles is also important for ion exchange. Coincidentally, grain size appears also to be a major factor governing the structure and distribution of biological communities in the NE Irish Sea. Redox processes are strongly influenced by the activity of bacteria (e.g. sulphur cycle species) and are tied to microbial break down of organic matter. These lead to the formation of iron sulphides and promote conditions in which several contaminants are more tightly bound to sediment.

Bulk sediment mineralogy and available surface area are not well correlated with radionuclide content. Extractable radionuclides are typically in different fractions of the sediments; Cs in clays, U in carbonates, clays and organic matter and Th in iron oxides. Most of the Cs appears to be tightly bound, suggesting that further losses from the sediment may decline significantly with time. Radionuclides are distributed through the fine grained sediment matrix and occur in discrete hot particles. However, unlike previous studies, no evidence of well-developed tabular forms consisting of probable spent fuel debris were seen. Instead, the hot particles were gel-like organic grains with high Mg content, pelleted mud or consisted of rims around shell fragments. Diagenesis appears to be a significant factor in fixing radionuclides; original fuel fragments may have dissolved and been refixed, with the high Mg perhaps reflecting the Mg-alloy casing of Magnox fuel rods. An appreciable proportion of α- and β-emitting radionuclides are bound to shell surfaces where they are closely associated with pyrite and glaucony authigenesis. Modelling suggests that 10% of Pu is potentially mobile under oxidising conditions. Some Pu release would, therefore, be expected under storm-induced oxidation or that produced by bioturbation. This is consistent with observed loss of some Pu from the sediments over time.

Microbial activity also acts to bind sediment particles through formation of surface films and can help prevent erosion and hence redistribution of contaminated sediments. Bioturbation has a significant impact on movement of contaminants vertically within the sediment column. This is particularly apparent on the mud patch, 15-20km off Sellafield, but is still important, though to a lesser degree, in the more radioactive inshore sediments, 3-4 km offshore. It also introduces local oxidising conditions which can affect speciation and hence contaminant binding. Certain species, principally the mud shrimps, are seen to be effective in redistributing radionuclides. Echiurian worms are also major bioturbators, but experiments to assess their efficiency in mixing sediment proved unsuccessful. Other species appear to be much less effective mixers of sediment and associated contaminants. Modelling techniques were used to estimate the degree of radionuclide mixing. This could, in future, be tied to information on species density and geographical distribution to quantify the overall impact of bioturbation.

Shell fragments become locally reducing sites due to break down of organic components and microbial boring and can locally concentrate radionuclides. Biological processes appear to be much more important in the subtidal zone than in the intertidal sediments. Their effect is most notable in the surface oxygenated sediments, where sedimentary structures are all but obliterated. At greater depth structures are preserved, indicating less efficient biological mixing. Radionuclide profiles and Pu isotope ratios show that mixing is by no means complete. Although burrows are apparent at surface in the intertidal zone, sedimentary laminations are well preserved indicating that physical processes are more important here.

In general, radionuclides are the most apparent contaminants in the NE Irish Sea. Heavy metals are present locally at enhanced levels, but in general the sediments are fairly pristine in terms of these elements. There is some evidence for entry of contaminants from present and former industry along the Cumbrian coast into the Solway. Organic contaminants such as PAHs reflect normal global marine levels, primarily due to burning of fossil fuels with minor petroleum-derived components.

Deeper coring has extended our knowledge of the volume of contaminated sediment, but has yet to fully define it. However, uncontaminated sediment has been found at depths as little as 30cm relatively close to high water mark, whereas further out coring to 3m is still within the contaminated zone. The new cores allow known inventory estimates for radionuclides in the intertidal zone to be revised upwards by a factor of 4.5 for the Solway Firth and 3.5 for Morecambe Bay and the Duddon Estuary.

Arising from this project, a number of significant gaps in knowledge and areas requiring further study have been identified. These are outlined briefly below.

7. Recommendations for future work

1. Sea bed mapping of the eastern Irish Sea is based largely on old data (pre-1970) and is thus of poorer quality than for the western Irish Sea. Use should be made of extensive Hydrographic Office survey data for the E Irish Sea to better define sediment distribution and sedimentation regimes in the area most affected by Sellafield-derived contaminants. This would help fulfil the DEFRA vision to deliver a joined-up approach to seabed mapping as it could underpin coordinated approaches to mapping.
2. It would be worth considering acquisition of modern high quality sidescan and multibeam sonar for the NE Irish Sea. This could usefully be done as part of a larger direct investigation of the effect of storms on the mud patch using a wide range of techniques. This could be tied to further hydrodynamic modelling and validation of models (see below).
3. In parallel with storm surge simulations and as part of other contracts a three dimensional general purpose sediment transport model has been developed and used as part of other projects in shelf edge regions (Davies and Xing 2002, Xing and Davies 2002). This model, which includes wave-current interaction is currently being modified to take account of “wetting and drying” in the eastern Irish Sea. Subsequently it could be applied on a 1km grid to investigate sediment movement in the region, as a follow up to the present contract where the processes initiating sediment movement were examined.
4. To complement such a study, as shown in the results from the present contract, it would be essential to measure currents into and out of the eastern Irish Sea to the north and south of the Isle of Man (see Jones and Davies (2002) for detail) as well as measuring bed stress in the “mud patch” region. This might be done under the auspices of the POL Coastal Observatory project.
5. Collection of deep vibrocore samples (e.g. using the BGS 6m vibrocorer) is needed in offshore and intertidal sand areas of the NE Irish Sea to fully establish the depth of contamination and complete estimates of radionuclide inventories. Carbon dating of selective cores would be useful to verify low sedimentation rates and the extent of reworking of Holocene shells

6. Having successfully demonstrated the potential of the field and mesocosm approach, similar techniques should be used in future to determine the ecological / environmental relevance of biological processes, by:

Quantifying and modelling the nature, rates and scale of biological reworking to include a broader range of species, densities and sites.

Examining relationships between specific types of bioturbation, radionuclide distributions/fluxes and erodibility/resuspension, by incorporating measurements of additional parameters such as threshold shear strength and porosity. Since biological activity usually increases in summer it would be worthwhile to investigate how these inter-relating features vary with season.

Comparing impacts of bioturbation on fluxes of dissolved radionuclides in sediment, relative to movement of particulate material.

Examining macrobiological influences on the geochemical associations of radionuclides and resultant impact of these associations on mobility, bioavailability and genotoxicity of radionuclides. This is important in the light of the need, under the OSPAR convention , to ensure that non-human biota are also adequately protected.

For each of these objectives it would be useful to compare the behaviour of radionuclides of contrasting chemistries and particle affinities, based on ^{137}Cs and ^{241}Am. Extending the approach to other contaminants (metals) in the same cores would provide valuable comparisons of behaviour and insights into geochemical interactions.

7. Chemistry

It is predicted that changes in redox regime from a reducing state to an oxidising state may release bound heavy metals or radionuclides. Studies into the kinetics of release, and potential re-immobilisation via sorption to iron oxyhydroxide surfaces may be useful in determining the true extent that sediments may act as a sink and source of these anthropogenic pollutants to the ocean.

8. Microbiology

Although analyses showed the presence of sulphur cycle organisms with depth in the core, their activity is unknown. Hence their significance and efficiency in catalysing geochemical reactions controlling contaminant mobilisation cannot be determined. The significance of iron cycle bacteria should also be assessed.

A broadening of chemical analyses to include detailed assessments of the total organic carbon and inorganic carbon would assist in assessing controls on microbial activity. Such information could also be used to calculate maximum biomass in sediments and possible maximum effects on mobilisation.

9. Further detailed investigations of the effects of diagenesis on binding of radionuclides to the surface of shelly material would be very valuable. This study has indicated that early diagenetic alteration of shells has a significant effect on ‘fixing’ radionuclides in the offshore sediments. Further evaluation of the process needs to be carried out to establish which radionuclides are involved, in what quantities and to establish whether the fixation is reversible.

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