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Geochemistry and Budgetary Considerations of ^{14}C in the Irish Sea

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Abstract

Sellafield nuclear fuel reprocessing plant has been discharging ^{14}C as a component of the low level liquid radioactive waste into the Irish Sea since 1952. This ^{14}C is of radiological importance due to its long half-life, mobility in the environment and propensity for entering the food chain. Unlike the overall tend towards lower discharge activities since the peak in discharge activity during the 1970s (for example ^{137}Cs and ^{241}Am), the discharge activities for ^{14}C have increased since 1994/95 due to a change in discharge policy from mainly atmospheric discharges to mainly marine discharges. In contrast with other Sellafield derived radionuclides (for example ^{137}Cs and ^{241}Am), the behaviour of ^{14}C in the Irish Sea is, however, poorly understood despite an increase in research effort in recent years. This study was therefore undertaken to improve our understanding of temporal variations in ^{14}C specific activities in the biogeochemical fractions of the water column and biota in the Irish Sea and North Channel in relation to the Sellafield discharges. The project also determined a budget of Sellafield derived ^{14}C in the sediments of the NE Irish Sea and measured the flux of this ^{14}C from the Irish Sea.

Before the contribution of Sellafield derived ^{14}C to any carbon fraction can be made the activity of the marine background must first be estimated. The dissolved inorganic carbon (DIC) fraction of the water column, mussel, seaweed, crab, flatfish and roundfish samples were collected annually from the west coast of Co. Donegal, Ireland, and from these, the average current marine background activity was estimated to be approximately 253 Bq kg^{-1} C.

There were clear signs of incorporation of Sellafield derived ^{14}C to the biogeochemical fractions (dissolved inorganic carbon or DIC, dissolved organic carbon or DOC, particulate inorganic carbon or PIC and particulate organic carbon or POC) of the water column in seawater from the NE Irish Sea (Nethertown and St. Bees Head site) and North Channel (Portpatrick), although ^{14}C specific activities of the biogeochemical fractions of the water column in the North Channel were lower than those found close to the point of discharge.

Temporal trends in DIC specific activities at Nethertown bore no relationship to temporal trends in the discharge activities. In contrast with the Nethertown site temporal trends in the biogeochemical fractions (DIC, PIC and POC) at the St. Bees Head site rapidly responded to temporal trends in the discharge activity, with the most rapid changes in specific activity being exhibited by the DIC, followed by the POC. In the North Channel trends in the DIC specific activities were similar to those for the discharge activities, although a 1-2 month lag time was apparent before peaks in the discharge activity were seen in the DIC specific activities at the North Channel. Temporal trends of ^{14}C specific activities for the other biogeochemical fractions (DOC, POC and PIC) at Portpatrick did not bear any relationship to the temporal trends in the discharge.

Using the monthly discharge data and monthly specific activities in the DIC at Portpatrick the data can be modelled to give a flow rate of 4.6 km^3 d^{-1} through the North Channel (David Prandle Pers. Comm.). This is in good agreement with the flow rate of 5 km^3 d^{-1} used in previous studies to estimate the removal of Sellafield derived radionuclides from the Irish Sea through the North Channel.

Using the flow rate of 5 km^3 d^{-1} an estimated removal from the Irish Sea during the 2 year study period of 11.4 ± 0.7 TBq in the DIC fraction, 0.9 TBq in the DOC fraction, <0.01 TBq in the PIC fraction and 0.07 TBq in the POC fraction was calculated. This gave a total of 12.4 TBq of ^{14}C removed from the Irish Sea through the North Channel, approximately 100% of the total Sellafield discharges during the study period.

This approach did not take into account the standing crop of ^{14}C present in the Irish Sea at the beginning of the study. To encompass this a simple modelling approach (assuming negligable transfer of ^{14}C from the DIC to other biogeochemical fractions) was used to estimate the halving times for the activity in the NE Irish Sea at the beginning of the study. Using a halving time of one month the estimated removal of ^{14}C from the NE Irish Sea in the form of DIC during the study period was 10.5 TBq, while using variable halving times the estimated removal was 10.8 TBq. These estimates were in good agreement with that during the sampling period of 11.3 TBq and with the estimated removal of 12.4 TBq using a flux of 5 km^3 d^{-1}.

The ^{14}C specific activities found in mussel flesh and shell during this study were higher then the ambient background activities of mussel flesh and shell found at Burtonport, showing uptake of Sellafield derived ^{14}C by mussels. The ^{14}C specific activities for mussel flesh at Portpatrick were lower in the North Channel than those found close to the point of discharge. Temporal variations in the specific activity of mussel flesh and shell at Nethertown showed a rapid response to variations in the discharge activities, although the activity of the shell material had a longer response time than that of the flesh. In contrast, trends in the mussel flesh activities at Portpatrick did not show any response to trends in either the discharge activities or DIC or POC specific activities.

Analysis of 7 Pederson cores and 5 Van Veem grabs from a range of locations and sediment types in the NE Irish Sea showed that there had been a recent input of ^{14}C enhanced (Sellafield derived) organic material to the surface (0-2 cm) sediments of all cores and 3 of the grabs. The ^{14}C specific activities of the inorganic carbon fraction of the sediments was lower than that of the organic carbon fraction of the sediments in both core and grab samples. For the surface (0-2 cm) sediments a trend of increasing ^{14}C specific activity with latitude in both the inorganic and organic carbon fractions of the cores was observed. This trend was not repeated in the grabs. ^{137}Cs and ^{241}Am specific activities were determined in these cores and grabs. As with the organic and inorganic ^{14}C specific activities, the specific activities of the surface sediment (0 - 2 cm) showed a trend of increasing activity with latitude in the cores. This trend was not repeated in the grab samples.

Inventories (Bq m^{-2}) were calculated for ^{137}Cs and ^{241}Am and for upper inorganic and organic (0 and 98 Bq kg^{-1}C, respectively) ^{14}C in each of the cores. Plotting these inventories against latitude shows an increase in ^{137}Cs and ^{241}Am and organic ^{14}C with latitude, however, the inorganic ^{14}C does not follow this trend.

It was apparent that the basic trends in specific activity and inventories with latitude were broadly similar for the radionuclides studied (with the exception of the inorganic inventories with latitude) despite the differences in biogeochemistry and transfer routes into the sediments, this is consistent with net movement of contaminated sediment from the south to the north within the sample area.

^{137}Cs:^{241}Am activity ratios in the surface sediments (0-2 cm) and ^{137}Cs:^{241}Am inventory ratios both showed an overall trend of decreasing value with latitude for the cores. Ratios of <1 indicate prolonged exposure to seawater, also consistent with the concept of a northwards movement of the contaminated sediment, with lower ^{137}Cs:^{241}Am activity ratios of the more northerly cores reflecting a greater distance of transport and a corresponding greater contact time with seawater.

While the ^{137}Cs:^{241}Am activity ratios of the grabs are lower than those of the surface sediments (0-2) of the cores, the trend of increasing activity ratio with latitude was not repeated for the ratio for the grabs, with the northernmost and southernmost grabs having the highest ^{137}Cs:^{241}Am activity ratios.

Declaration

With the exception of $\delta^{13}C$ MS analysis of sample CO_2 (carried out in the NERC, Isotope Geosciences Unit, SUERC), the final vialling of benzene (which was carried out by Mr. R. Anderson, SUERC), analysis of graphite targets (carried out at the University of Arizona AMS facility), preparation of KCFC columns containing dissolved ^{137}Cs from seawater for γ counting and analysis of plutonium in sediments (both carried out by Mr. J. Donnelly, SUERC), the work in this thesis is the original work of the author and has not been submitted in whole or in part for any other degree.

Preliminary reports of some of the data from Section 3.2 has been accepted for publication in a peer-reviewed journal (Gulliver *et al.* 2001).

Pauline Gulliver

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The candidate would like to thank Drs. MacKenzie and Cook for their unfailing help and advice during this study.

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Thank you to all those that helped with the sampling program (especially, Alison, Caroline, Phil and Gordon) and those that helped carry carboys of seawater.

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Chapter 1

INTRODUCTION

1.0 Overview

This thesis describes a study of the biogeochemistry of anthropogenic ^{14}C which is discharged into the Irish Sea as a component of the liquid effluent from the Sellafield nuclear fuel reprocessing plant in north west England. The main focus of the research involved a study of temporal variations in ^{14}C specific activities in the biogeochemical fractions of seawater and in the biota from the Irish Sea and the North Channel and of the possible relationship of these variations to the Sellafield discharge pattern. The research also entailed investigation of ^{14}C transfer to, and post-depositional behaviour in, the sediments of the Irish Sea. Subsidiary aspects of the work included characterisation of ^{14}C at a remote site in the north west coast of Ireland, which was considered to be representative of the ambient "background" activity of the north east Atlantic. The results of the study are useful for developing a conceptual biogeochemical model for ^{14}C in the Irish Sea and the implications for human population radiation doses are evaluated.

1.1 Natural Production of ^{14}C.

^{14}C is the only naturally occurring radioisotope of carbon and is naturally present at low concentrations in the environment in comparison to the stable isotopes ^{12}C and ^{13}C (^{12}C = 98.9%; ^{13}C =1.1%; ^{14}C = 1 atom per 10^{12} stable atoms). ^{14}C is a weak beta emitter with an E_{max} of 156 keV and a half-life of 5730 ± 40 years (Godwin 1962). It is produced in the upper atmosphere when cosmic-ray produced neutrons react with ^{14}N nuclei (Libby 1946) *via* the following reaction:

$$^{14}N(n,p)^{14}C$$

Natural production of ^{14}C is estimated to be of the order of 0.92×10^{15} - 1.4×10^{15} Bq y^{-1} (Light 1973; UN 1977; Bush *et al.* 1983). The rate of natural production of ^{14}C is subject to both long term (millennial scale) and short term (decadal to century scale) variations. Long term variations are due to changes in the cosmic ray flux incident on the earth, caused by changes in the earth's magnetic dipole moment. Increases in the earth's magnetic dipole cause increased deflection of the cosmic ray flux, which lowers the number of cosmic ray produced neutrons penetrating the upper atmosphere and so lowers the rate of ^{14}C production (Elasser *et al.* 1956; Mazaud *et al.* 1991). Short term variations in the rate of ^{14}C production are attributed to variations in sun-spot activity (Stuiver 1961; 1982; de Jong *et al.* 1979; Suess 1970b; Baxter and Walton 1971; Bruns *et al.* 1980). Periods of high sunspot activity result in a lower cosmic ray flux, with a consequently lower production rate of ^{14}C in the upper atmosphere. Cyclical variations in ^{14}C production, with periods between 11 and 400 years have been reported (Suess 1970a; Baxter and Farmer 1973; Damon *et al.* 1973).

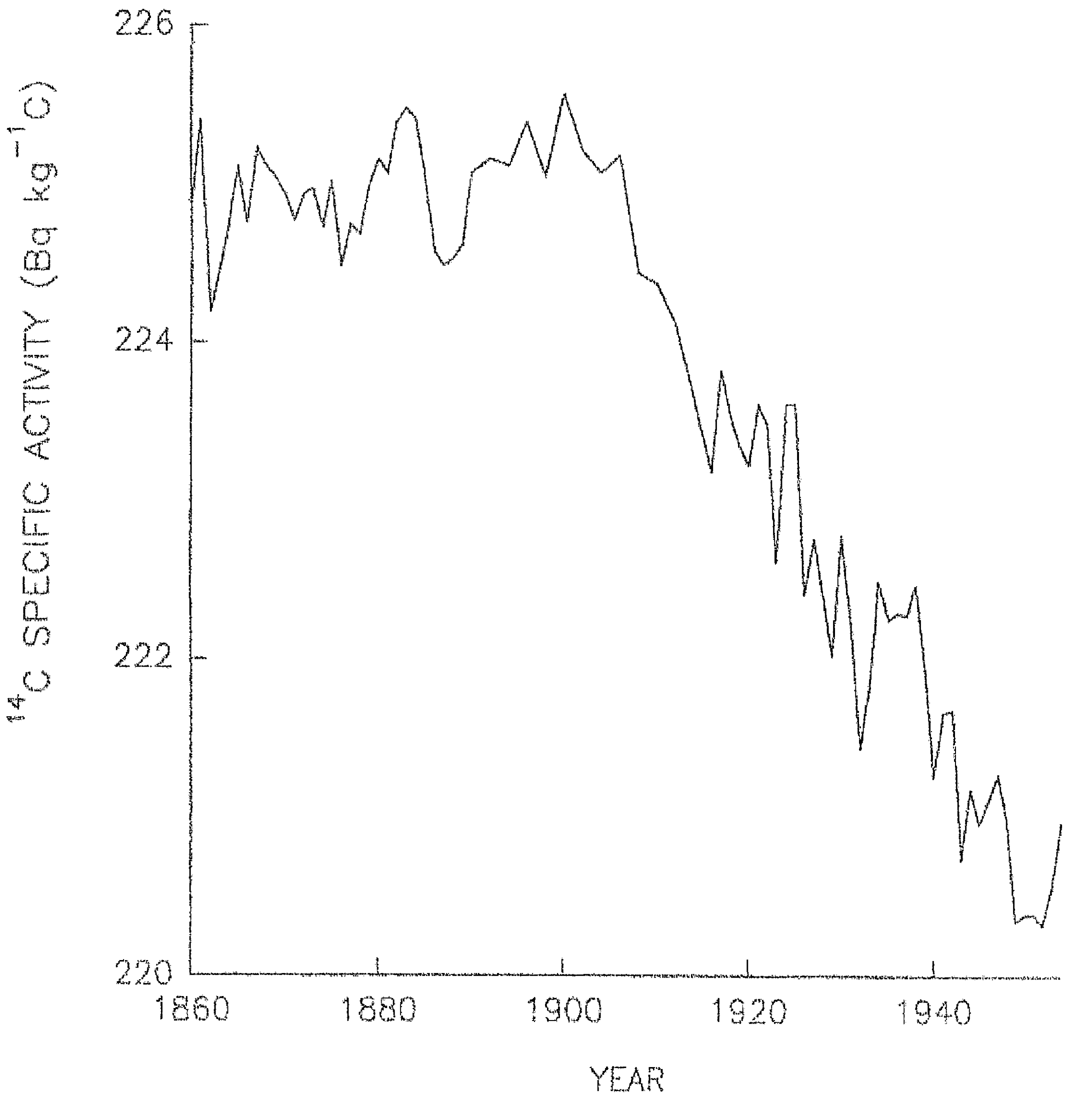
The ^{14}C formed in the upper atmosphere is oxidised to $^{14}CO_2$ which then enters the global carbon cycle. ^{14}C primarily enters the oceanic carbon cycle *via* ocean-atmosphere exchange of (^{14}C labelled) CO_2 but also *via* river runoff and precipitation, giving rise to small but detectable activities in all global oceanic carbon reservoirs.

1.2 Anthropogenic Perturbation of Environmental ^{14}C Activities.

In addition to natural variations in ^{14}C production, two anthropogenic influences have induced global variations in environmental ^{14}C activities; i) combustion of fossil fuel and ii) atmospheric nuclear weapons testing. In addition, ^{14}C has been released from nuclear fuel cycle processes but this has not had a major impact on the global ^{14}C cycle.

The Suess Effect, which started with the onset of the industrial revolution, was caused by large scale releases of "dead" CO_2 (ie. no ^{14}C present) as a consequence of the combustion of coal and oil, resulting in an increase in the atmospheric ^{12}C:^{14}C ratio and hence a decrease in the atmospheric ^{14}C specific activity. The temporal decrease in atmospheric ^{14}C specific activity over the period 1860 to 1950 AD is evidenced by decreasing tree-ring activity over this period. Tree-ring data for the atmospheric activity of the Northern Hemisphere for the period 1860 to 1950 were reported by Damon *et al.* (1973) and Stuiver and Quay (1981) and are presented in Figure 1.1. Suess (1953, 1955) first described this effect and it is now commonly referred to as the Suess Effect. By 1950, the ^{14}C specific activity in the atmosphere had fallen by 3% and 2% in the Northern and Southern Hemispheres, respectively (Suess 1955). The difference in activity between the two hemispheres is due to the higher consumption of fossil fuels in the Northern Hemisphere, the time it takes for atmospheric mixing between the two Hemispheres and the greater atmosphere to ocean flux of CO_2 in the Southern Hemisphere (Young and Fairhall 1968). Stuiver and Quay (1981) determined that the decreasing specific activity of ^{14}C in the atmosphere during the period 1890 - 1950 was due mainly to the Suess Effect and that only approximately 0.3% of the decrease was due to natural variation.

Figure 1.1 Atmospheric ^{14}C specific activity between 1860 and 1950 (Damon *et al.* 1973 and Stuiver and Quay 1981)



While CO_2 emissions to the atmosphere have increased from 1950 to the present (Keeling *et al.* 1982; Rotty and Masters 1985), the global trend in atmospheric ^{14}C specific activity during that period was not dominated by the Suess Effect but by the production of ^{14}C in atmospheric nuclear weapons testing.

Nuclear weapons testing began in New Mexico in 1945 and, since then, tests have been carried out in the atmosphere, underground and, in a limited number of cases, underwater. Atmospheric detonations of nuclear weapons produce ^{14}C by the neutron activation of atmospheric ^{14}N ($^{14}N(n,p)^{14}C$), with subsequent oxidation to $^{14}CO_2$ and entry into the global carbon cycle. Underground detonations of nuclear devices produce approximately 50% less ^{14}C per Mt than atmospheric detonations, due to neutron capture by the surrounding soil and water (Lassey *et al.* 1988; Taylor *et al.* 1990). The most important periods of atmospheric nuclear weapons testing were 1954 - 1958 and 1961 - 1962. In 1963, a partial atmospheric test ban treaty was signed by the former Soviet Union, Great Britain and the United States and since then, only a limited number of atmospheric tests have been carried out (Carter and Moghissi 1977), the last having taken place in 1980. The estimated production of ^{14}C due to atmospheric nuclear weapons testing up to 1980 is 2.2 -3.5 x 10^{17} Bq (Lassey *et al.* 1988; Taylor *et al.* 1990) (Figure 1.2).

The majority (70%) of the fallout from atmospheric nuclear weapons testing was released into the stratosphere of the Northern Hemisphere (Eisenbud 1987; UNSCEAR 1993) and was then globally dispersed, resulting in low-level global contamination. Fallout deposition in the Northern Hemisphere was greater than that in the Southern Hemisphere, since most of the tests were carried out in the Northern Hemisphere, and there is a finite mixing time for total mixing of the stratosphere on a global scale. The maximum input of ^{14}C to the stratosphere occurred in 1961-1962, but the maximum atmospheric specific activity was recorded in the Northern Hemisphere in 1964 when it reached approximately double the atmospheric ^{14}C specific activity prior to the beginning of atmospheric weapons testing (Figure 1.3), showing that a time of two years was needed for complete mixing between the stratosphere and the troposphere on a global scale.

The ^{14}C produced was dispersed globally in the form of $^{14}CO_2$ and subsequently incorporated into the global carbon cycle and dispersed into different global carbon reservoirs, resulting in a gradual decrease in atmospheric ^{14}C specific activity since 1964, to an ambient level in the UK terrestrial environment of 259 Bq kg^{-1} C in 1992 (Otlet *et al.* 1997).

Studies have been carried out to estimate the collective dose to the global population from atmospheric weapons testing and ^{14}C is of major significance in this context. UNSCEAR (1993) calculated that the collective effective dose from nuclear weapons testing to the global population was 3 x 10^{17} man Sv (UNSCEAR 1993), with ^{14}C contributing 70% of the dose, and the other main contributors being ^{137}Cs, ^{90}Sr, ^{95}Zr and ^{106}Ru.

Figure 1.2 The estimated annual and cumulative ^{14}C production from nuclear weapons tests (1945-1980)

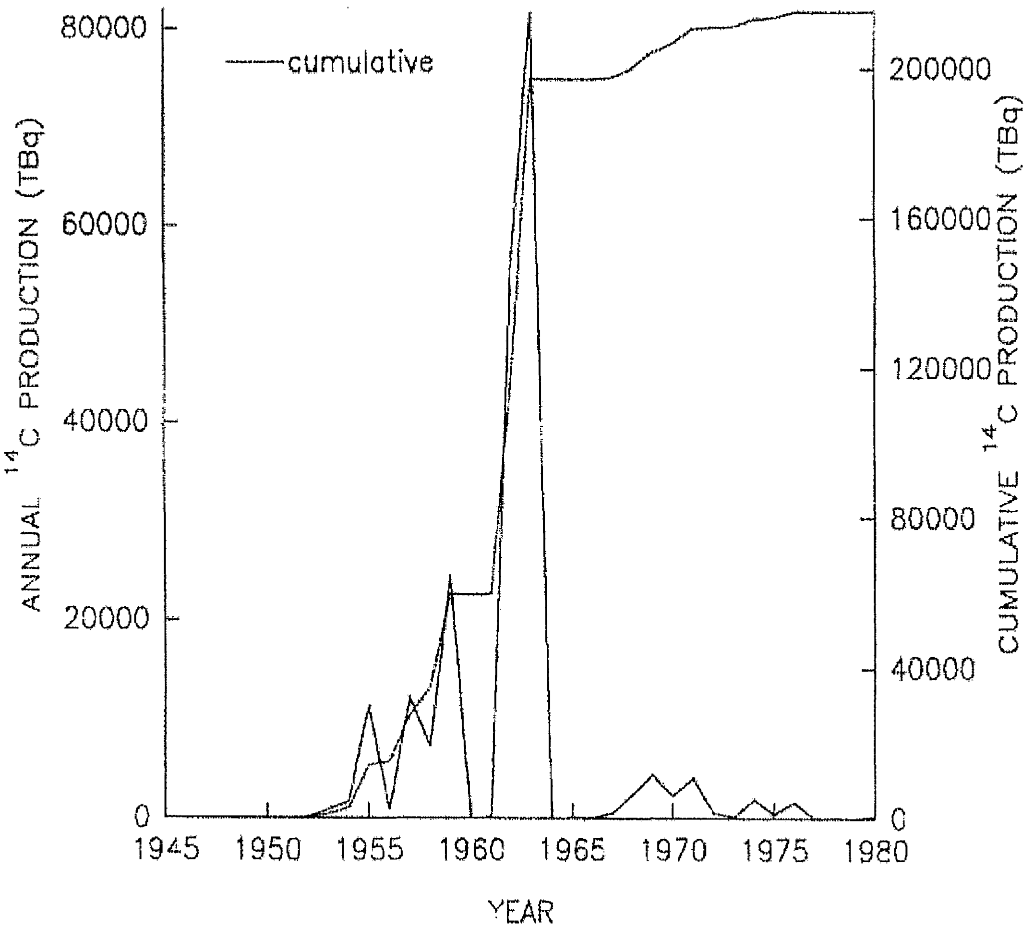
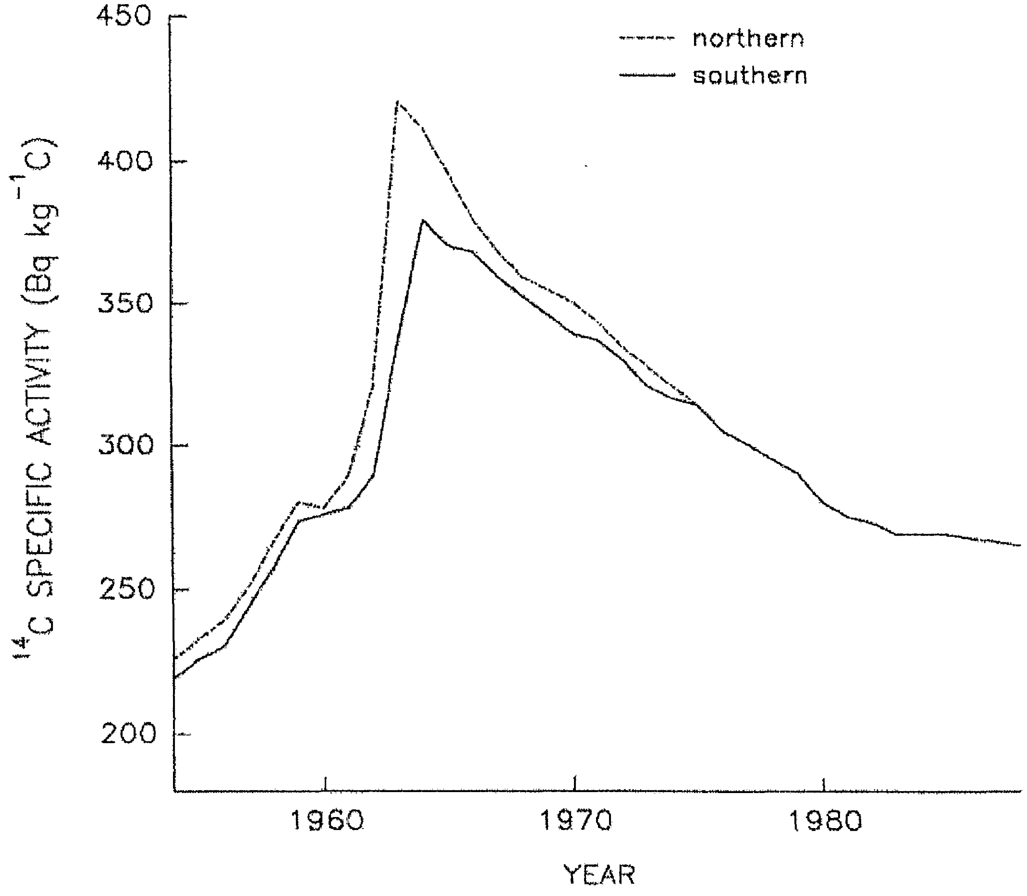


Figure 1.3 The atmospheric ^{14}C specific activity in the Northern and Southern hemispheres (1954-1990)



1.3 ^{14}C in the Nuclear Fuel Cycle

The nuclear fuel cycle comprises a range of operations including, mining and milling of uranium ore, purification and isotopic enrichment of uranium, fuel element fabrication, reactor operations, re-processing and disposal of spent fuel, disposal and storage of waste and decommissioning of reactors. Most ^{14}C produced during the nuclear fuel cycle is formed during normal reactor operations. ^{14}C is produced in nuclear reactors *via* a number of different routes, with the main mechanism being the $^{14}N(n,p)^{14}C$ reaction (Table 1.1).

Table 1.1 Mechanisms for production of ^{14}C in a nuclear reactor.

$\mathbf{^{14}N(n,p)^{14}C}$	(Overall main route of production)
$^{13}C(n,\gamma)^{14}C$	
$^{17}O(n,\alpha)^{14}C$	
$^{16}O(n,^{3}He)^{14}C$	
$^{15}N(n,d)^{14}C$	
Ternary fission	(produces a small % of total)

Estimation of ^{14}C production from normal reactor operations is difficult since the most important contribution comes from ^{14}N impurities in the reactor materials and accurate assessment of the level of nitrogen impurities is difficult (Bush *et al.* 1984). ^{14}C is produced in the moderator, coolant and structural materials of a nuclear reactor and the location of production determines the fate of the ^{14}C, with that produced in structural materials being unlikely to be released to the environment until reactor decommissioning. ^{14}C produced in the moderator and coolant is released to the environment during normal reactor operations or stored on ion-exchange resins which are used to clean up the coolant and are subsequently deposited in low-level waste repositories. ^{14}C produced in the fuel and fuel cladding is transferred to the reprocessing plant where some will be released to the environment during reprocessing. Annual global production of ^{14}C by the nuclear power industry was estimated by Begg (1992), to be 1470 TBq y^{-1} using data from annual production rates of ^{14}C, and installed capacity data (IAEA 1991). Therefore, potential production of ^{14}C by the nuclear power industry is of a similar order of magnitude to natural production, although releases of ^{14}C from the nuclear power industry to the environment are estimated to be approximately 50% of total production (Begg 1992). Estimates show that ^{14}C is the greatest contributor to the collective effective dose to the global population from nuclear industry discharges of radionuclides (UNSCEAR 1993). In comparison however, ^{14}C released by the nuclear industry to the environment up to 1985 is estimated to be equivalent to only 1% of the ^{14}C produced by nuclear weapons testing (Lassey *et al.* 1988).

Gas cooled reactors (Magnox and AGRs) are the most common type of nuclear power reactor in the UK. The main production of ^{14}C in AGRs is in the moderator *via* the $^{14}N(n,p)^{14}C$ but there is also a contribution from the cladding, fuel and coolant, with estimated production from these sources of 3.48, 1.18, 0.64, and 0.03 TBq/GW(e)y, respectively (Bonaka 1980, McNamara *et al.* 1998). In AGRs, the ^{14}C produced in the coolant is released as CO_2. ^{14}C produced in the moderator is expected to remain dominantly in the reactor until decommissioning, although some is released to the coolant through graphite corrosion. Graphite corrosion is expected to contribute more to the gaseous ^{14}C discharge than that produced in the coolant (Kelly *et al.* 1975; Bonaka 1980; Bush *et al.* 1984). The level of ^{14}C in gaseous and solid wastes from reactor operations and nuclear fuel recycling were calculated by McNamara *et al.* (1998) based on the production rate estimates by Bush *et al.* (1984), and are shown in Table 1.2. These include solid and gaseous, but not liquid waste routes. There are no estimates of ^{14}C activities in liquid waste releases from AGRs in the literature, but monitoring of radionuclides in the marine environment by the Ministry of Agriculture Fisheries and Food (MAFF) shows that ^{14}C activities in some marine species are elevated above ambient background activities (20 Bq kg^{-1} wet weight, as defined by MAFF 1995) in the vicinity of nuclear power producing facilities (MAFF 1995 -99) (Table 1.3). The dominant ^{14}C release to the environment from nuclear power operations occurs at the fuel reprocessing stage (NEA 1980). Reprocessing is carried out in Great Britain at the Sellafield and Dounreay nuclear fuel reprocessing plants, with Sellafield being by far the larger facility. The main focus of this study is on the geochemistry of ^{14}C discharged in the low-level liquid radioactive waste stream to the Irish Sea from the Sellafield nuclear fuel reprocessing plant. A full discussion of the liquid effluent ^{14}C discharges from Sellafield is given in Section 1.8.

Table 1.2. ^{14}C waste arising from UK graphite moderated reactors (TBq/GW(e)yr).

Reactor Type	Reactor Gaseous waste	Reactor Solid waste	Reprocessing Gaseous Waste	Reprocessing Solid Waste
AGR	0.55	5.37	0.37	1.85

Table 1.3 ^{14}C activities (Bq kg^{-1} wet weight) measured by MAFF in biota in the vicinity of some nuclear power producing facilities. Contribution from natural sources estimated to be 20 Bq kg^{-1} wet weight (MAFF 1995)

Year	Sample type	Nuclear power producing facility	^{14}C Activity (Bq kg^{-1} wet weight)
1996	Plaice	Hartlepool	39
1996	Crabs	Hartlepool	38
1996	Crabs	Torness	34
1996	Crabs	Sizewell	39
1998	Native Oysters	Bradwell	21
1998	Cod	Hartlepool	57
1998	Plaice	Hartlepool	46
1998	Crabs	Sizewell	46

1.4 The Oceanic Carbon Cycle.

The global carbon cycle (Figure 1.4) has both a biological and non-biological component. On time scales in the range of thousands of years, the only significant global transfer of carbon is between the continental biosphere, the atmosphere and the oceans (Duplessy 1986). The total amount of carbon found in any one of these reservoirs at any one time is dependent on the prevailing climatic conditions. For example, during the last glaciation there was a decrease in the amount of carbon in the continental biosphere due to the expansion of glaciers in high latitudes, deserts in low latitudes and a decrease in precipitation, while at the same time there was a corresponding increase in the amount of atmospheric carbon (Adams *et al.* 1990; Duplessy 1986). Atmospheric CO_2 has an important role in climate control and is well known in its role as a greenhouse gas. The oceans contain a great deal more CO_2 than the atmosphere, 36,600 and 781 Gt respectively (Sundquist 1993; Chester 1990; Pilson 1998), so small changes in the concentration of CO_2 in the oceans can have large effects on the concentration of CO_2 in the atmosphere and hence on global climate. As this study is concerned with the biogeochemistry of ^{14}C within the marine environment, the following section will focus on the oceanic carbon cycle (Figure 1.5).

There are five main carbon fractions in the oceans; dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate organic carbon (POC), particulate inorganic carbon (PIC) and volatile organic carbon or VOC. The VOC fraction is often disregarded due to the fact that its overall budget is small in comparison with that of the total carbon pool (Pilson 1998). The distinction between dissolved and particulate carbon fractions is operationally defined, with the dissolved carbon fraction commonly being defined as that which passes through a filter of 0.22 μm mesh size, while particulate carbon is described as that which is retained on a filter of 0.22 μm mesh size, but other authors may define the DOC as that which passes through a filter of 0.45 μm mesh size (Chester 1990). Carbon enters the worlds oceans through river discharge, dry deposition of carbon containing particles from the atmosphere and ocean-atmosphere gaseous exchange (Williams 1975; Duce and Duursma 1977; Baes *et al.* 1985; Richey *et al.* 1980; Schlesinger and Melack 1981; Meybeck 1982). Estimated inputs of carbon to the ocean are shown in Table 1.4. Carbon is removed from the oceans via ocean-atmosphere exchange and sedimentation of boiogenic particles to the ocean floor.

Table 1.4 Inputs of carbon to the world oceans

Source	Inorganic C (Gt C y^{-1})	Organic C (Gt C y^{-1})
Rivers	0.4 (Baes et al. 1985)	0.2-1.0 (Richey et al. 1980; Schlesinger and Melack 1981; Meybeck 1982)
Ocean-atmosphere exchange	70 (Saundquist 1993)	N/A
Dry deposition	N/A	0.2-1.0 (Williams 1975; Duce and Duursma 1977)
Wet deposition	N/A	6 x 10^{-3} (Duce and Duursma 1977)

The vertical structure of the oceans is such that a number of different water bodies can be identified by physical characteristics such as their density (a function of the temperature and salinity of the water body). The surface layer (surface to approximately 200 m depth) forms approximately 2% of the total volume of the oceans and is characterised by being of relatively low density, well lit and well mixed by wind and waves. Circulation in surface ocean waters is

Figure 1.4 The Global Carbon Cycle. Principal reservoirs (Gt) and fluxes (Gt y^{-1}) of carbon (Sundquist 1993).

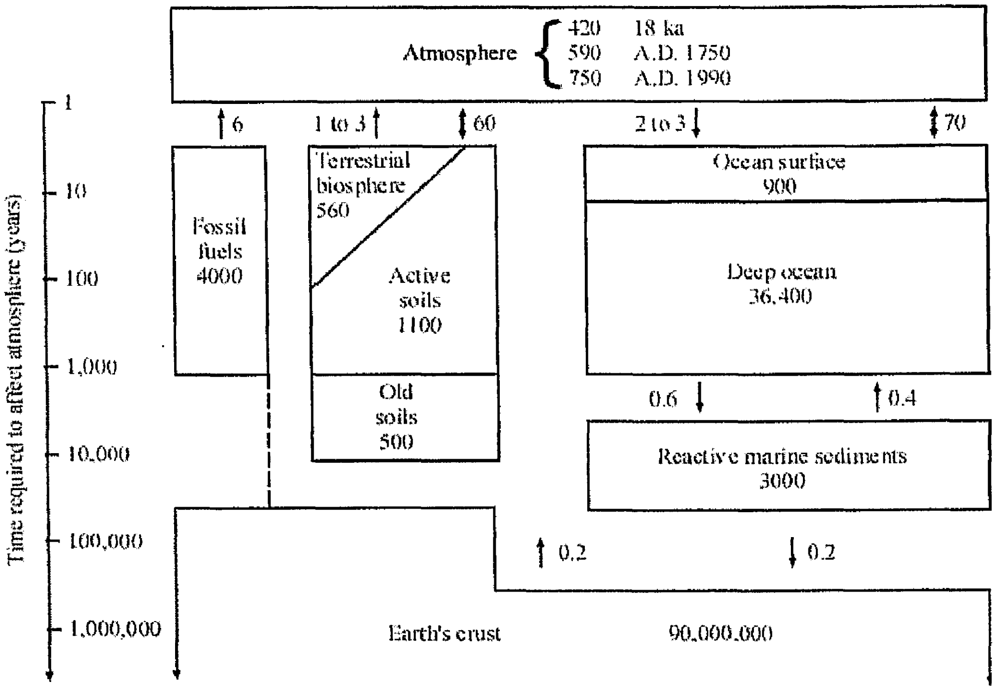
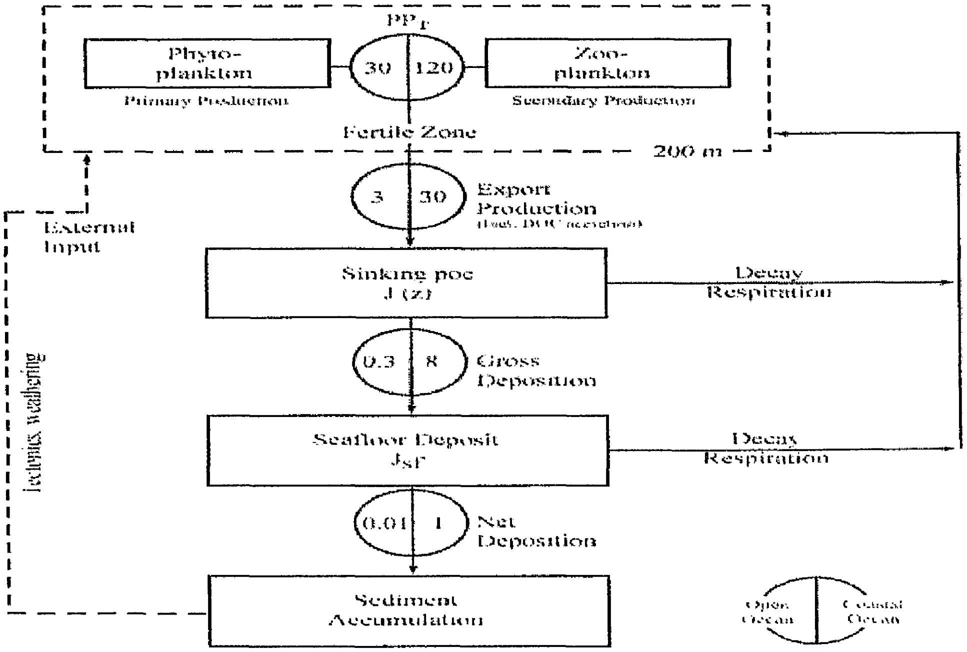


Figure 1.5 Schematic representation of the oceanic carbon cycle (Berger *et al.* 1989). Units of net primary production (PP_T) are in g m^{-2} y^{-1} of carbon.



wind driven and there is more horizontal than vertical mixing (Chester 1990; Pilson 1998).Between the surface waters and deep waters there is a boundary region (normally called the thermocline) which is characterised by rapid changes in temperature and salinity. The themocline accounts for approximately 18% of the volume of the ocean and acts as a barrier to mixing between the surface mixed layer and stratified deep ocean water (Solomon *et al.* 1985; Chester 1990; Gross 1990; Pilson 1998).

Deep water forms 80% of the volume of the oceans. Deep water is formed in the Arctic and Antarctic regions and is characterised by low temperature and high salinity. This gives the water body a higher density than surrounding surface waters and so causes it to sink (down welling). The water body then flows laterally by so called thermohaline circulation. Deep waters formed in different locations are characterised by different temperatures and salinities which result in water bodies of varying densities (Baes *et al.* 1985; Chester 1990; Gross 1990; Pilson 1998). Once formed, these deep water bodies are removed from atmospheric exchange, thus preserving the isotopic signature of the atmosphere at the time of formation. Hence ^{14}C labelled CO_2 incorporated from the atmosphere into a deep water body can be used to estimate the age of this water.

DIC

The DIC is the largest fraction of carbon in the oceans. Atmosphere-ocean exchange of CO_2 is of importance because the flux of CO_2 from the atmosphere is the largest source of carbon to the oceans. The concentration of CO_2 in surface oceanic waters depends on the equilibrium which exists between the partial pressure of CO_2 in the atmosphere and the partial pressure of CO_2 dissolved in the surface oceans. At equilibrium conditions, CO_2 is dissolved in oceanic waters according to Henry's Law.

$$[G] = H_G \times pp(G)$$

Where [G] is the concentration of gas G in solution; pp(G) is the partial pressure of gas G and H_G is the Henry's Law constant for gas G -which is a function of temperature and salinity. CO_2 is driven across the atmosphere-ocean boundary when the partial pressure of CO_2 in the atmosphere exceeds that of CO_2 dissolved in oceanic surface waters. On a global scale there is a net flux of CO_2 into the oceans from the atmosphere (Pilson 1998). The transfer rate is increased by the presence of waves on the surface of the ocean which "inject" bubbles of air to depths of up to 10 m below the surface. At depth, these bubbles are subjected to the pressure of the overlying water column which increases their internal pressure to greater than 1 atmosphere. Under this increased pressure, the gases in the bubble then dissolve into the surrounding water. Atmospheric CO_2 can only penetrate the surface waters of the ocean, so while surface water of the ocean equilibrates with the atmosphere within a few years, the remainder of the ocean traps CO_2 at the rate at which surface water sinks and is mixed with deep water. (Duplessy 1986; Broeker 1982).

Once dissolved in seawater, CO_2 becomes part of the total dissolved inorganic carbon or DIC pool which is composed of CO_2, carbonate, bicarbonate and carbonic acid which exist in a complex equilibrium with each other (Eqn. 1).

$$CO_2 + H_2O \leftrightharpoons H_2CO_3 \leftrightharpoons HCO_3^- + H^+ \leftrightharpoons CO_3^{2-} + H^+ \qquad \text{Eqn 1}$$

The level of partitioning between the elements of the DIC pool depends on the temperature and pH of the water column. The carbonate system is responsible for 95% of the acid-base buffering of the oceans over its natural pH range of between 7.9 and 8.4 (Pilson 1998). On time scales of up to several thousand years, the pH of seawater is mostly controlled by this system *via* changes in the various components of the CO_2/carbonate system. However, on geological time scales, oceanic pH is controlled by the chemical equilibrium between the water column and the minerals present in the underlying sediment.

The rate of CO_2 uptake by the oceans, was studied in a series of oceanic surveys undertaken in the 1970s and 1980s such as Geochemical Ocean Sections Study (GEOSECS), Vertical Transport and Exchange (VERTEX) and Transient Tracers in the Oceans (TTO).The results of these studies have been interpreted by a number of methods to estimate the flux of CO_2 from the atmosphere to the surface mixed layers of the oceans (Broeker *et al.* 1985; Munnich and Roether 1967; Stuiver 1980; Quay and Stuiver 1980). Most of these studies used CO_2 labelled with ^{14}C produced during atmospheric nuclear weapons testing. The penetration of this labelled CO_2 to depth in the ocean was used to estimate the flux of CO_2 into the ocean from the atmosphere. An average flux of 20-23 moles m^{-2} y^{-1} was estimated for the years 1962-1972, although there are regional flux variations, with the flux of CO_2 in the oceans being greater in high latitudes where winds are stronger and down welling of surface water occurs and in the southern hemisphere where there is a larger area of ocean across which ocean-atmosphere exchange of CO_2 can occur.

DIC is removed from the water column by organisms either for production of organic carbon *via* photyosynthesis (POC) or for the precipitation of skeletal support structures composed of calcium carbonate. Many of these physical structures are formed by planktonic species and form the bulk of the PIC, but the precipitation of calcium carbonate by coral reefs also removes calcium carbonate from the ocean. The physical structure of a coral reef is formed by precipitation of calcium carbonate by the coralline animals themselves and by calcareous red algae. Both are important in terms of formation of the reef and act as binding agents. Also found in coral reefs and other shallow sea areas are green calcareous algae such as *Halimeda* (Hills-Colinvaux 1980) which secrete calcium carbonate. These species can form significant calcareous deposits (Jensen *et al.* 1985).

PIC

In the open ocean, the PIC pool is composed primarily of the biogenic calcium carbonate produced *in situ*, or autochthonously, by planktonic organisms such as Foraminifera, Coccolithophorids and Pteropods. These creatures deposit calcium carbonate either as calcite or aragonite. The resulting shells, or plates, reflect the isotopic composition of the water in which they are formed, which in turn has implications relating to the climate at the time of formation. These shells are therefore a snapshot of the isotopic chemistry of the surface waters of the ocean at their time of formation. Coastal waters not only contain PIC produced autochthonously but are also influenced by terrestrial PIC which enters the sea *via* river run-off (Table 1.4).

Carbonate is removed from surface waters by the sinking of PIC to the sea floor to form carbonate sediments. It can be seen from the isotopic composition of these carbonate sediments that most of the carbonate deposited is biogenically produced within the ocean (Pilson 1998). Carbonate sediments (>30% carbonate) cover nearly half of the area of the sea floor. In regions of deep water (>4000 m in the Pacific and >4500 m in the Atlantic) there are no calcium carbonate deposits, due to the increasing solubility of calcium carbonate with increasing pressure and decreasing temperature, which causes deep waters to be under saturated with respect to calcium carbonate. The depth at which PIC (calcite and aragonite) disappears from the water column is termed the carbonate compensation depth.

The estimated accumulation rate of calcium carbonate in modern oceans is 32 x 10^{12} mol y^{-1} (or 0.38 Gt C y^{-1}) (Milliman 1993; Milliman and Droxler 1995), of which 11 x 10^{12} mol y^{-1} (0.13 Gt C y^{-1}) is deposited in deep sediments, 14.5 x 10^{12} mol y^{-1} (0.17 Gt C y^{-1}) is deposited in coral reefs and shallow sea ecosystems with the remaining 6.5 x 10^{12} mol yr^{-1} (7.8 x 10^{-2} Gt C y^{-1}) being predominantly deposited on the continental slopes.

POC

Particulate organic carbon (POC) in the ocean is composed of both living and detrital matter. As with the PIC fraction of seawater, in the open ocean most of the POC is produced autochthonously by marine phytoplankton. These are mostly single-celled algae, diverse in morphology, evolutionary history and biochemical behaviour, however, all the photosynthetic forms convert sunlight into chemical energy, which is used to synthesize the organic constituents of life from CO_2, water and nutrients (Fogg 1975; Chester 1990; Libes 1992).

Because of the requirement for light, photosynthesis is limited to the top 100 m or so of the surface ocean, which is referred to as the photic zone. Primary production, *ie* the amount of inorganic carbon transformed into organic carbon, varies geographically and nutrient supply is generally believed to be the limiting factor in most marine systems (Neinhuis 1981; Pilson 1998) although temperature can also play a limiting role in mid-high latitude regions.

Degens and Mooper (1976) and Berger *et al.* (1988, 1989) compiled many measurements of primary production in order to map variations in primary production throughout the world oceans. These compilations show that coastal regions and areas of upwelling (where nutrient laden waters rise to the surface) have much higher primary production rates than the central ocean gyres (Strickland 1965). Many estimates of total net primary production have been made and values range between 27 and 50 Gt C y^{-1} with approximately 80% occurring in the open ocean and 20% in the coastal regions (Williams and Druffel 1987; Martin *et al.* 1987; Berger 1989) although the true value may exceed this (Pilson 1998). According to Parsons (1975) POC in the open ocean may be considered largely to be autochthonous as POC input from rivers is confined mainly to the coastal regions.

Particulate material sinks through the water column where much of it is either consumed by deep dwelling organisms and/or degraded by bacteria. Once POC reaches the sediments, it is further metabolised by benthic fauna and bacteria. The greatest preservation of organic carbon occurs in shallow, rapidly sedimenting regions, such as continental shelfs and deltic fans, where as much as 10% of the primary production may be buried in the sediments, whereas in deep, slowly sedimenting regions, such as the abyssal sediments, as little as 0.01% of primary production may be buried (Berner 1982; Calvert *et al.* 1991). Berner (1982) estimated the final burial rates for POC to be 0.126 Gt C y^{-1} with the majority of this (0.110 Gt C y^{-1}) being buried in shallow shelf and deltic sediments. This figure is equivalent to approximately 0.25% of primary production.

DOC

The DOC pool is the second largest carbon pool in the oceans. However, it is the most difficult to analyse accurately with different values for DOC being obtained depending on the method used (Menzel and Vacaro 1964; Armstrong *et al.* 1966; Sharpe 1973; Sugimura and Suzuki 1988). The problems involved in the analysis of DOC were discussed in an international workshop held in 1991 and the results of this workshop are available in Volume 41 of the journal Marine Chemistry. There is still much to learn of the biogeochemical cycling of the different compounds of which the DOC is comprised.

DOC is produced autochthonously by the exudation of organic compounds by phytoplankton, excretion by zooplankton, the loss of organic compounds by zooplankton while grazing and the breakdown of detrital material by microbial activity (Williams and Druffel 1988; Chester 1990). It is estimated that up to 10% of the carbon fixed during photosynthesis is released as DOC (Pilson 1998).

Terrestrial DOC is transported to the sea by rivers at a rate of approximately 0.2 ± 30 % Gt C y^{-1} (Pilson 1998, based on results from Meybeck 1982). Studies using the amount of lignin in marine sediments and the $\delta^{13}C$ value of DOC in the open ocean suggest that approximately 10 % of marine DOC is terrestrially derived (Eadie *et al.* 1978; Meyers-Schulte and Hedges 1986; Williams and Druffel 1987). However, there is some debate as to what amount of the DOC from rivers escapes from the coastal zone to mix into the open ocean. In some studies very high molecular weight DOC appears to flocculate and settle out on first mixing with seawater, while other studies show conservative mixing of DOC (Mantoura and Woodward 1983).

40-80% of DOC is composed of high molecular weight organic molecules such as humic and fulvic acids. These are extremely variable in structure and elemental composition. Approximately 20% of the DOC is composed of labile organic molecules such as lipids, carbohydrates and amino acids which are rapidly utilised by the bacterial communities in the sea (Chester 1990; Pilson 1998). These bacteria can form bacterial mats and/or are consumed by larger organisms transforming the DOC to POC.

1.5. Stable carbon isotope values in the coastal marine environment

While the bulk of marine carbon resides in the open oceans, this study focuses on the Irish Sea, a coastal sea which lies between Great Britain and Ireland. The carbon fractions in coastal seas are the same as those found in the open ocean, however, in coastal seas terrestrially derived carbon will be incorporated into the marine carbon fractions and may account for a large percentage of the carbon to be found in that fraction. The effect of DIC input from river runoff on the overall DIC concentration (mg C l^{-1}) of the oceans is negligible, however, in areas of high freshwater input such as estuaries, dilution can be important and the total concentration of DIC can be lower than that of the open ocean. In addition there may be some deviation from the marine $\delta^{13}C$ stable isotopic signature of between -1 and +1 ‰ (relative to the PDB standard), as the $\delta^{13}C$ value for DIC in freshwater can vary between -5 and -10 ‰ (relative to the PDB standard) (Michener and Schnell 1994). Variations in the $\delta^{13}C$ signal for the DIC can indicate the presence of fresh water influence.

Freshwater inputs can also affect the concentrations and $\delta^{13}C$ values of POC, PIC and DOC in coastal waters. The $\delta^{13}C$ value (‰) for marine produced organic carbon is between - 18 and - 22 ‰ (relative to the PDB standard) while terrestrially derived organic mater has a $\delta^{13}C$ value of between - 24 and - 32 ‰ (relative to the PDB standard)

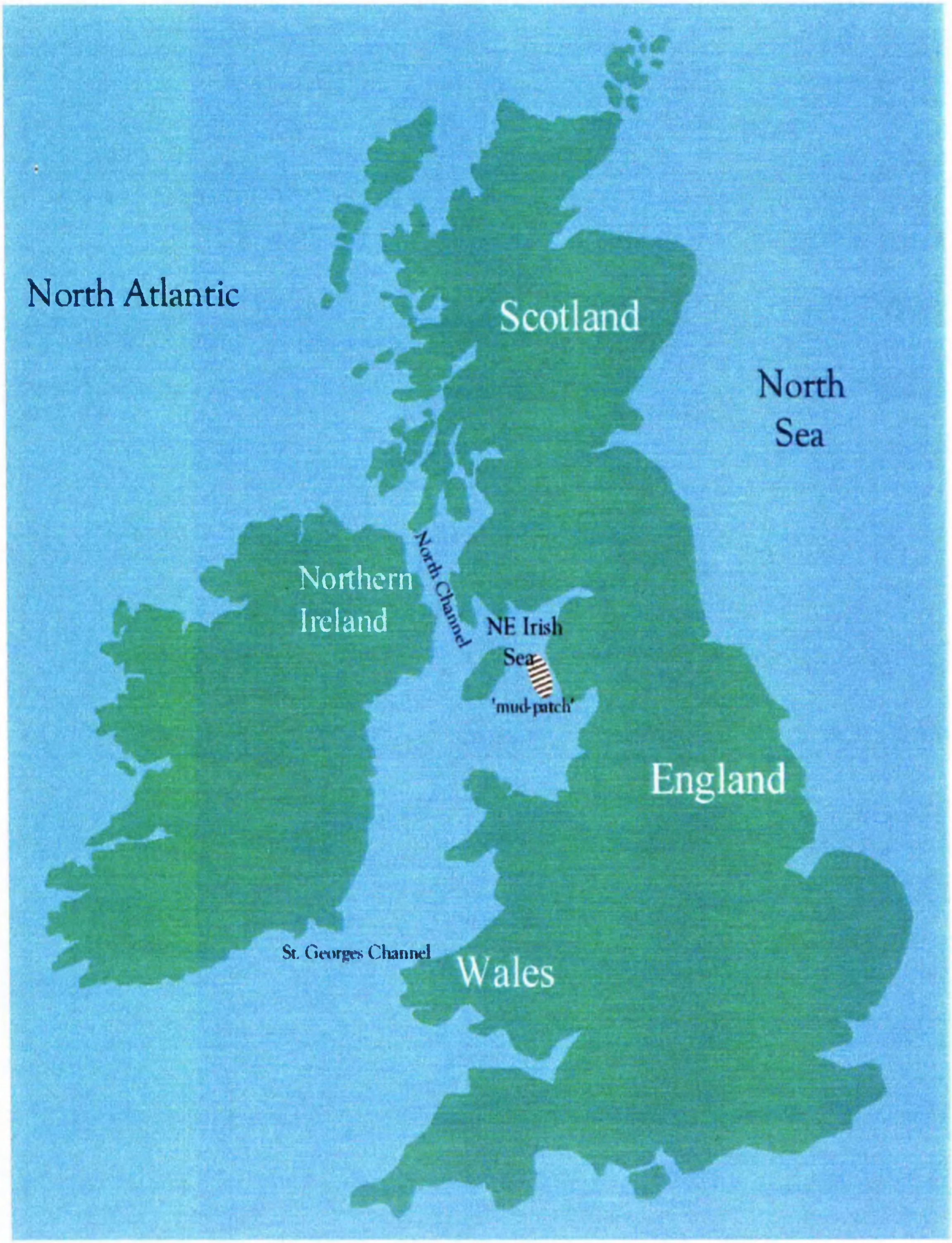
The various biogeochemical fractions of carbon in the nearshore marine environment are influenced by a number of factors such as 1) open ocean water 2) river input, 3) primary production by phytoplankton, reflecting the isotopic concentrations of the DIC (Michener and Schnell 1994), 4) secondary production by zooplankton (reflecting the isotopic composition of the food source which could be marine and/or terrestrially derived), 5) excretory products from phyto and zooplankton and 6) "sloppy feeding" by zooplankton which results in organic compounds being released directly from the prey to the water column. These factors all contribute to the stable isotope value (‰ relative to PDB) and the ^{14}C activity of the various fractions.

The concentrations of the biogeochemical fractions vary seasonally. Increases in phytoplankton populations and subsequent increases in zooplankton concentrations dominate the isotopic signature of the POC and DOC fractions in the spring and summer due to increased primary production. Increased rainfall in the winter results in an enhanced input of terrestrially derived carbon from river runoff to the marine environment, potentially dominating the isotopic signature of the biogeochemical fractions during the winter months. The isotopic compositions of the biogeochemical fractions will vary from place to place as they are dependant on 1) species composition, 2) underlying geology, 3) land use and 4) rainfall of the river catchment areas. There are also interannual variations in the concentrations and isotopic compositions of the biogeochemical fractions as some of the above factors can vary from year to year.

1.6. Physical characteristics of the Irish Sea.

The Irish Sea is a semi-enclosed body of water (Figure 1.6) which is connected to the North Atlantic by two narrow channels to the north and south (the North Channel and St. Georges Channel, respectively). In this study, the focus was placed on the NE Irish Sea because it is the initial environmental compartment receiving the Sellafield liquid effluent discharge, and on the North Channel, because this is the main exit for water from the Irish Sea.

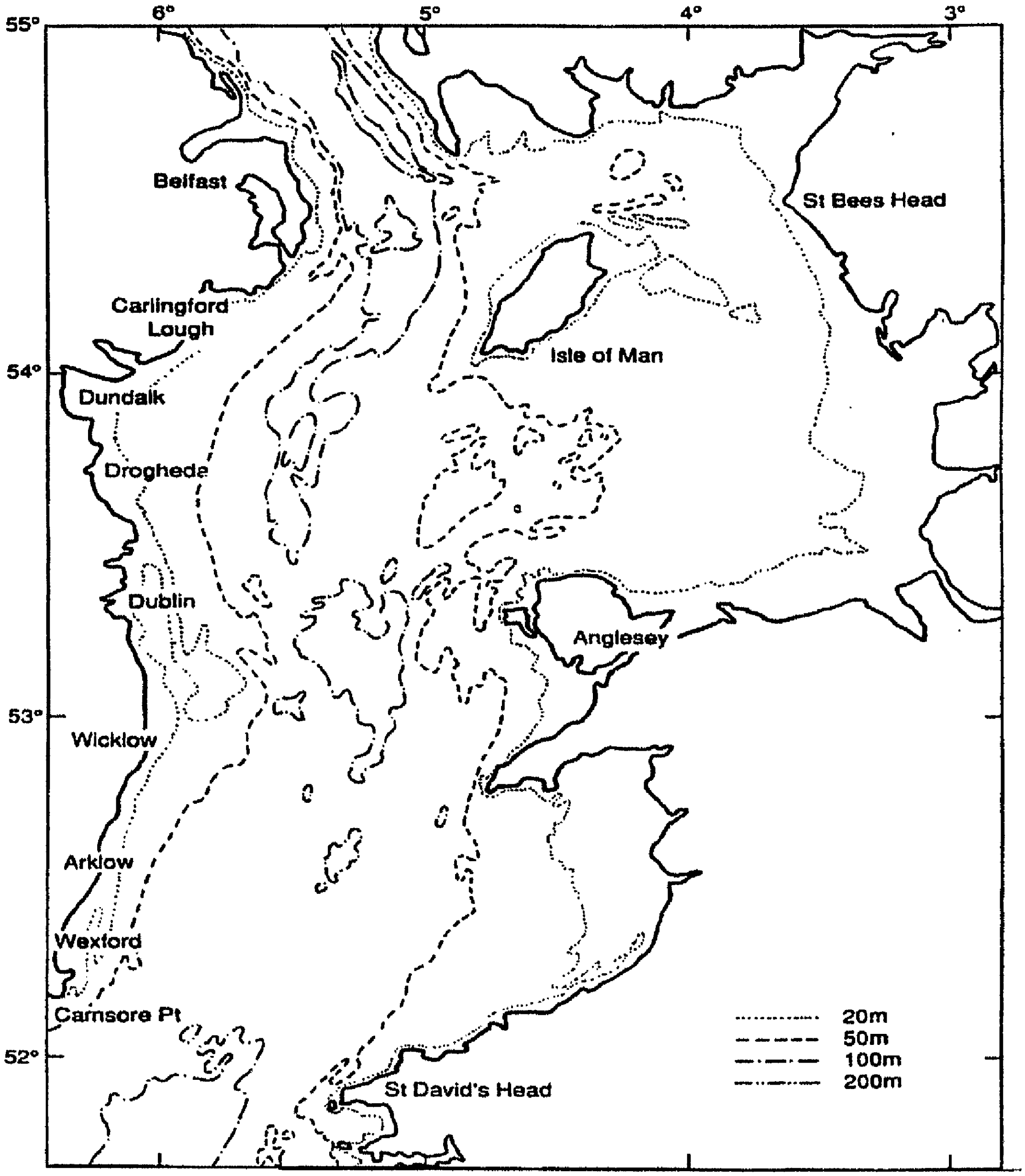
Figure 1.6 Map of the British Isles with details of the Irish Sea



1.6.1 Topography

Topographically, the Irish Sea can be divided into two systems: a deep north/south trough to the west and shallow embayments to the east (Figure 1.7). The water depth exceeds 275 m along the axis of the trough, while in the embayments of Cardigan Bay and the Eastern Irish Sea, the water depth is less than 50 m. It is estimated that 80% of the volume of water in the Irish Sea lies to the west of the Isle of Man (Dickson and Boelens 1988).

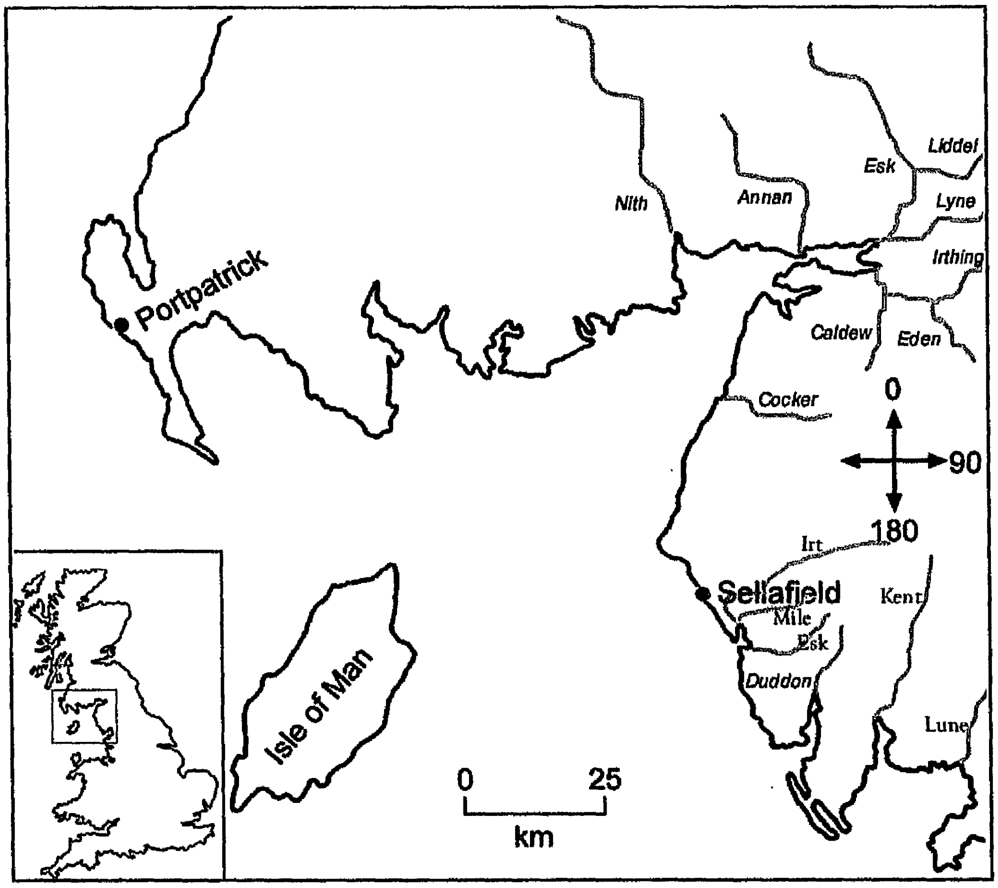
Figure 1.7 Bathymetry of the Irish Sea



1.6.2. Salinity distributions and freshwater input

Overall, the salinity distributions in the Irish Sea are related to: 1) the input of Atlantic waters through St. Georges Channel to the Irish Sea, with salinity decreasing from south to north (Bowden 1950), and 2) freshwater input which lowers salinity near river mouths and in estuaries (Jones and Falkard 1970; Kennington *et al.* 1999).

Figure 1.8 Rivers entering the NE Irish Sea



The volume of freshwater entering the Irish Sea averages 32 km^3 y^{-1} (Irish Sea Study Group 1990) which is small in comparison to the total volume of the Irish Sea (2430 km^3, Dickson and Boelens (1988)). Precipitation accounts for one-quarter of the total freshwater input (8 km^3 y^{-1}), with the remaining freshwater input coming from rivers (24 km^3 y^{-1}) (Irish Sea Study Group 1990). There is a high degree of temporal variability in precipitation and river discharge, but in general, the highest inputs of freshwater to the Irish Sea occur during the winter months. Several rivers (Derwent, Eden, Esk, Annan, Ribble) discharge into the NE Irish Sea from NW England and Southern Scotland (Figure 1.8) while Atlantic water enters the Irish Sea from the south west. Consequently, waters along the Cumbrian and south Scottish coasts are less saline than those along the east coast of the Isle of Man (Kennington *et al.* 1999; Jones and Folkard 1970 and Allen *et al.* 1996)

1.6.3. Temperature

Surface seawater temperatures vary depending on the season. Irish Sea water is coldest in February/March (5 - 8 ^{0}C) and warmest in August/September (13 - 17 ^{0}C). The variation in water temperature is more marked in shallow waters than in deeper waters, such that shallow waters are cooler in winter and warmer in summer.

1.6.4. Tides

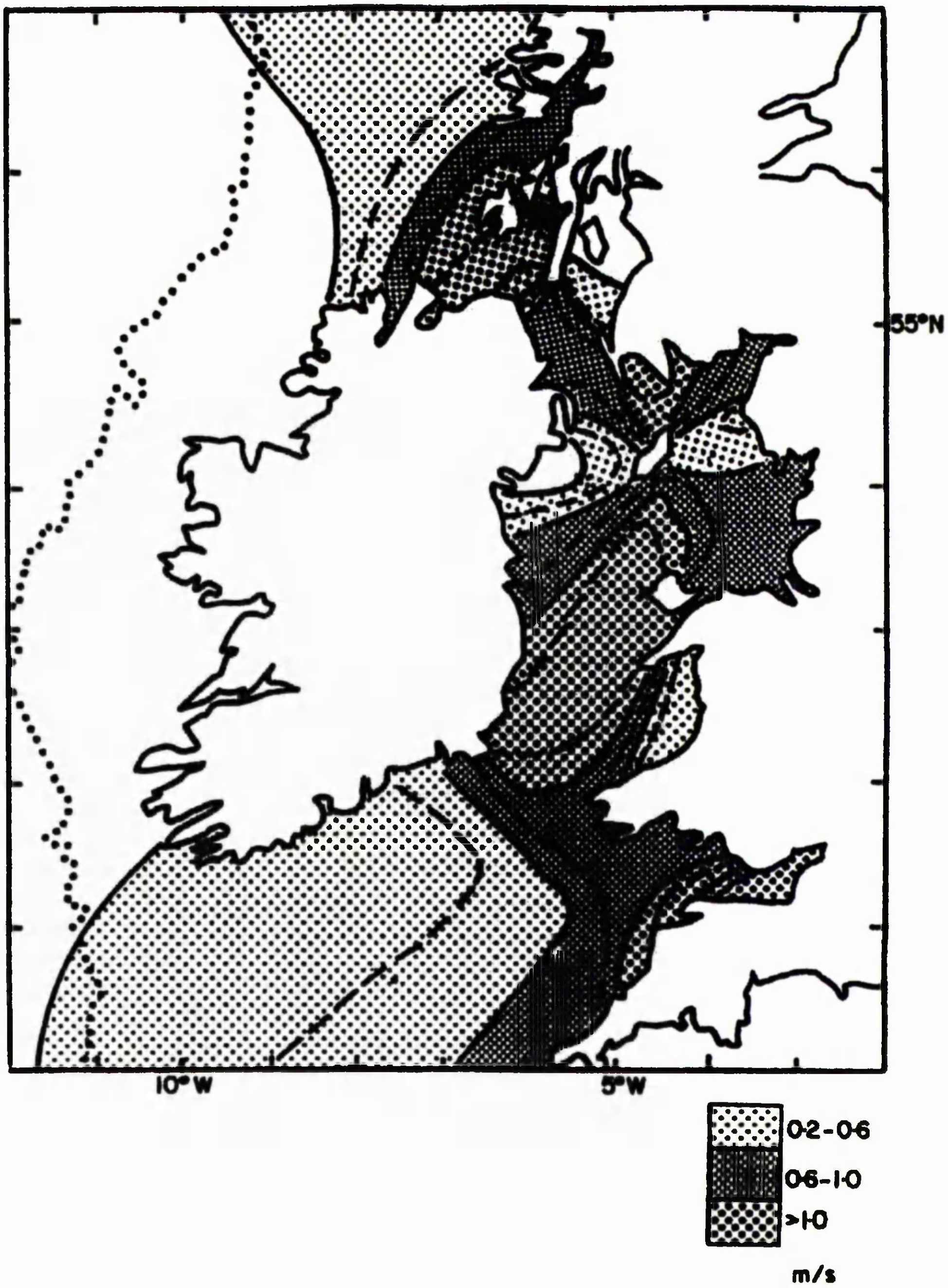
Tides enter the Irish Sea through the North Channel and St. Georges Channel and meet to the west of the Isle of Man, causing a tidal node at that location (Figure 1.9). Tidal amplitudes and currents vary around the tidal node, with the North Channel having low amplitude but high currents (0.6-1.0 ms^{-1}) and the NE Irish Sea having high amplitude (mean spring range is 8 m) but low currents (0.2 - 0.6 ms^{-1}) (Irish Sea Study Group 1990)

1.6.5.Stratification of the water column

Stratification of the Irish Sea is affected by salinity distributions in the winter and temperature and salinity distributions in the summer. Simpson and Hunter (1974) argued that the spatial pattern of seasonal stratification in the Irish Sea is controlled by tidal mixing, and that the intensity of stratification is related to the water column depth and tidal mixing, with increased strength in stratification being related to increased depth and decreased tidal currents. The weak tidal currents of the NE Irish Sea are not capable of overturning stratification of this area, however, the shallow depth of the NE Irish Sea embayment causes stratification of the water column to be easily overturned by wind action. Therefore stratification in the NE Irish Sea is not as strong the stratification which forms the gyre in the western Irish Sea in the summer months (Hill *et al.* 1997).

Gowen *et al.* (1995) reported weak stratification of the southern end of the North Channel for 2-3 months in the summer of 1992.

Figure 1.9 Tidal velocity distributions in the Irish Sea



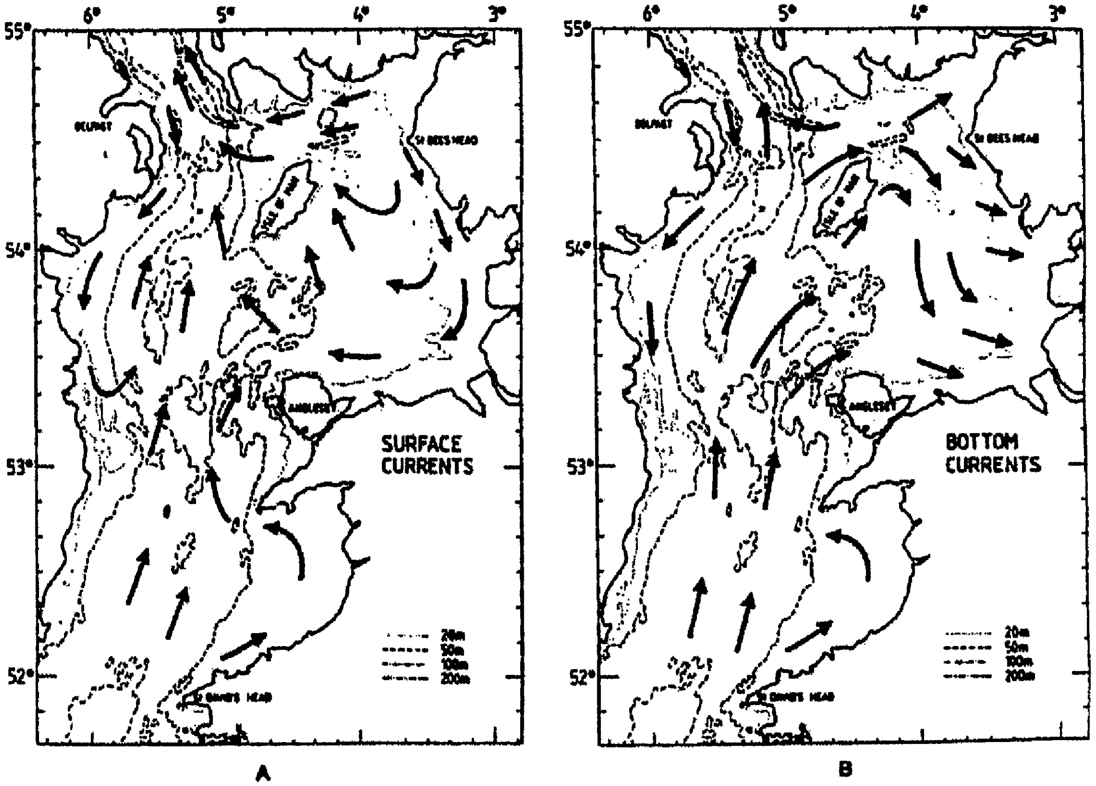
1.6.6. Water Circulation

Using salinity measurements, Bowden (1950) showed that North Atlantic seawater enters the Irish Sea through St. Georges Channel and flows northwards to exit through the North Channel. Subsequent studies using tracer budgets such as salinity and dissolved ^{137}Cs and ^{99}Tc activities as well as hydrodynamic modelling have shown that the net long-term circulation in the Irish Sea is northwards with basin averaged speeds of between 1 -2 cm s^{-1} (Bowden 1950; Jefferies *et al.* 1973; Wilson 1974; Jefferies *et al.* 1982; Ramster and Hill 1968; Howarth, 1982; Prandle 1984). Based on the estimated net residual flow, estimates of one year were calculated for the time it would take for water to traverse the length of the Irish Sea (Ramster and Hill 1969; Howarth 1982). On short time scales, however, (days to months) the net flow is much more variable in terms of both flux and direction of flow (The Irish Sea Study Group 1990) and it is important not to consider the movement of water in the Irish Sea to be continuously northwards.

Ramster and Hill (1969) (Figure 1.10) published a diagram of surface and bottom water circulation based on short duration moored current meters in the western Irish Sea and surface and bottom drift card returns, however, it is argued by Hill *et al.* (1997) that because the long-term circulation (approximately 1-2 cm s^{-1}) is not much larger that the background "noise" due to wind blown water movement and tidal currents (approximately 1 cm s^{-1}) it is not possible to determine an accurate, organised circulation pattern based upon the original observations. Studies of the activity and distribution of radionuclides (*eg.* ^{137}Cs, ^{99}Tc and ^{14}C) in sessile inter-tidal biota and in the water column show that, while the general movement of radionuclides is northwards, some southwards movement also occurs (Begg 1992; Begg *et al.* 1991; 1992; Jefferies *et al.* 1973; Jefferies *et al.* 1982; Leonard *et al.* 1997) but these studies do not indicate whether this movement is due to long term net circulation (Ramster and Hill 1969) or short term wind and tide induced water movement (Hill *et al.* 1997).

The studies by Jefferies *et al.* (1973; 1982) were used to describe the long term circulation and residence times of water in the Irish Sea and concluded that a residence half-time for water of 200 days was applicable for the NE Irish Sea and a residence half-time for water of about 1 year applied for the whole northern Irish Sea. This agrees with the estimate of residence times for water in the eastern Irish Sea by Dickson and Bolens (1988) of over a year.

Figure 1.10 (A) Surface and (B) bottom water circulation patterns in the Irish Sea



1.6.7. Sediment distributions

The distribution of surface sediments in the Irish Sea is shown in Figure 1.11. The distribution of sea floor sediments is related to the near bed currents, with muddy sediments being associated with weak currents and gravely sediments being associated with strong currents. Gravel can be seen to stretch through the Irish Sea from St. Georges Channel to the entrance to the North Channel. Sandy sediments lie to the east and west of the gravel and cover a large area of the seabed and form extensive regions of sand waves (Irish Sea study group 1990). The large mud patch to the west of the Isle of Man is associated with the low tidal currents that contribute to the formation of a summer gyre in this region. There is also an area of muddy sediments in the NE Irish Sea (commonly referred to in the literature as the Sellafield "mud-patch") off the Cumbrian coast. Both these areas are important for shrimp fisheries as the species *Callianessa subterranea* lives in soft muds. The sediments in these areas have been studied by a number of workers (Belderson 1964; Belderson and Stride 1969; Pantin 1977, 1978; Mauchline 1980; Johnson 1983) and the consensus was that these are areas of active sedimentation. However, Kirby *et al.* (1983) challenged this view in a review of previous work and concluded that much of the evidence for accumulation was circumstantial and that there was no evidence of a source of fine grained particles for addition to the mud patches. It is possible, in the case of the Western Irish Sea mud-patch, that the summer gyre will retain small particles such as plankton and act as a sort of funnel for particles to the sea bed of this area until the structure of the gyre breaks down during winter months. Whether or not this provides enough sediment to the Western Irish Sea mud-patch for it to be considered an area of active sedimentation is not yet known.

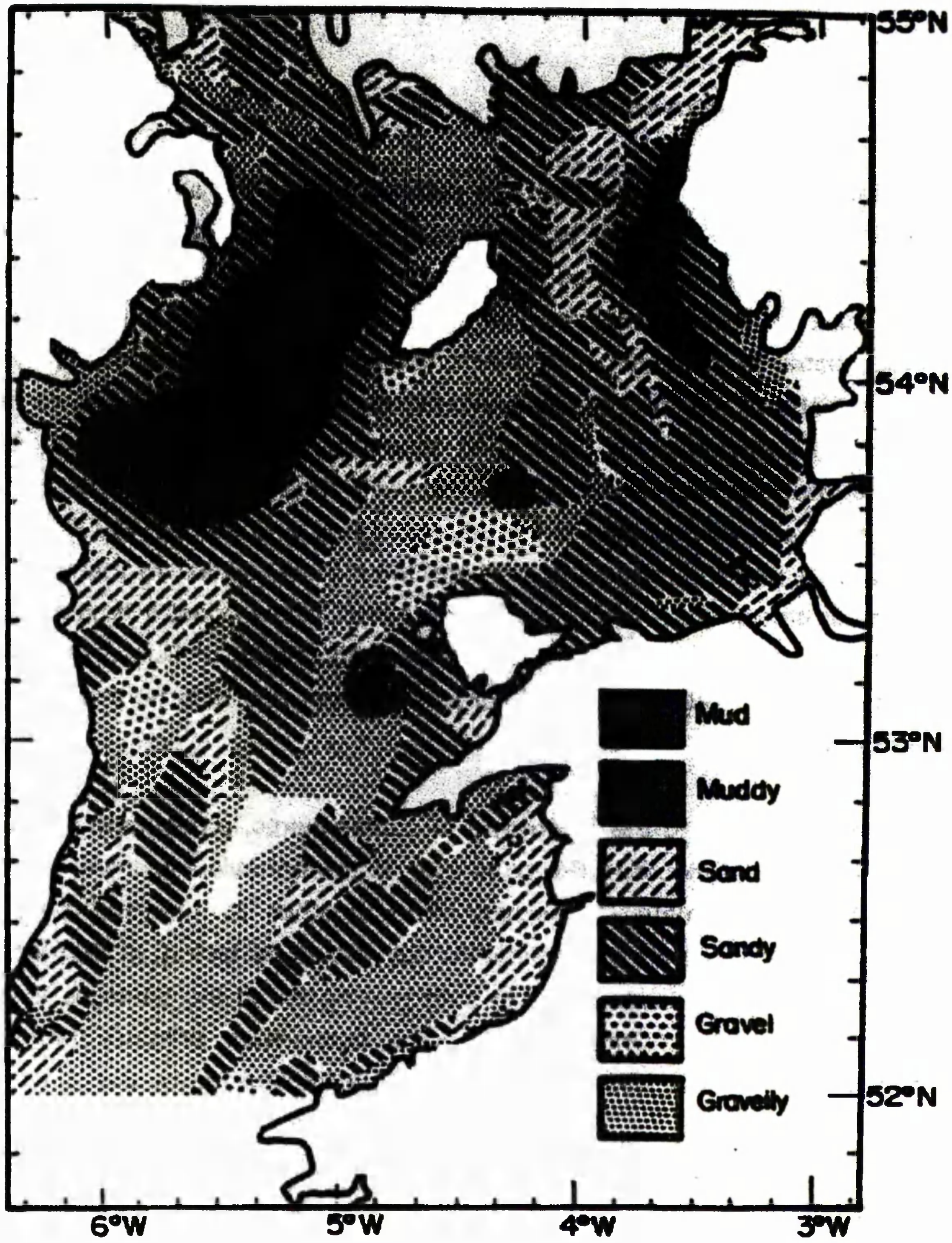
In an attempt to establish the rate of sediment accumulation, Kershaw (1986) used bulk inorganic ^{14}C ages from two cores collected in the NE Irish Sea. These cores had similar age distributions and showed near constant ages from the surface to the base of the core (12,500 ± 1,000 y BP). This ^{14}C distribution was attributed to bioturbative mixing of the sediments in the NE Irish Sea, which can occur to a depth of 140 cm (Kershaw *et al.* 1983, 1984; Kirby *et al.* 1983; Williams *et al.* 1981). In a subsequent study using radiocarbon ages of the shell of the gastropod *Turritella communis* (Riso), Kershaw *et al.* (1988) estimated that the rate of sedimentation in the NE Irish Sea was of the order of 0.02 - 0.3 cm y^{-1}over the past 3,000 - 4,000 years.

The Sellafield "mud-patch" has been shown to contain significant activities of particle reactive radionuclides discharged from Sellafield (Jefferies *et al.* 1973 ; Hetherington 1975; Nelson and Lovett 1978; Baxter *et al.* 1979; Day and Cross 1981; Pentreath *et al.* 1984) which has effectively labelled the sediments. A number of studies have shown that these sediments are undergoing redistribution to coastal sites (Aston *et al.* 1981; Aston and Stanners 1982; Hunt 1985; MacKenzie *et al.* 1987; McDonald *et al.* 1990; MacKenzie and Scott 1993; Pulford *et al.* 1998; MacKenzie *et al.* 1999). The distribution of Sellafield derived radionuclides within the NE Irish Sea will be discussed in more detail in Section 1.11.

1.7 Water flux through the North Channel

The flux of water through the North Channel is important because it regulates the rate at which contaminant radionuclides from Sellafield are removed, mainly in the dissolved phase, from the Irish Sea. The tidal range in the North Channel is low but the tidal currents here are

Figure 1.11 Sediment distribution in the Irish Sea.



amongst the highest in the Irish Sea area, which contributes to the vertically well mixed nature of the North Channel water column (Knight and Howarth 1999), with surface to bottom temperature variations rarely exceeding 1^0 C. Over long time periods (> several months) the net flow through the North Channel is south to north, however, over shorter time periods, the flow is more complicated, oscillating with a tidal rhythm (Brown and Gmitrowicz 1995; Knight and Howarth 1999; Davies and Hall 2000; Young *et al.* 2000). Water movement in the North Channel is not entirely controlled by tidal dynamics but is also heavily influenced by wind forcing (Howarth 1982; Prandle, 1976; Brown and Gmitrowicz 1995). There is also evidence of mass incursions of North Atlantic water into the Irish Sea through the North Channel during specific storm conditions. Variations in the short term oscillations and flows were investigated by Brown and Gmitrowicz (1995) who described the overall flow through the North Channel to be northwards with a flux of water between 9.5 and 12.1 $km^3\ d^{-1}$ (Table 1.5). They described the transverse structure of water flow through the North Channel to be complicated, with short term (days) changes in the direction of flow, a persistent southerly influx of water from the Atlantic along the western side of the North Channel of between 2.6 and 4.3 $km^3\ d^{-1}$ and of a persistent northerly outflow on the eastern side of the North Channel. Work by Leonard *et al.* (1997) on the distribution of ^{99}Tc in the NE Irish Sea and North Channel supports the presence of a northerly flow of Irish Sea water along the eastern coast of the North Channel.

Estimates of water flux through the North Channel have been examined using a number of methods (Table 1.5) with the range of estimates being between 1.7 and 12.1 $km^3\ d^{-1}$ (0.02 and $0.14 \times 10^6\ m^3\ s^{-1}$). For the purposes of removal of Sellafield derived radionuclides from the Irish Sea, a flux of 5 $km^3\ d^{-1}$ has been used previously (Pentreath *et al.* 1985; Cook *et al.* 1997).

Once water from the Irish Sea passes northwards through the North Channel it runs along the Scottish Shelf and forms a major constituent of the Scottish Coastal current (Hill and Simpson 1986; McKay and Baxter 1986), eventually rounding the northern Scottish coast as a component of the Fair Isle Current (Turrell and Henderson 1990) and passing into the North Sea. This water subsequently forms part of the Norwegian coastal current that runs along the Scandinavian shelf and then enters Arctic waters (Kershaw and Baxter 1995; Leonard *et al.* 1998; Aarkrog *et al.* 1999; Kershaw *et al.* 1999).

Table 1.5 Estimates of water flux through the North Channel of the Irish Sea.

Author	method	period of measurement	flux km^3 d^{-1}
Bowden (1950)	Salinity distribution	-	1.7
McKay and Baxter (1985)	^{137}Cs budgets	1978 -1981	7.8
Jefferies *et al.* (1982)	^{137}Cs budgets	10.71 - 12.75	3.5
Jefferies *et al.* (1982)	^{137}Cs budgets	01.76 - 05.78	7.9
Howarth (1982)	Cross channel telephone cables	-	4.3
Howarth (1982)	Current metre measurements	07.79 - 09.79	-14.7
Brown and Gmitrowocz (1995)	Current metre measurements	03.85 - 04.85	9.5
Brown and Gmitrowicz (1995)	Current metre measurements	04.85 - 06.85	12.1
Knight and Howarth (1999)	ADCP and OSCR HF Radar	07.93 - 08.94	6.7
Young *et al.* (2000)	Hydrodynamic model	-	2.0

ADCP - Acoustic Doppler Current Profilers

OSCR HF Rader - Ocean Surface Current High Frequency radar

Section 1.8 Discharges of low level liquid radioactive waste from the Sellafield nuclear fuel reprocessing plant to the Irish Sea

A number of nuclear establishments are authorised to discharge, under licence, low-level liquid radioactive waste into British coastal waters (Figure 1.12). The nuclear establishments at Sellafield, Springfields and Capenhurst and the nuclear power generating facilities at Heysham, Chapelcross and Wylfa discharge liquid radioactive waste into the Irish Sea. Of these, the nuclear fuel reprocessing plant at Sellafield is by far the largest contributor of liquid radioactive waste to the Irish Sea (BNFL 1990 -1999; Gray *et al.* 1995).

The Sellafield nuclear fuel reprocessing plant (formerly known as Windscale) is located on the north west coast of England (Figure 1.12) and was commissioned as part of the UK's nuclear weapons programme in the 1940s to produce plutonium for military purposes (Dunster 1998).

Releases of low level liquid radioactive waste from Sellafield have exhibited pronounced temporal variations in response to variations in the quantities of fuel being reprocessed and advances in effluent treatment procedures. Initial liquid effluent discharges were the result of reprocessing of fuel from the Windscale piles. Construction of these air cooled reactors began in 1947 and the first reactor achieved criticality in 1950 and the second in 1951. Both reactors were closed in 1957 after a fire in one of the piles. The primary plutonium separation plant became fully operational in 1952 and began reprocessing irradiated fuel from the piles, which had been stored in an open water pond up to this point. The commissioning of the primary separation plant in 1952 marked the start of liquid radioactive effluent discharges to the Irish Sea *via* pipelines (these are referred to in this text as "the pipeline") which extend approximately 2.5 km from the high water mark (Gray *et al.* 1995).

In order to assess the dispersion of the liquid radioactive discharges from reprocessing, two studies of the hydrology of the Irish Sea began in 1947. The first was a short term (12 h) tracer experiment using fluorescent dye , while the other was a longer term study using drift bottles. These studies concluded that tidal action would move the effluent parallel to the coast, but that long term dilution and removal of the radioactive effluent from the area would depend on wind driven turbulent diffusion and the net long term northerly circulation (Seligman and Scott 1948; Seligman 1955; Dunster, 1998).

The quantity of fuel reprocessed at Sellafield and associated discharges of low level liquid radioactive waste increased markedly with the development of the UK's nuclear power production program. Initially, reprocessing involved fuel from Magnox reactors, but more recently, fuel from AGR and light water reactors has been reprocessed in the Thermal Oxide Reprocessing Plant (THORP). The commissioning of THORP increased the throughput of spent fuel at Sellafield. The majority of spent fuel that is reprocessed at Sellafield comes from within the UK, but some also comes from abroad.

Figure 1.12 Nuclear establishments in the British Isles

Since the beginning of reprocessing in 1952 there have been significant changes in liquid effluent treatment processes before it is discharged into the Irish Sea. The concern over the total activity discharged into the Irish Sea in the 1970s prompted the termination, in 1980, of the practice of discharging medium active liquors, as well as the development of the following improved methods of treatment for the various low level effluent waste streams, prior to discharge (BNFL 1992a, 1992b, 1996; Gray *et al.* 1995).

1. The site ion-exchange effluent plant (SIXEP) which was brought on line in 1985. In this facility, the storage pond water from the Magnox plant is treated by passing it through a series of sand filters and clinoptilolite (a natural clay with a high cation exchange capacity). The SIXEP plant successfully reduced the activities of ^{90}Sr, ^{137}Cs and ^{134}Cs in the discharges.
2. The salt evaporator also began operations in 1985 and allowed the concentration and storage of salt bearing liquors from the reprocessing waste stream.
3. The enhanced actinide removal plant (EARP) commenced operations in 1994 and uses a ferric oxide scavenging process, to reduce further discharges of actinides *eg* ^{241}Am and plutonium isotopes.

Currently, the main sources of low level liquid radioactive waste are:

1 Storage pond water from the Magnox plant which is treated in SIXEP.

2 Storage pond water from THORP which is monitored and discharged directly to the sea.

3 EARP discharges, consisting of treated Magnox and THORP effluents.

4 Dissolver off-gas scrubber liquors from THORP which are treated to remove ^{14}C before monitoring and discharge.

5 Remaining process liquors which are routed to the site effluent treatment plant (SETEP) where effluent is held for monitoring of its composition prior to discharge.

6 Minor waste streams, such as surface drainage water and laundry effluent which account for less than 0.1% of the total liquid radioactive discharge. The radionuclides in the liquid effluent discharge which are of interest within this study are ^{14}C, ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239/240}$Pu. Figures 1.13 to 1.17 illustrate the annual discharge histories

Figure 1.13 ^{14}C discharges from Sellafield to the Irish Sea (1967 - 1998)

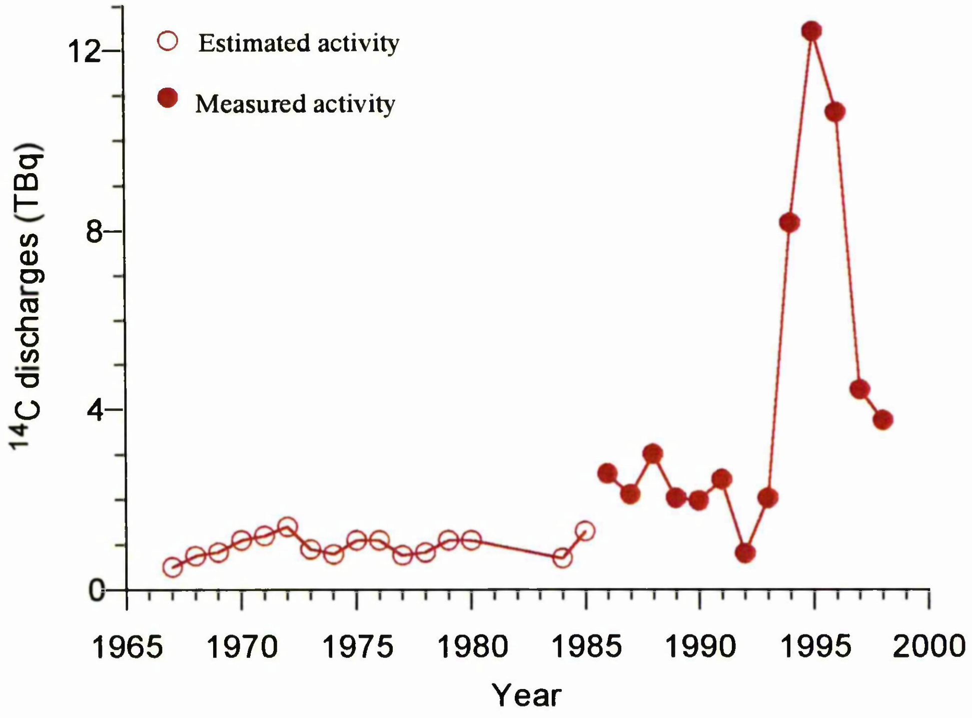


Figure 1.14 ^{137}Cs discharges from Sellafield to the Irish Sea (1952 - 1998)

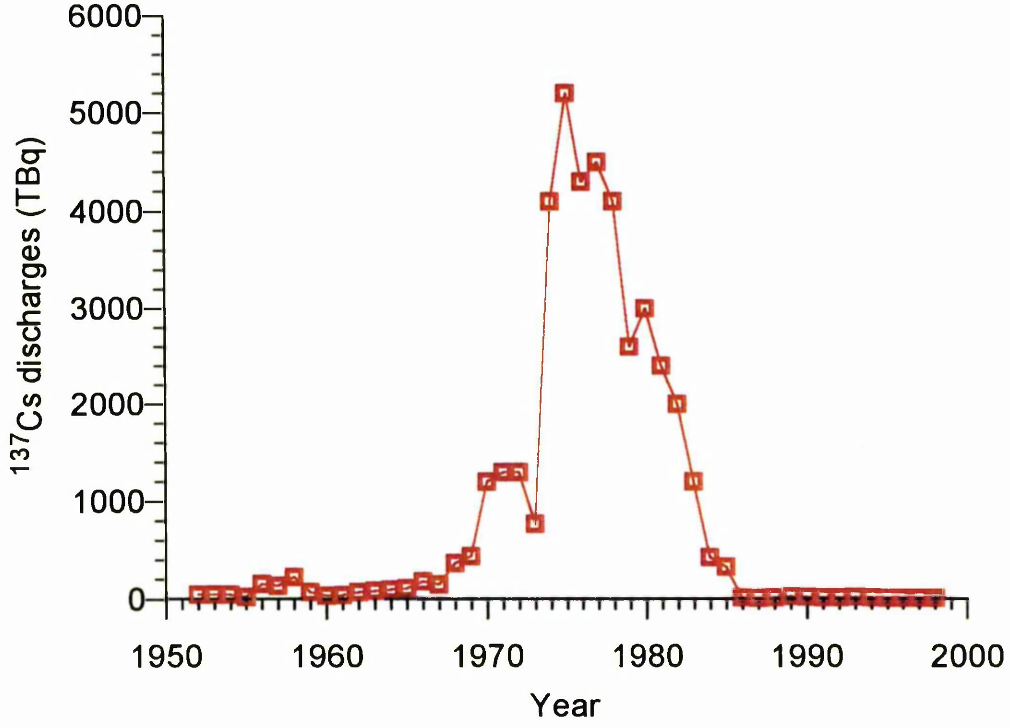


Figure 1.15 ^{241}Am discharges from Sellafield to the Irish Sea (1952 - 1998)

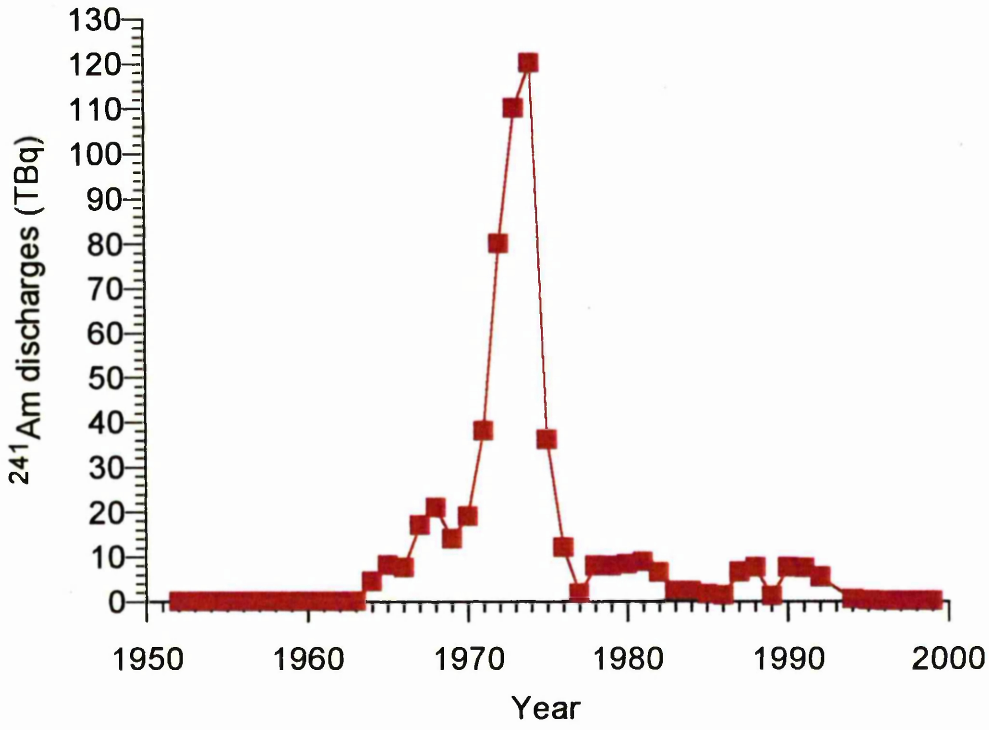


Figure 1.16 ^{238}Pu discharges from Sellafield to the Irish Sea (1952 - 1992)

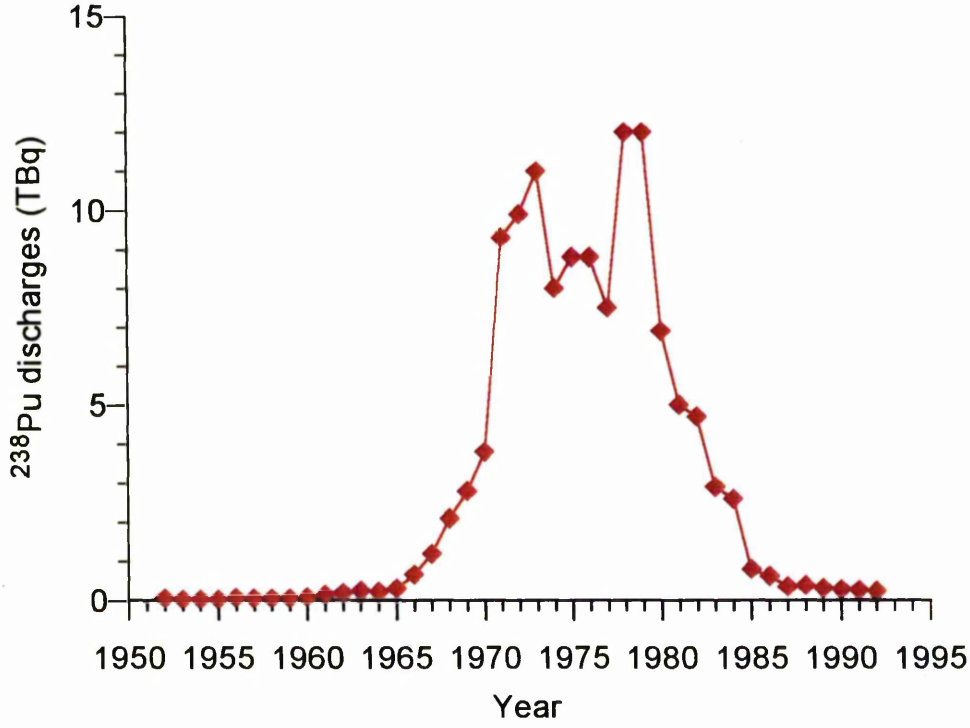
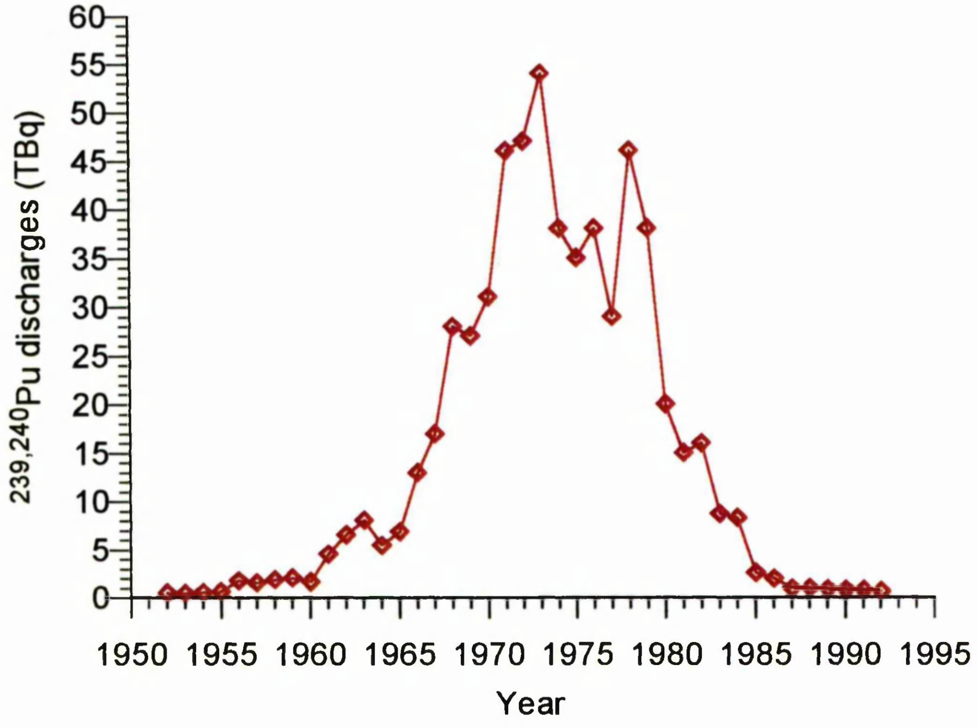


Figure 1.17 ^{239,240}Pu discharges from Sellafield to the Irish Sea (1952 - 1992)



of each of these radionuclides. The annual discharges of ^{137}Cs, ^{241}Am and plutonium have all decreased since their peak in the 1970s (early 1980s) to current annual discharges of a few TBq of ^{137}Cs, <0.5 TBq of ^{241}Am and <1 TBq of plutonium isotopes.

From Figure 1.13 it can be seen that the temporal trend in the activity of ^{14}C discharges is markedly different from those of other radionuclides. In general, the trend has been towards decreasing discharges since the peak in the 1970s, but in the case of ^{14}C, discharges have increased in recent years. Activities of ^{14}C discharged were not monitored prior to January 1984 and discharges for the years 1967 to 1983 were estimated.

The increase in ^{14}C discharges is due to the increase in fuel throughput since commissioning of the THORP plant and, to a larger extent, to a change in policy in 1994 from mainly atmospheric release of ^{14}C to a mainly marine route of discharge. The activity of ^{14}C discharged annually, prior to 1994, was between 1 and 2 TBq while discharges in 1994 and 1995 were 8.2 and 12.4 TBq, respectively, in response to changing effluent treatment procedures as discussed above.

The low level liquid radioactive waste is initially acidic and is neutralised by addition of ammonium hydroxide before discharge at high water. As the effluent is less saline than seawater, it forms a body of low density water on the top of the water column and this stratification remains for approximately 3-4 days before being mixed into the waters of the NE Irish Sea (Hetherington, 1975; Dyer, 1986).

1.9 Definitions, Conventions and Reporting ^{14}C Data

Various conventions can be used when reporting ^{14}C data and this section defines the various conventions and units used in ^{14}C research (Stuiver and Polach 1977).

The Primary Modern Reference Standard for ^{14}C measurements is wood grown in AD 1890 (and therefore uncontaminated by fossil fuel CO_2 -Suess Effect) whose activity was measured post-1950 and corrected for ^{14}C decay to correspond to AD 1950. In practice, all laboratories use a Secondary Modern Reference Standard against which sample activities are determined. The Secondary Standard commonly in use is Oxalic Acid SRM 4990C which is distributed by the National Institute of Standards and Technology, Gaithersburg, USA. This reference material consists of a 1000-lb lot of oxalic acid prepared by fermentation of French beet molasses using *Aspergillus niger*. 0.7459 times the specific activity of this material (normalised to a ^{13}C value of -25 ‰) is equal to the activity of the decay corrected AD 1890 wood which in turn equates to 226 Bq kg^{-1} of carbon.

Most laboratories, in their calculations, use an activity value A_{ON} which is 74.59% of the measured net oxalic acid activity (A_{OX}), normalised for ^{13}C fractionation according to

$$A_{ON} = 0.7459 A_{OX}\{1-\{2(25+\ ^{13}C)/1000\}]$$

(Measurements of ^{13}C are made by stable isotope mass spectrometry and are relative to the PDB standard).

Percent Modern equates to the activity ratio A_{SN}/A_{ON} x 100% where A_{SN} is the normalised sample activity. However the activity A_{ON} depends on the year of measurement (y) and has to be corrected for decay between 1950 and the year (y) of actual measurement. The *absolute international standard activity* is given by

$$A_{abs} = A_{ON} e^{-\lambda(y-1950)}$$

where y is the year of oxalic acid measurement and $= 1/8276\ y^{-1}$ is based on the physical half-life of ^{14}C (5730 y).

For geochemical and environmental ^{14}C studies, the term *absolute percent modern* (pM) is commonly used. This is defined as

$$\text{Absolute pM} = A_{SN}/A_{abs} \times 100\%$$

Thus, 100% modern is effectively the specific activity that prevailed in 1890.

1.10. Distribution of Sellafield derived radionuclides in the water column of the Irish Sea.

1.10.1 ^{137}Cs

Discharges of Sellafield derived liquid radioactive effluent have resulted in measurable activities of a number of radionuclides in the waters of the NE Irish Sea. This study is primarily concerned with the geochemical behaviour of ^{14}C, however, comparatively little research has been carried out so far on its behaviour in the Irish Sea. In contrast, the behaviour of ^{137}Cs is well understood and a large body of research exists on its geochemistry within the Irish Sea (Jefferies *et al.* 1973; 1982; Wilson 1974; Baxter *et al.* 1979; Prandle 1984; Begg *et al.* 1991; Bradley *et al.* 1991; McCartney *et al.* 1994; Cook *et al.* 1997; Leonard *et al.* 1997). Work by Begg (1992) has shown that activity distributions of ^{137}Cs and ^{14}C show similar, though not identical, trends in the water column with distance from the pipeline. It is therefore helpful to study ^{137}Cs activities in the water column in conjunction with ^{14}C.

^{137}Cs has been discharged from the Sellafield nuclear fuel reprocessing plant since it began operations in 1952 (Gray *et al.* 1995). The peak in ^{137}Cs releases occurred in the 1970s (Figure 1.14) with the discharge of ^{137}Cs in 1975 being 5,270 TBq. Since that time, the discharges have decreased to a few TBq y^{-1} between 1990 and 1999 (BNFL 1976 -1999; Gray *et al.* 1995).

It has been estimated that during the period of peak discharges, following release, approximately 10% of the ^{137}Cs became associated with fine grained sediments of the Sellafield "mud-patch", while the remaining 90% remained in solution and underwent widespread dispersion by the tidal currents of the Irish Sea (Pentreath *et al.* 1984; Miller *et al.* 1982; Murray *et al.* 1978; Jefferies *et al.* 1973; Prandle 1976; 1984).

The activities of dissolved ^{137}Cs in Irish Sea waters reported by Jefferies *et al.* (1973), were highest close to the Sellafield pipeline and lowest in St. Georges Channel. They also observed that while the dissolved ^{137}Cs activities in the waters of the North Channel were lower than those reported for waters adjacent to the Sellafield pipeline, a tongue of high activity water could be seen to move from Sellafield through the North Channel and then clockwise around the Scottish coast. In further studies, dissolved ^{137}Cs has been used as a conservative tracer of water movement from the Irish Sea, around the Scottish coast to the North Sea and then north to Arctic waters (McKay and Baxter 1986; Kershaw *et al.* 1999; Kershaw and Baxter 1995; Aarkrog *et al.* 1999; Leonard *et al.* 1998). Kershaw and Baxter (1995) estimated transit times from Sellafield to the North Channel and East Coast of Scotland of 1 and 2-3 years respectively, while the corresponding transit times reported by Leonard *et al.* (1997) using ^{99}Tc as the tracer were shorter at 3-6 and 9 months, respectively.

A number of workers have used dissolved ^{134}Cs/^{137}Cs activity ratios to assess the flux of water through the North Channel (Jefferies *et al.* 1973; Prandle 1976; Jefferies *et al.* 1982) as discussed in Section 1.7 of this work.

As the discharges of ^{137}Cs have decreased since the 1970s, the activities of ^{137}Cs in the waters of the Irish Sea and North Channel have decreased such that the activities in 1992 were approximately 250 to 350 mBq l^{-1} close to Sellafield and <50 mBq l^{-1} in the North Channel (Cook *et al.* 1997) in comparison to 29.9 Bq l^{-1} in 1979 close to Sellafield (Hunt and Kershaw 1990) and 1.2 Bq l^{-1} in 1981 in the North Channel (McKay and Baxter 1986). Subsequent to the period of peak discharges, the annual loss of ^{137}Cs through the North Channel, as reported by Pentreath *et al.* (1984) and Cook *et al.* (1997), was higher than the reported discharges from Sellafield for the year prior to that in which the studies were conducted. Both Pentreath *et al.* (1984) and Cook *et al.* (1997) concluded that this additional source of ^{137}Cs to the water column was due to the desorption of ^{137}Cs from the sediments of the NE Irish Sea, which will be discussed in greater detail in Section 1.11.1.

1.10.2. ^{14}C

While there is a large body of work relating to the environmental behaviour and distribution of a number of Sellafield derived radionuclides (including ^{137}Cs, ^{241}Am and Pu radioisotopes) both in and beyond the Irish Sea, until recently, little research effort had focussed on ^{14}C. Despite the fact that the total discharges of ^{14}C from Sellafield are low in comparison with the total discharge of other components of the low-level liquid radioactive waste, recent concern over the radiological implications of ^{14}C discharges has prompted a number of studies investigating the distribution and behaviour of Sellafield derived ^{14}C in the Irish Sea (Begg *et al.* 1991; 1992; Begg 1992; Cook *et al.* 1995; 1998; Wolstenholme *et al.* 1999;

Wolstenholme 1999).

Water Column -DIC

As stated before, seawater contains four carbon fractions, DIC, DOC, PIC and POC. The ^{14}C discharged from Sellafield to the NE Irish Sea is in a mainly inorganic form (Cook *et al.* 1995) and indeed Begg *et al.* (1991) and Cook *et al.* (1995) found the DIC fraction to contain the highest ^{14}C activity of the four carbon fractions of seawater.

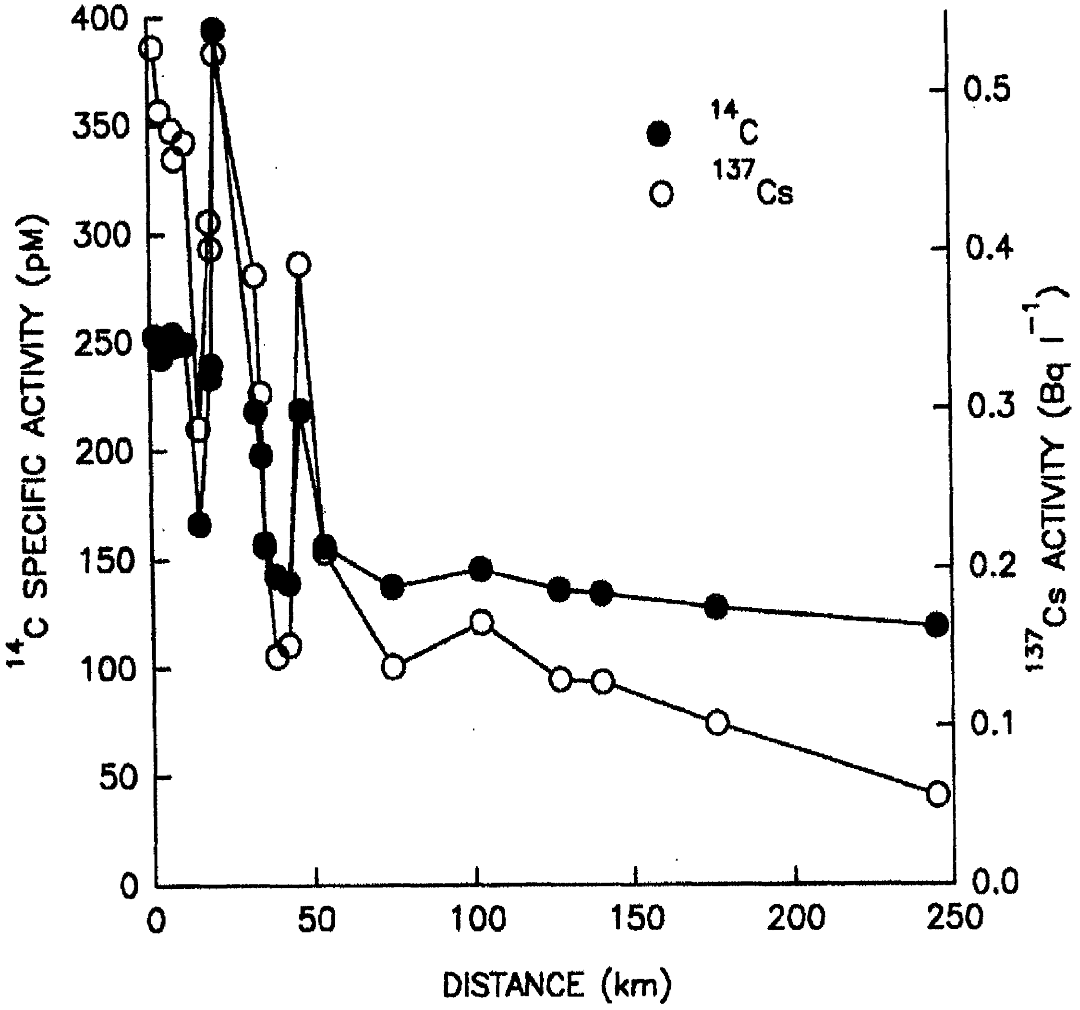
The study of Begg *et al.* (1992) aimed to determine the behaviour and environmental distribution of anthropogenically produced ^{14}C released into the aquatic environment from Sellafield and Amersham (Cardiff). During this study, from 1989 to 1991, water samples were collected over a large geographic area and were analysed for dissolved ^{137}Cs, the ^{14}C activity of the DIC fraction of the water column and to a lesser extent the ^{14}C activity of the other biogeochemical fractions of the water column (DOC, PIC and PIC).

While the ^{14}C activity of the DIC at each site was above the ambient background at this time of approximately 115.4 ± 0.4 pMC, in the study of Begg *et al.* (1991), the range of ^{14}C activities showed geographic variations from approximately 250 pMC near Sellafield to 119.7 ± 0.8 and 118.7 ± 0.5 pMC in St. Georges Channel and Scottish Coastal waters, respectively. Based on the ^{14}C activity of the DIC, Begg (1992) and Cook *et al.* (1995) concluded that the ^{14}C was discharged in a mainly inorganic form. Consistent enhancements above ambient background of between 200 to 250 pMC from sites on a transect which ran from Earnse Point, 40 km south of Sellafield, to the Scottish coastline, showed evidence of immediate enhancement of the DIC close to the point of discharge and subsequent transport both south and north of Sellafield. The activity of the DIC entering the Irish Sea through St. Georges Channel during the same study was close to ambient background at 119.7 ± 0.8 pMC and Begg *et al.* (1991) concluded from this that enhanced ^{14}C activities in the Irish Sea were due to discharges from Sellafield and that the influence of discharges of ^{14}C from Amersham (Cardiff) were negligible in waters outside the Severn Estuary, a conclusion that was supported by the work of Cook *et al.* (1998).

As discussed in Section 1.10.1, ^{137}Cs is an extensively used radiotracer of water movement and hydrography, due to its conservative behaviour in seawater (Jefferies *et al.* 1982; Prandle 1984; McKay and Baxter 1986). Begg *et al.* (1991) showed that the distribution of ^{14}C and ^{137}Cs activities in Irish Sea water exhibit a similar distribution relative to both distance and direction from the point of release (Figure 1.18). By mapping the observed activities of these radionuclides in the Irish Sea (apart from one observation) Begg *et al.* (1991) showed that both ^{14}C in the DIC and dissolved ^{137}Cs exhibited a trend of decreasing activity with increasing distance from Sellafield, with activity contours running parallel to the Cumbrian coast and a tongue of high activity water just north of Sellafield. The $^{14}C/^{137}Cs$ ratios in seawater showed decreasing values with increasing distance from the point of discharge (>250 close to Sellafield falling to 180 in the North Channel and approximately 60 off the west coast of Scotland) indicating differences in the behaviour of ^{14}C relative to that of ^{137}Cs. Begg *et al.* (1991) argued that the change in $^{14}C/^{137}Cs$ activity ratios with distance could be due either to the ^{14}C activity in the DIC being influenced by biological uptake and/or the ^{137}Cs activity being increased by desorption from the sediments.

From a study of ^{14}C activities above ambient background in the DIC and in biota of the NE Irish Sea coastline Begg *et al.* (1991, 1992) concluded that the ^{14}C discharged from Sellafield was distributed both to the north and south of Sellafield, but that the bulk of the ^{14}C was removed by the prevailing current system northwards through the North Channel. They also concluded that like ^{137}Cs, ^{14}C in the DIC behaves in a mainly conservative manner in seawater. Subsequent to the work of Begg *et al.* (1991) and Cook *et al.* (1995), Cook *et al.* (1998) reported considerably higher ^{14}C activities in the DIC fraction of seawater at three sites close to Sellafield of 8,814± 77, 5,145 ± 45 and 935 ± 8 Bq kg^{-1} C (or approximately 3,900, 2,300 and 400 pMC respectively) and an activity of 430 ± 4 Bq kg^{-1} C (or approximately 200 pMC) reported for the North Channel, which was approximately one third higher than that previously reported for the same site by Cook *et al.* (1995). The activity found at St Georges Channel (252 ± 3 Bq kg^{-1} C of approximately 111.5 pMC) was similar to those found by Cook *et al.* (1995) and Begg *et al.* (1991). These increases in ^{14}C activity in seawater within the Irish Sea were attributed to the increased ^{14}C discharges from Sellafield in 1994/95.

Figure 1.18 Distribution of dissolved ^{137}Cs and ^{14}C DIC activities in the Irish Sea (Begg *et al.* 1991)



The study by Cook *et al.* (1998) was designed to investigate marine background ^{14}C activities in British and Irish Coastal waters. Apart from locations in the Irish Sea, the sampling sites were chosen for remoteness from anthropogenic influence. They concluded that the ^{14}C ambient background in the marine environment (in 1995) due to natural production and atmospheric weapons testing was 247 Bq kg^{-1} C, and that the influence of Sellafield discharges on the Burtonport site (West coast of Ireland) was negligible and that this was therefore, a suitable site for estimation of ^{14}C ambient background. The ^{14}C activities in samples from the north coast of Scotland were also close to the Burtonport value for the ambient background. However, it must be noted that this study was carried out in 1995, not long after the increase in ^{14}C discharges from Sellafield and the transit time for Irish Sea water to reach the east Scottish coast has been estimated by some authors as being as long as 1 to 2 years (Kershaw and Baxter 1995; Dahlgaard, 1995) while other authors have estimated a shorter transit time of approximately 9 months (Leonard *et al.* 1997), so it is possible that the increase in ^{14}C discharge activity from Sellafield may not have reached the locations in the north of Scotland or the east coast of England at the time of sampling.

In a more recent study, Wolstenholme *et al.* (1999) analysed the ^{14}C activity of DIC on six separate occasion at two sites, termed Sellafield (MIRMAID regions 10 and 11) and Sellafield North (MIRMAID regions 23 and 24) (Kirby *et al.* 1983) in the Irish Sea, between February 1995 and November 1996. The ^{14}C activities in the DIC at the Sellafield sampling site were variable and ranged between 247 ± 3 and 1,677 ± 9 Bq kg^{-1} C (~ 105 to 706 pMC) while the activities at the Sellafield North site were higher and ranged between 859 ±4 and 10,991 ± 57 Bq kg^{-1} C (~360 to 4,668 pMC). Wolstenholme *et al.* (1999) concluded that the very high activity of 10,991 ± 57 Bq kg^{-1} C was due to either a "packet" of incompletely mixed effluent, or that the whole Irish Sea area was transiently enriched to this degree. Unfortunately there was no sample collected at the same time at the Sellafield site to provide a comparison. Wolstenholme (1999) compared the activities of ^{14}C in the DIC with monthly discharge data supplied by BNFL and concluded that there was a short response time in the DIC activity of the water column to the ^{14}C discharges, presumably because the discharge is in an inorganic form. Due to the difference between the frequency of recorded (monthly) discharge data relative to that of the sampling intervals, which was approximately quarterly, it was not possible to assess precisely the time interval between the changes in discharge and the changes in the activity of the DIC.

Other Biogeochemical fractions

Begg *et al.* (1991) and Cook *et al.* (1995) presented results for the analysis of ^{14}C in the four biogeochemical fractions of seawater (Figure 1.19). The seven sites sampled between 1989 and 1991 give a good indication of the range of ^{14}C activities in each of the fractions prior to the rise in ^{14}C discharge in 1994/95. In comparison with the DIC activities, which were all above modern, only one of the POC activities was above modern at 188.3 ± 1 pMC (~425.6 Bq kg^{-1}

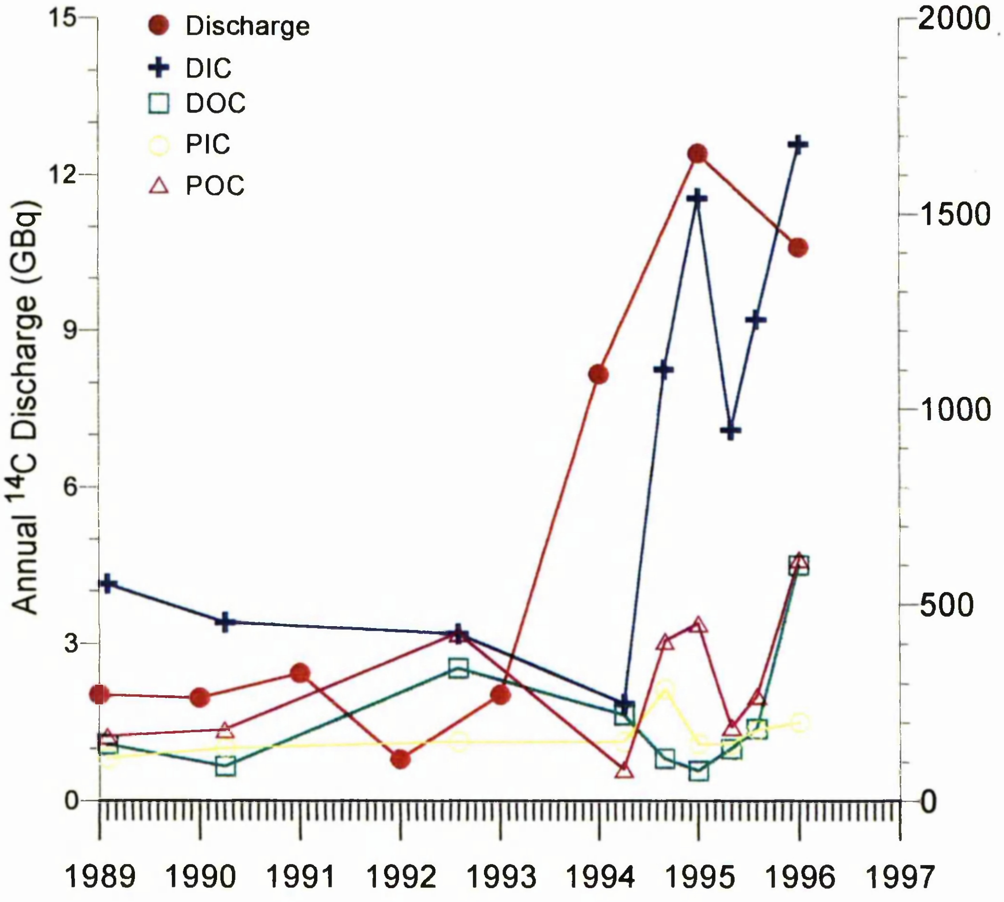
C) while the remaining samples ranged between 51.9 ± 0.6 and 80.4 ± 1 pMC (~117.3 and 181.7 Bq kg^{-1} C). Enrichment of the POC above ambient background had been expected as Begg *et al.* (1992) had found enhanced activities in the flesh of intertidal biota to the north and south of Sellafield, which feed directly on components of the POC. It must be noted that the only enriched POC sample was collected in the summer and Cook *et al.* (1995) speculated that as the DIC and POC were not significantly different from each other at this time, the POC derived directly from the DIC, indicating a quick turnover of carbon between the two biogeochemical fractions. This could be explained if the POC was dominated by phytoplankton which directly utilise the DIC *via* photosynthesis. If this was true then there are implications of seasonality in the ^{14}C activity of the POC, DOC and PIC due to peaks in phytoplankton production at certain times of the year. The ^{14}C activity of the DOC and PIC fractions (with the exception of the DOC fraction in June 1993) were also depleted relative to the ambient background activity for the early 1990s of approximately 260 Bq kg^{-1} C (Lassey *et al.* 1988; Begg 1992), at 47.9 ± 0.5 to 100.3 ± 1.5 pMC (~106 to 227 Bq kg^{-1} C Bq kg^{-1} C) for the PIC and 33.2 ± 0.5 and 149.0 ± 0.8 pMC (~75 to 337 Bq kg^{-1} C) for the DOC.

Samples obtained from two trawls for mixed plankton in the NE Irish Sea in 1989 had higher ^{14}C activities than corresponding POC samples (Cook *et al.* 1995), indicating that the POC contained some older organic material, possibly of terrestrial origin or resuspended sedimentary material.

The ^{13}C values of between -19.3 and -26.4 ‰ and -23.8 to -29.9 ‰ (relative to the PDB standard) of the POC and DOC, respectively (Begg 1992) indicate that there is some input of terrestrial carbon to the organic fractions of the water column (marine production ^{13}C values are typically between -18 and -22 ‰ and terrestrial ^{13}C values between -24 and -32‰). This terrestrial carbon could contain lower ^{14}C activities and so dilute the ^{14}C activity of contemporary marine production. Such inputs would be variable as they depend on river input to the marine environment.

Wolstenholme (1999) analysed the biogeochemical fractions of seawater at the Sellafield and Sellafield North sites between February 1995 and November 1996. In Figure 1.19 the activities of the four biogeochemical fractions at the Sellafield site are compared to the results reported for samples collected in the vicinity of Sellafield by Cook *et al.* (1995). The activities of the PIC, POC and DOC on each occasion were depleted relative to the DIC activity for both studies. In comparison to the activities of the DIC, POC and mixed plankton reported by Cook *et al.* (1995), the ^{14}C activities reported by Wolstenholme (1999) are higher (apart from the DIC at the Sellafield site and the POC at both sites in February 1995), ranging between 247 ± 3 and 10,991 ± 57 Bq kg^{-1} C (105.1 ±1 and 4,662 ± 24 pMC) for the DIC, 80 ± 1 and 736 ± 4 Bq kg^{-1} C (36 ±0.4 and 322 ± 2 pMC) for the POC and 774 ± 3 and 1,247 ± 5 Bq kg^{-1} C (343 ± 1 and 547 ± 2 pMC) for the mixed plankton trawls.

Figure 1.19 Measured ^{14}C activities in the DIC, DOC, PIC and POC fractions of the water column in the vicinity of Sellafield (Cook *et al.* 1995; Wolstenholme 1999).



The DOC and PIC fractions had lower activities than those of the DIC, POC and mixed plankton on all occasions and did not show the same response to the increase in ^{14}C discharge exhibited by the DIC and POC. Wolstenholme (1999) concluded that all the carbon containing reservoirs and the plankton at both sites exhibited higher activities in this study than those found by Cook *et al.* (1995) due to the increased ^{14}C discharges from Sellafield in 1994, but that the slower responses of the DOC and PIC fractions were due to incorporation of older material into these carbon fractions, which diluted the Sellafield derived signal.

1.11 Distribution of Sellafield derived radionuclides in the sediments of the Irish Sea

The work off Wolstenholme (1999) concluded that the distribution of Sellafield derived ^{14}C in the organic carbon fraction of Irish Sea sediments could be described by dividing the sediment column into zones of differing mixing intensity. Depth of mixing intensity was based on arguments developed by MacKenzie *et al.* (1999) using ^{137}Cs:^{241}Am activity ratios where ratios of <2 were indicative of high intensity mixing, ratios of 2-6 were indicative of medium intensity mixing and ratios of <6 were indicative of low intensity mixing. The approach of MacKenzie *et al.* (1999) to determine the depth of mixing zones was adopted in this study. So while the focus of this work is to study the behaviour of ^{14}C the use of other radionuclides to determine the physical mixing of the sediment studied means that the discharge history, environmental behaviour and long term fate of ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239,240}Pu$ are also important.

1.11.1 ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239,240}Pu$ distributions

The following section is a condensation of the large body of work that describes the distributions and behaviour of Sellafield derived radionuclides in the sediments of the NE Irish Sea.

The highest activities of liquid effluent released from Sellafield to the Irish Sea occurred in the 1970s (Gray *et al.* 1995) when discharges were two to three orders of magnitude greater than they are currently (Section 1.8). There were large temporal variations in the activities of individual radionuclides discharged as well as in the radionuclide activity ratios. For example, $^{238}Pu/^{239,240}Pu$ and $^{241}Am/^{239,240}Pu$ activity ratios for annual discharges (1952-1990) varied from

0.029 to 0.361 and 0.13 to 3.16, respectively, giving ratios for the time integrated discharge of 0.182 and 1.55, respectively.

The environmental inventories of ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu discharged by Sellafield between 1952 and 1990 were approximately 3.6×10^4, 9.4×10^2, 1.1×10^2 and 6.1×10^2 TBq respectively, with approximately 3.6×10^2 TBq of the ^{241}Am being derived from the decay of discharged ^{241}Pu (Gray *et al.* 1995).

During the period of high discharges, almost all of the ^{241}Am, along with approximately 90% of the plutonium isotopes (in the highly insoluble +4 oxidation state) and 10% of the ^{137}Cs were immediately incorporated into the fine grained sediments of the Sellafield "mud-patch", located close to the point of discharge. The remaining 10% of the plutonium, in the soluble +5 oxidation state remained in solution and was carried out of the Irish Sea together with 90% of the ^{137}Cs (Jefferies *et al.* 1973; Hetherington 1975; Nelson and Lovett 1978; Baxter *et al.* 1979; Day and Cross 1981; Pentreath *et al.* 1984).

Subsequent lateral dispersion of this contaminated sediment to a larger area of the NE Irish Sea and surrounding coastal areas has been important, both in terms of the long term dispersion and dilution of the radionuclides and of increased human exposure to anthropogenic radioactivity in the coastal environment. Hunt (1985) demonstrated that after the major input of radionuclides in the 1970s, dispersion and mixing of the contaminated sediment resulted in a gradual reduction in radionuclide concentrations in intertidal sediments in the vicinity of Sellafield. On the basis of observed ^{238}Pu:^{239,240}Pu activity ratios, he concluded that sediment-associated plutonium was removed from the marine environment around Sellafield on a timescale of one to two decades. By 1987, the dispersion processes had resulted in substantial lateral re-distribution of radionuclides in the offshore surface sediments of the NE Irish Sea as reported by McDonald *et al.* (1990), who observed that samples from a 60 km transect, extending northwest from the centre of the "mud-patch", exhibited effectively constant activity ratios. They also observed that specific activities varied mainly in response to grain size, rather than distance from Sellafield. In an extensive summary of data generated by the MAFF (now CEFAS) Lowestoft laboratory, McCartney *et al.* (1994) also observed that the nature of the underlying sediment had a strong influence on radionuclide concentrations and this was highlighted by a strong correlation between ^{137}Cs concentrations and the silt content of the sediment. The authors further noted that in 1988, significantly enhanced concentrations of radionuclides persisted in a restricted area of sediment in the immediate vicinity of the Sellafield outfall, with ^{239,240}Pu activities in excess of 2000 Bq kg^{-1}. Some of the conclusions from these studies were supported by MacKenzie *et al.* (1999) who showed, from a series of surface sediment samples running north-west from Sellafield to the North Channel, that the relative importance of individual size fractions in determining the fate of the contaminant radionuclides was not only dependent on the radionuclide concentrations but also on the percentage of the total mass of sediment that each fraction represents. This supported the findings of Eakins *et al.* (1990) in their investigation of intertidal sediments. Thus, for the higher activity samples from the "mud patch", the clay and silt size fractions were dominant in determining the fate of Sellafield derived radionuclides, but coarser sediment fractions were of equal or more importance at other locations.

In the early 1980s, it was established that onshore transport of contaminated sediments resulted in deposition of Sellafield waste radionuclides in the estuarine intertidal sediments of north west England (Aston *et al.* 1981; Aston and Stanners 1982). Subsequently, MacKenzie *et al.* (1987) demonstrated that transport of contaminated particles was, in fact, the dominant mechanism of supply of Sellafield waste radionuclides to the intertidal areas of south west Scotland. It was further observed that there was an order of magnitude decrease in the efficiency of the particle transport process in areas to the west of Burrow Head (54^0 38' N; 04^0 21' W), relative to those to the east of this point. Two key observations of this work were that, (a) within the suite of samples analysed from the Scottish coast of the Irish Sea, variations in radionuclide concentrations were dominantly attributable to variations in sediment grain size and (b) over a distance of about 100 km, strong linear correlations existed between the specific activities of ^{137}Cs, ^{239,240}Pu and ^{241}Am in surface sediments. MacKenzie *et al.* (1987) and MacKenzie and Scott (1993) concluded that these observations were compatible with the supply of particle-associated radionuclides to different intertidal locations from a common pool of well-mixed contaminated sediment, but that they were incompatible with transport of the radionuclides in solution, which would have resulted in large spatial variations in the activity ratios of radionuclides with contrasting solubility characteristics, such as ^{137}Cs and ^{241}Am. The dominant role of particle-associated transport of radionuclides to the intertidal areas of the Irish Sea was further evidenced by the observation that, since the late 1970s, radionuclides deposited in saltmarshes and intertidal areas of north west England and south west Scotland exhibited activity ratios that were representative of the time integrated Sellafield discharges (Kershaw *et al.* 1990, 1992; MacKenzie *et al.* 1994; MacKenzie and Scott 1993; Pulford *et al.* 1998).

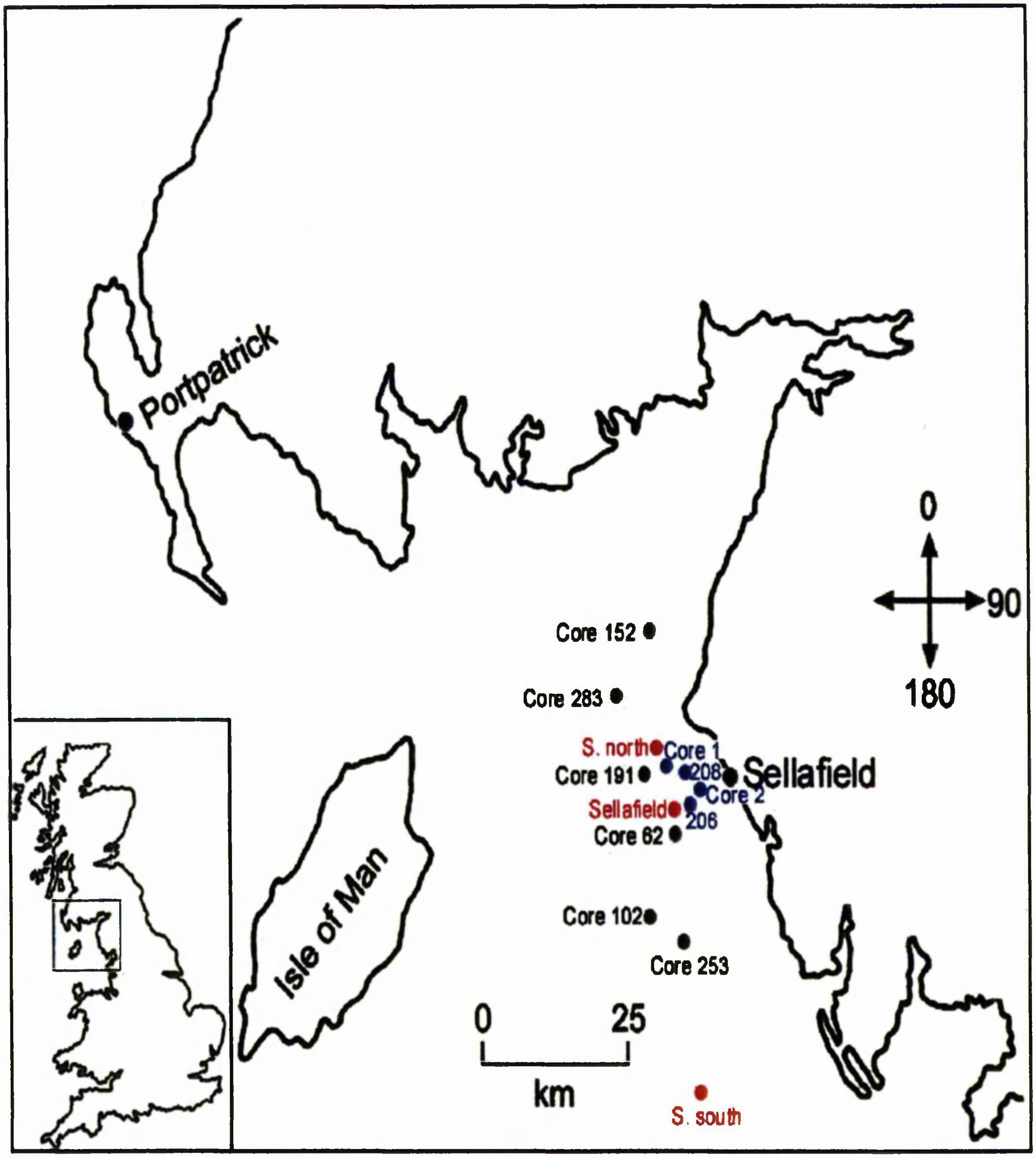
The sediments of the NE Irish Sea have been shown to be subject to intensive biological mixing (Kershaw *et al.* 1983; 1984; 1988; Woodhead 1988; MacKenzie *et al.* 1998) (for example by the Thalassinid shrimp, *Callianessa subterranea* and the echiuran worm, *Maxmuelleria lankesteri*) and there is evidence of biological mixing of Sellafield radionuclides to a depth of 1.4 m in the Sellafield "mud-patch" (Kershaw *et al.* 1983; 1984). The sediments of the NE Irish Sea are also subject to disturbance by trawling which reduces the amount of cohesion between clay particles in the "mud-patch" area. Moreover, due to the shallow nature of the NE Irish Sea embayment (<50 m), these sediments will also be subject to disturbance by storm action (Irish Sea Study Group 1990; Williams *et al.* 1981). Studies by Woodhead *et al.* (1988) and MacKenzie *et al.* (1998) on the vertical distributions of the short half-life radionuclides ^{60}Co ($t_{½}$ = 5.3 y), ^{134}Cs ($t_{½}$ = 2.06 years), ^{106}Ru ($t_{½}$ = 367 days) and ^{144}Ce ($t_{½}$ = 284 days) showed that the ^{60}Co was transported vertically and mixed to a depth of up to 18 cm on a timescale similar to its half life. Based on the mixing of the other three radionuclides in the surface sediments, they concluded that a timescale of the order of >1 year was required for complete homogenisation of past Sellafield discharges in the surface sediment (<10 cm). In addition, the study showed that the sediments were indicative of a highly mixed system with respect to the long lived radionuclides such as ^{241}Am, ^{238}Pu and $^{239/240}$Pu and the activity ratios of these radionuclides in the sediment column reflected the time integrated Sellafield discharge ratios rather than the annual discharge activity ratios. On the basis of the ^{137}Cs:^{241}Am ratio and radionuclide specific activity profiles in the sediment column MacKenzie *et al.* (1998) argued that the sediment could be viewed as having zones of differing intensities of mixing with increasing depth.

Redissolution of radionuclides from the sediment to the overlying water column has been of importance since the 1980s due to the fact that the discharges during this period were approximately two orders of magnitude lower than those in the 1970s, resulting in low dissolved radionuclide concentrations in the water column relative to those in the underlying sediments. Operation of the law of mass action has resulted in re-dissolution of radionuclides from the sediment, consistent with reversible sorption (Hunt and Kershaw 1990). Hunt and Kershaw (1990) calculated the loss of radionuclides from the sediment to the water column by the process of desorption to be: 1,300 ± 700 TBq of ^{137}Cs between 1983 and1988, 8 TBq of Pu(α) between 1979 and 1987 and 2.5 TBq of ^{241}Am between 1976 and 1987. Pentreath *et al.* (1984) calculated losses of plutonium *via* desorption from the sediments of between 1.33 and 2.55 TBq per annum through the North Channel between 1973 and 1979. This calculation was based on a flow rate of 5 km^3 day^{-1} through the North Channel and measured surface seawater concentrations of plutonium. The authors noted, however, that the extent to which surface water is representative of the total water column is unclear. MacKenzie *et al.* (1994) calculated halving-times of 4-7 years for the activities of plutonium isotopes and ^{241}Am in sediment deposited in intertidal areas, with the corresponding halving-time for ^{137}Cs being 3-4 years. The lower halving-time for ^{137}Cs was attributed to significant re-dissolution. McCartney *et al.* (1994) calculated that the specific activity of ^{137}Cs in the surface 5 cm layer of sediment of the "mud-patch" decreased by approximately 75% between 1983 and 1988. The authors attributed this decrease to desorption of ^{137}Cs from the sediments to the water column and did not consider any decrease in specific activity as a consequence of sediment redistribution. In agreement with this, MacKenzie *et al.* (1998) also suggested that up to 77% of the ^{137}Cs originally deposited in surface sediments (<10 cm depth) and about 15% of that in deeper layers had been lost by redissolution to the overlying water column, indicating that a K_d of the order of 10^4 –10^5 is applicable to radiocaesium in this system. Based on the dissolved and particle-associated activities from samples collected in the NE Irish Sea and North Channel, Cook *et al.* (1997) concluded that as a consequence of re-dissolution and subsequent aqueous phase transport, the activity of ^{239,240}Pu in Irish Sea sediments was subject to a halving period of 350 years while that for ^{137}Cs was 23 years, reflecting the contrasting solubilities of these species. Following the approach of Pentreath *et al.* (1984), losses through the North Channel were calculated to be 1.19, 0.22 and 86 TBq during 1992 for dissolved ^{239,240}Pu, ^{238}Pu and ^{137}Cs, respectively. These values are greater than the activities discharged from Sellafield during the year prior to sample collection for this study and confirm that re-dissolution is indeed occurring at a significant rate.

1.11.2 ^{14}C

The initial studies of ^{14}C in the Irish Sea by Kershaw (1986) and Kershaw *et al.* (1988) (Figures 1.20 and 1.21) were not designed as a pollution investigation, but were intended to estimate the sediment accumulation rates of the Sellafield and western Irish Sea mud patches

Figure 1.20 Location of cores in the Irish Sea Cir 191 and 62 after Kershaw (1986) (black text); Cores 152, 283, 253 and 102 after Kershaw *et al.* (1988) (black text); Core 1 and 2 after Cook *et al.* (1995) (blue text); 206 and 208 (grabs after Begg 1992) (blue text) and S. South, S. North and Sellafield after Wolstenholme (1999) (red text).



in the manner of Erlenkeuser (1980) and to assess the significance of the rate of accumulation with respect to permanent burial of Sellafield derived radionuclides. Kershaw (1986) presented radiocarbon results from analysis of the bulk inorganic carbon fraction of two NE Irish Sea sediment cores, collected in 1983 using a Kasten corer (Figures 1.20 and 1.21). Core Cir 5/83-62 (referred to as Cir 62 in this text) was 144 cm in length with a surface (0-10 cm) ^{14}C age of 13,030 ± 400 y BP. The ages of the deeper sections ranged from 11,700 ± 300 to 13,230 ± 260 y BP. Core Cir 5/83-191 (referred to as Cir 191 in this text) was 166 cm in length with a surface (0-9 cm) ^{14}C age of 11,820 ± 150 y BP. The ages of the deeper sections ranged from 11,680 ± 210 to 12,640 ± 230 y BP. Thus, throughout the lengths of both cores, the ^{14}C age was near constant, with both exhibiting age reversals. Therefore, Kershaw (1986) deemed them unsuitable for use in the estimation of sedimentation rates.

Kershaw (1986) concluded that the near-constant radiocarbon ages implied that the sediment at both sites had been subjected to intensive mixing on the time scale of the half-life of ^{14}C which is consistent with evidence of intense and rapid mixing as discussed in section 1.11.1. The average age of 12,500 ± 1,000 y BP of these cores is compatible with deposition in pre Holocene times. Evidence based on the estimated age (5,700 y BP) of the material arriving at the surface sediment of a site in the western Irish Sea, suggested that the sediments may contain material of terrestrial or re-worked origin and so the deposition age could be considerably younger than the observed ^{14}C age. However, the stable carbon isotope data for the three cores presented by Kershaw (1986) indicated that the sedimentary carbonate was of marine origin, with the $\delta^{13}C$ values of the cores ranging from -0.1 to 1.1 ‰ (relative to the PDB standard). This demonstrates that there is little, if any, terrestrial carbonate in the cores and it is more likely that the material has been reworked and may have been eroded and redistributed several times.

Kershaw (1986) concluded that biological mixing of the sediments of this area had blurred any geochemical signal to the point where no sensible conclusions could be made regarding the current depositional environment of the NE Irish Sea. He also concluded that it was quite likely that the vertical distributions of Sellafield derived radionuclides in the sediments of the north Irish Sea were due predominantly to biological redistribution, rather than to the active sedimentation of freshly contaminated particles.

In a subsequent study, Kershaw *et al.* (1988) analysed the bulk inorganic fraction of the sediment as well as the shells of the gastropod, *Turritella communis* (Riso), (these shells are common throughout the sediments of the NE Irish Sea), in four cores from the NE Irish Sea (Figures 1.20 and 1.22). While the ^{14}C ages and age distributions of the inorganic sediment in cores 253, 102 and 152 generally agreed with those found in the previous study (Kershaw 1986) there was a greater range of ages in these cores (15,330 ± 480 to10,310 ± 190 y BP in core 253; 13,230 ± 120 to 11,400 ± 100 y BP in core 102 and 620 ± 150 to 12,000 ± 110 y BP in core 152). Core 283 was the shortest, at 60 cm, and the ^{14}C ages in this core were similar at all depths. The stable isotope data from these cores also agreed with the data from the previous study, with δ^{13}C values between - 0.8 and + 0.8 ‰, supporting the theory of a marine origin for the carbonate in the sediments of this area. The ages of the *T. communis* shells in cores 253, 102 and 152, were much younger (approximately 4,300 to 300 y BP) than the bulk inorganic carbon fraction of the sediment at corresponding depths. Apart from core 102 and one instance at the bottom of core 152, the radiocarbon ages of the shells indicated a trend of increasing age with increasing depth in the sediment. Using the ^{14}C ages derived from the *T. communis* shells, (corrected for the marine reservoir age of 405 ± 40 y BP Harkness 1983),apparent accumulation rates of0.08, 0.02 and 0.27 cm y^{-1} were calculated for cores 152, 253 and 102, respectively. Core 102 had a more variable age profile for *T. communis* shells,

Figure 1.21 ^{14}C activities in the sediment column reported by Kershaw (1986)

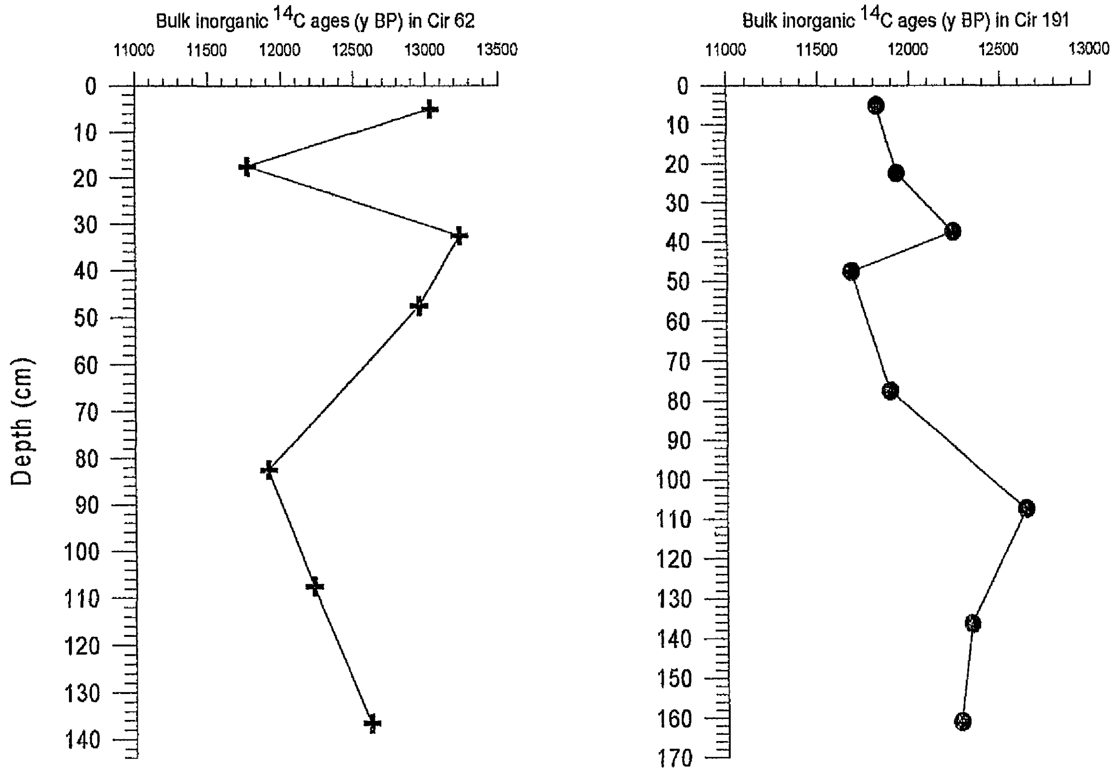
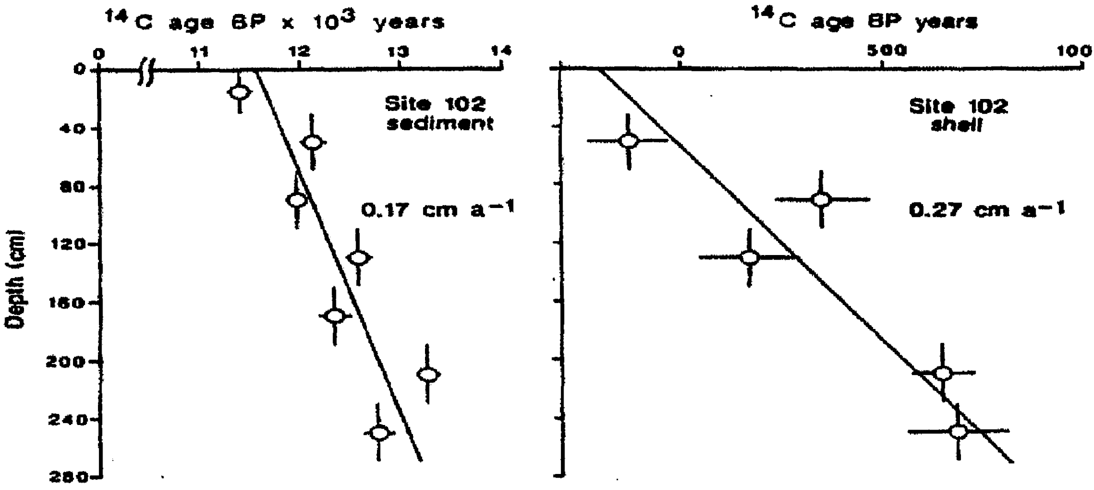
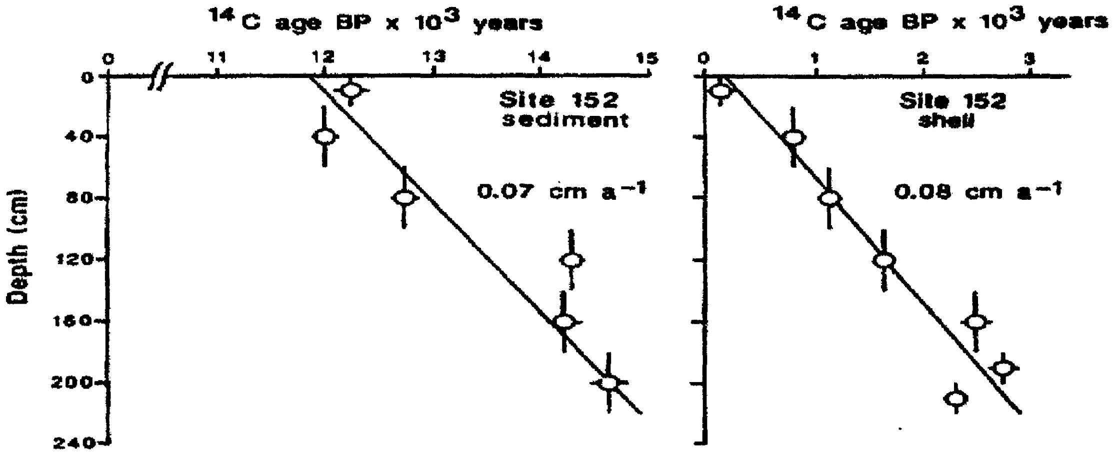


Figure 1.22 ^{14}C activities in the sediment reported by Kershaw *et al.* (1988). (a) core 102, (b) core 153 and (c) core 253.

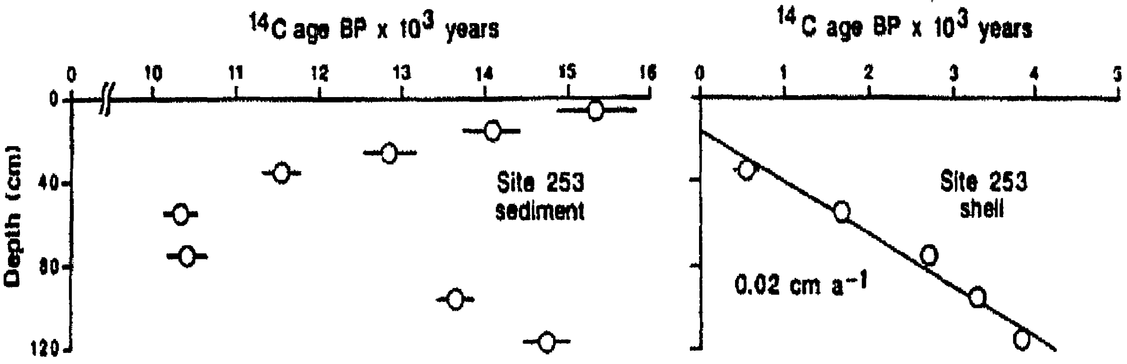
(a) core 102



(b) core 152



(c) core 253



with the ages of the two lowermost samples (190-230 cm and 230-270 cm) and the two middle samples (70-110cm and 110-150 cm) not differing significantly from each other. Furthermore, the estimated sedimentation rate of 0.27 cm y^{-1} for this core was much higher than those derived for the other cores. The presence of shells with a reservoir corrected age of < 700 years at 2 m depth was interpreted by Kershaw *et al.* (1988) as evidence of enhanced sedimentation at the site of core 102 and they suggested that southward movement of fine grained sediments from the Solway Firth and Wigtown Bay could have been the source of sediment, as suggested by Pantin (1978). The doubts as to whether or not there is a contemporary source of fine grained sedimentary material available for transport to the NE Irish Sea bed (Kirby *et al.* 1983), combined with the erratic intervals in ^{14}C age distributions within the sediment core questions the validity of this sedimentation rate. Kershaw *et al.* (1988) concluded (based on the radiocarbon data) that recent, net sedimentation had taken place in at least three sites in the NE Irish Sea (cores 102, 152 and 253), but that the rate of accumulation was not rapid enough to completely bury the total quantity of contaminant radionuclides adsorbed or deposited on the surface sediments. They also concluded that bioturbation is a more important factor than the accumulation of particles in the distribution of Sellafield derived radionuclides in the sediments of the NE Irish Sea. Kershaw *et al.* (1988) also concluded from this and the previous study (Kershaw 1986) that the influence of the ^{14}C discharges from Sellafield up to that point had little obvious effect on the ^{14}C activity of the bulk inorganic carbon fraction of the sediments, however, as the initial (pre-Sellafield) age of the sediments is not known, it is difficult to agree with this conclusion. The studies by Kershaw (1986) and Kershaw *et al.* (1988) suggest that there is a discrepancy between different size factions of the sediment as exhibited by the younger ages of the *T. communis* shells, indicating that the bulk sediment is composed of a number of different carbon fractions of differing ^{14}C ages.

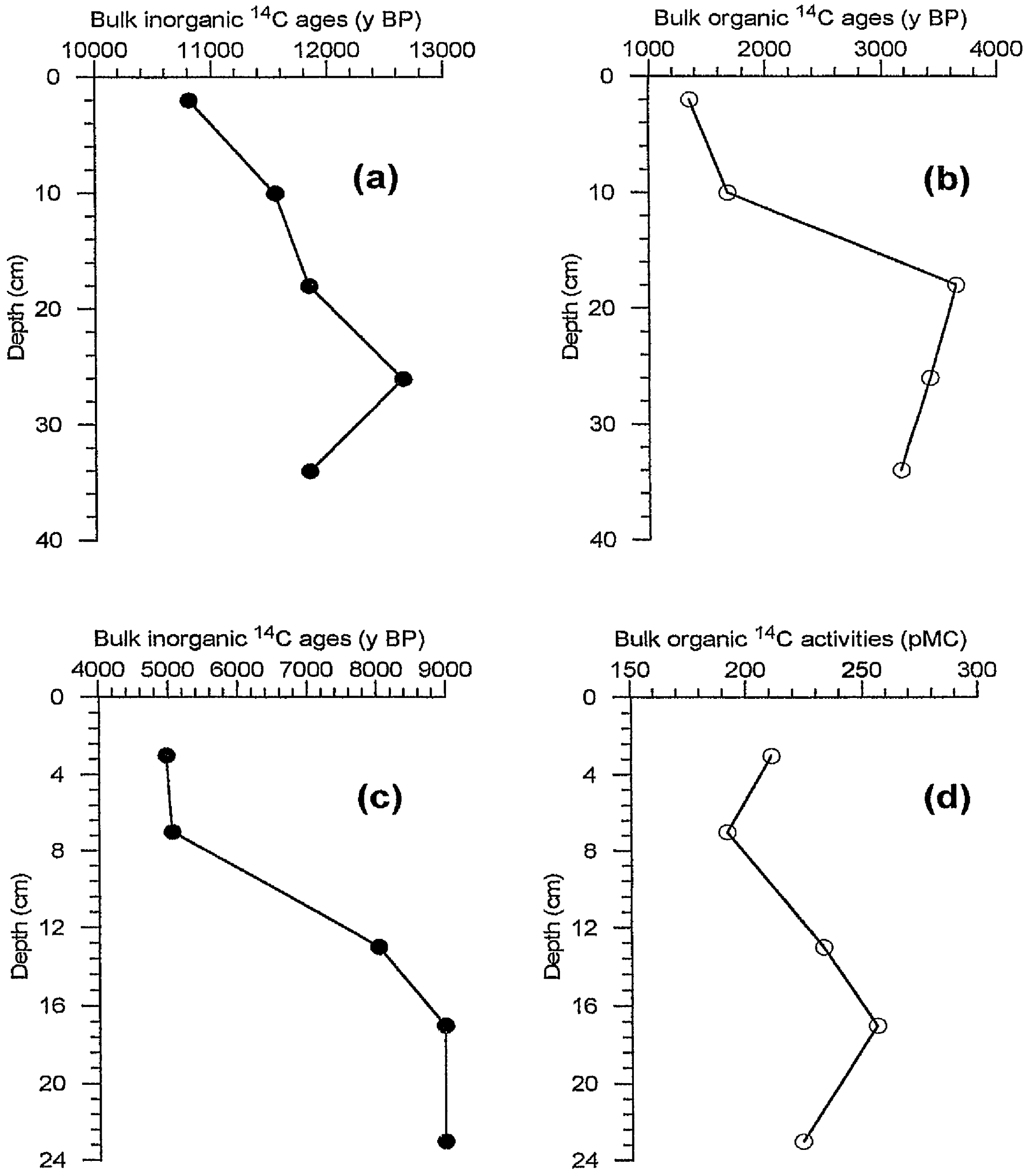
Subsequent work by Begg (1992); Cook *et al.* (1995); and Wolstenholme (1999); (Figure 1.20) took a different approach and included analysis of the organic as well as the inorganic carbon fraction of the sediment in an attempt to assess the influence of Sellafield derived ^{14}C on the sediments of the NE Irish Sea, rather than attempt to establish ^{14}C chronologies. Analysis of the cores and grab samples collected by Begg (1992) and Cook *et al.* (1995) will be considered together as they were collected (temporally) close together, prior to the rise in

^{14}C activity of the Sellafield discharges. In both the cores and grab samples, there was a marked difference in ages between the inorganic and the organic fractions of the sediment in the same depth interval. Core 2 (Cook *et al.* 1995) was only 25 cm in length and the inorganic ^{14}C ages were substantially younger (4,980 ± 100 to 8,980 ± 100 y BP) than those previously reported by Kershaw (1986) and Kershaw *et al.* (1988). In contrast, the organic carbon fractions were enhanced above the ambient background to the base of the core (192.2 ± 1.3 to 256.1 ± 0.9 pMC). This core was collected from close to the point of discharge from the Sellafield pipeline and provides unequivocal evidence of incorporation of Sellafield derived ^{14}C into the sediment. (Begg 1992) presented results for the inorganic and organic carbon fractions of the sediment from two grab samples collected at stations 208 and 206 (Figure 1.20) in order to investigate the geographic extent of this incorporation of Sellafield derived ^{14}C in the sediments. At 9,230 ± 230 and 8,460 ± 250 y BP, the inorganic carbon fraction of the grab samples were significantly older than those in core 2, but younger than those in cores collected by Kershaw (1986) and Kershaw *et al.* (1988). The organic carbon activities for the grabs were similar to those of the organic fraction of core C8, with both being above ambient background at 224.0 ± 4.6 and 223.5 ± 5.0 pMC (approximately 506 and 505 Bq kg^{-1} C) for stations 208 and 206, respectively.

In contrast, the ^{14}C activities of the inorganic fraction of the sediment in core 1 (Cook *et al.* 1995) were similar to the radiocarbon ages obtained by Kershaw (1986) and Kershaw *et al.* (1988), ranging between 10,810 ± 110 and 12,840 ± 150 y BP. The organic carbon activities for core 1 (Cook *et al.* 1995) were also significantly older (1,350 ± 55 to 3,640 ± 70 y BP) than those in core 2 (Cook *et al.* 1995). The difference in organic carbon activities between the cores may be explained by different sampling locations, with core 2 being collected closer to the discharge pipeline than core 1.

Cook *et al.* (1995) concluded that the difference in age between the inorganic and organic carbon fractions of the sediment (*ca.* 9,500 y BP at the top of the core and *ca.* 8,500 y BP at the base of the core) made it difficult to use the radiocarbon data for either the inorganic or organic fraction in calculations of sediment accumulation rates. They also concluded that the age reversals exhibited by the organic carbon fraction of the sediment in both cores 1 and 2, could be explained by dividing the sediment column into two boxes of different mixing rates, with a rapidly mixed box containing younger material at the surface and a less rapidly rates, with a rapidly mixed box containing younger material at the surface and a less rapidly mixed

Figure 1.23 ^{14}C ages (y Bp) and activities (pMC) in the sediment column reported by Cook *et al.* (1995). (a): inorganic sediment core 1; (b) organic sediment in core 1; (c) inorganic sediment in core 2; (d) organic sediment in core 2.



box containing older material at the base of the core. To explain the discrepancies in ^{14}C activity between the inorganic and organic carbon fractions of the sediment Cook *et al.* (1995) hypothesised that the trends observed in the inorganic carbon data were produced by mixing old, reworked carbonate (>12 ky, and possibly of infinite age) with biologically produced carbonate from the entire Holocene ($\delta^{13}C$ values were consistent with marine carbonate). The most recently produced carbonate is enriched in ^{14}C due to inputs from a variety of sources including Sellafield, Amersham (Cardiff) and nuclear weapons testing fallout, as demonstrated by observations of significant ^{14}C enrichments in mussel and winkle shells from intertidal areas of the Irish Sea by Begg (1992). The rate of dissolution of $CaCO_3$ shell material is slow, so any bulk carbonate sample will have an age that is a composite of the range of ages from recently produced material to possibly infinite age carbonate. The apparently old ages for the bulk inorganic carbon could be caused by the dominance of old material in the inorganic carbon fraction of the sediment.

The organic carbon fraction of the sediments is derived from riverine inputs of terrigenous material and Holocene marine production. During the past five decades, this current production material was enriched with contributions from Sellafield and Amersham (Cardiff) discharges and from nuclear weapons testing. The activity trends in the sediment column are brought about by intense mixing, and the younger ages relative to the bulk inorganic carbon fraction may be due to relatively fast oxidation of organic material (compared to the slow dissolution rate of carbonate). Thus, little old organic carbon will remain and the organic fraction will be dominated by recent inputs of material. From this, Cook *et al.* (1995) concluded that the differences in ^{14}C activity between the inorganic and organic components of the sediments cast serious doubts over the validity of deriving sedimentation rates for Irish Sea sediments based on either the bulk inorganic or organic carbon components.

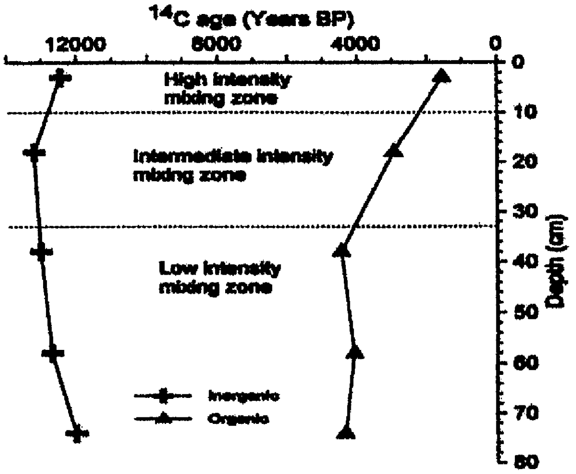
A further study of ^{14}C in the Irish Sea was undertaken by Wolstenholme (1999) (Figure 1.24) after the large increase during 1994/95 of ^{14}C activities discharged from Sellafield. Three cores from the positions shown in Figure 1.20, were analysed and interpretation of the ^{14}C results was based upon treatment of the radionuclide contaminated sediment as comprising a series of zones of decreasing intensity of mixing with increasing depth. On the basis of the arguments developed by MacKenzie *et al.* (1999), as discussed in Section 1.11.1, the ^{137}Cs:^{241}Am activity ratio was used to define three mixing zones for the Sellafield and Sellafield south cores: high intensity mixing zones from 0-10 and 0-15 cm, respectively, medium intensity mixing zones from 10-35 and 15-65 cm, respectively and low intensity mixing zones from 35 cm to the base of the core and 65 cm to the base of the core, respectively. Similarly, the Sellafield north core was divided into four mixing zones; a very high intensity mixing zone (0-20 cm), a high intensity mixing zone (20-55 cm), a medium intensity mixing zone (55-65 cm) and a low intensity mixing zone (65 cm to the base of the core).

The ^{14}C activities of inorganic and organic carbon fractions were determined for each of these mixing zones. In the Sellafield and Sellafield South cores, the inorganic carbon exhibited similar ^{14}C ages and age distributions to those observed by Kershaw (1986), Kershaw *et al.* (1988) and core 1 from Cook *et al.* (1995). The apparent ^{14}C ages of the inorganic carbon fraction in the high intensity mixing zone of the Sellafield North core were younger, (at 10,081 ± 121 and 10,047 ± 95 y BP) than the ages in the high intensity mixing zone of the other cores. The bulk inorganic carbon age for the other zones of the Sellafield North core were similar to those of the Sellafield and Sellafield south cores, suggesting a recent input of inorganic material with a younger ^{14}C age to the surface sediment in the area of the Sellafield North core.

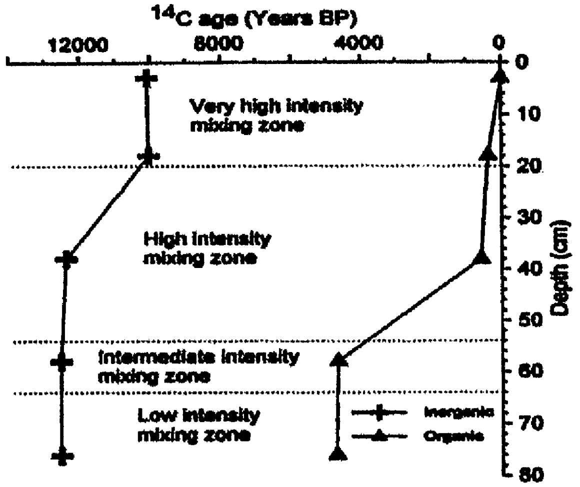
The bulk organic carbon fraction of the sediments in all three cores showed a consistent ^{14}C age offset from the bulk inorganic carbon fraction. Interestingly, Wolstenholme (1999) observed that the organic ^{14}C age in the lowest intensity mixing zone of all three cores (ranges from 4,100 ± 78 to 4,750 ± 151 y BP) was consistent with an average age for organic carbon produced at a constant rate throughout the Holocene. In each of the three cores, progressively younger ages for the organic carbon were observed in the intermediate and high intensity mixing zones. Wolstenholme (1999) argued that since Sellafield waste ^{137}Cs and ^{241}Am had been mixed to the bottom of each core, over the course of 43 years or less, any long-term steady state input of younger organic carbon at the surface would have been effectively homogenised with respect to the age of the organic carbon. It was therefore concluded that the observed profiles implied a recent perturbation of the system, consistent with the introduction of contaminant ^{14}C from Sellafield and possibly from weapons testing fallout. While the higher ^{14}C activities found by Cook *et al.* (1995) were not observed by Wolstenholme (1999) it must be noted that the ^{14}C activity of the organic fraction of the surface sediment in the Northernmost core was post-bomb in age (though not higher than the ambient background) at 242 Bq kg^{-1} C. Wolstenholme (1999) used the ^{14}C activities in the low intensity mixing zones of each core as background values which were subtracted from the ^{14}C activity in the overlying sediment to estimate inventories of Sellafield derived ^{14}C in the organic fraction of approximately 180, 167 and 592 Bq m^{-2} in the Sellafield, Sellafield south

Figure 1.24 ^{14}C activities in the sediment reported by Wolstenholme (1999). (a) Sellafield core; (b) Sellafield north core and (c) Sellafield south core.

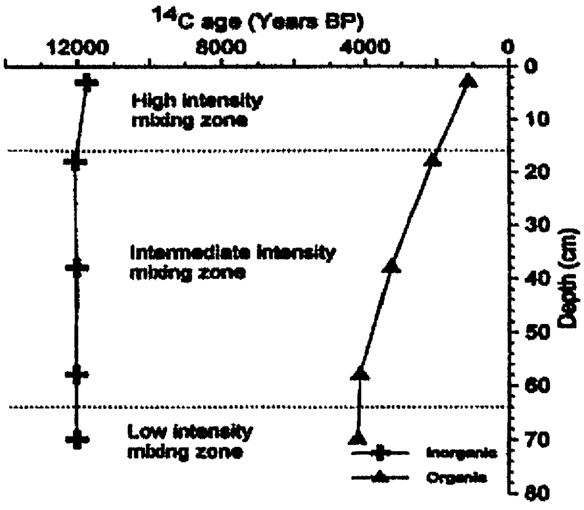
(a) Sellafield core



(b) Sellafield north core



(c) Sellafield south core



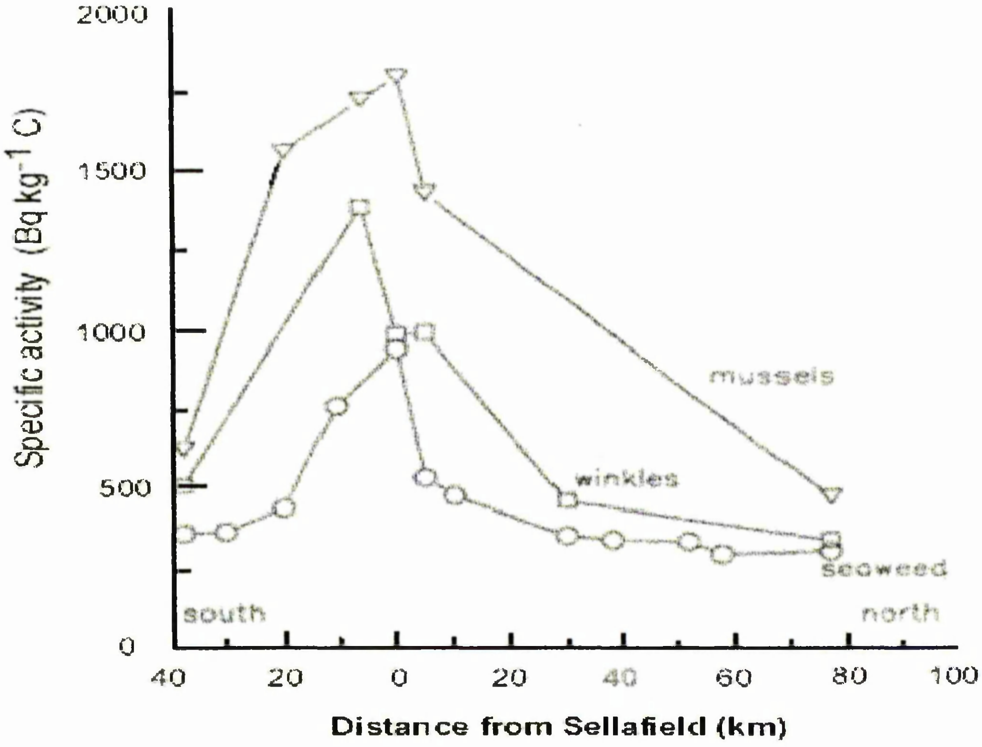
and Sellafield north cores respectively. This method was also applied to the inorganic carbon fraction for the Sellafield north core, giving an inventory of Sellafield derived ^{14}C in the inorganic carbon fraction approximately 106 Bq m^{-2}. Estimation of the excess ^{14}C activity incorporated into an area of 290 km^2 (Sellafield "mud-patch") was calculated as approximately 3.2×10^{10} and 9.5×10^{10} Bq for inorganic and organic carbon fractions respectively.

1.12 Distribution of ^{14}C activities in biota of British coastal waters.

Analysis of intertidal biota (*Mytilus edulis, Littorina littorea and Fucus* species) by Begg *et al.* (1992) showed that Sellafield derived ^{14}C was incorporated into the biota of the NE Irish Sea (Figure 1.25). The conclusion that a fraction of the Sellafield ^{14}C discharges moved south as well as north of the pipeline, based on the distribution of ^{14}C activities in the DIC, was supported by the spatial distribution of ^{14}C activities in the biota. All the biota analysed from this study had ^{14}C activities above the modern estimated ambient background activity of 260 Bq kg^{-1}. At each site in the NE Irish Sea, the mussels had the highest activity (401.2 ± 2 to 1,779.1 ± 7 Bq kg^{-1} C) and the seaweeds had the lowest (286.5 ± 3 to 937.4 ± 3 Bq kg^{-1} C). This trend decreased with distance from Sellafield with the biota collected in the Clyde Sea area having an activity of approximately 280 Bq kg^{-1} C.

As seaweeds utilise the DIC fraction of seawater during photosynthesis the ^{14}C activity above modern found in these sample supports the conclusion by Cook *et al.* (1999), that the ^{14}C discharge from Sellafield is in an inorganic form. The activities in the mussels (Begg *et al.* 1992), which are particle selective filter feeders, had higher activities than the POC activities presented by Begg *et al.* (1991) and Cook *et al.* (1995). The authors argued that as the POC samples were collected during winter months when phytoplankton numbers are smallest, the ^{14}C activity of the POC could be linked to primary productivity and so vary seasonally. Cook *et al.* (1995) and Wolstenholme (1999) presented ^{14}C activities in plankton trawls which were higher in activity than the POC activities and so they concluded that the ^{14}C activity in the material from the plankton trawls was more representative of the activity of the food source of the mussels. As the activity of mixed phytoplankton trawls is higher than that of the POC, this indicates that the POC is composed of a number of fractions of differing sources (such as terrestrial carbon) and ^{14}C activity as discussed in section 1.10.1.

Figure 1.25 Distribution of ^{14}C activities in biota in the Irish Sea 1988/1899 (Begg *et al.* 1992).



Cook *et al.* (1998) reported the ^{14}C activities in a range of biota including mussels and seaweed. Similar to the study by Begg *et al.* (1992), a trend of decreasing activity in biota with distance from the pipeline can be seen for samples collected in the Irish Sea. Samples for the study by Cook *et al.* (1998) were collected in 1995, after the increase in ^{14}C discharges from Sellafield. This increase is reflected in the higher ^{14}C activities of the mussels, winkles and *Fucus* species of the NE Irish Sea and North Channel compared to those reported by Begg *et al.* (1992). Cook *et al.* (1998) showed that the ^{14}C activity of mussels equilibrated more rapidly with the activity of the DIC than the other species of biota in the study, probably due to particle selective uptake of phytoplankton which are in equilibrium with the DIC.

Sites outside the Irish Sea in the study of Cook *et al.* (1998) were chosen to be remote from anthropogenic ^{14}C discharges in order to investigated the marine "background" ^{14}C activity around the British Isles due to ^{14}C natural production and fallout from nuclear weapons testing. An activity of 247 Bq kg^{-1} was estimated as the marine background activity for 1995.

Using these "background activities" Cook *et al.* (1998) calculated the contribution from the Sellafield and Amersham (Cardiff) discharges to the ^{14}C levels in the DIC and marine biota in the vicinity of these establishments. Cook *et al.* (1998) used the excess ^{14}C activities in the marine environment due to the Sellafield discharges to calculate the dose to the Sellafield critical group of seafood consumers.

Higher activities in the east coast of the British Isles were reported by Cook *et al.* (1998), a fact that could not really be attributed to Sellafield discharges as the activity in the biota of the NE English coast were higher than those of the NE Scottish coast. This indicates the likelihood of a release of ^{14}C from another source, *eg* nuclear power producing facilities, or a facility which uses a ^{14}C tracer.

1.13 Summary of previous work and aims of this study.

The following points summerize previous work investigating the behaviour of Sellafield derived ^{14}C in the Irish Sea by the following authors; Kershaw (1986), Kershaw *et al.* (1988), Begg (1992), Begg *et al.* (1991; 1992), Cook *et al.* (1995), Wolstenholme (1999) and Wolstenholme *et al.* (1999).

1) ^{14}C is discharged from the Sellafield nuclear fuel reprocessing plant to the Irish Sea in a mainly inorganic form. This ^{14}C has been shown to be directly incorporated into the DIC fraction of the water column (Begg 1991; Cook *et al.* 1995).

2) ^{14}C discharged from Sellafield behaves in a conservative manner in seawater, ^{14}C is distributed both to the north and south of Sellafield. Although the bulk of the discharged ^{14}C has been shown to be removed northwards and out through the Irish Sea *via* the North Channel by the prevailing current system (Begg *et al.* 1991).

3) Transfer of Sellafield derived ^{14}C from the DIC to the other biogeochemical fractions of the water column (POC, PIC and DOC) and biota of the Irish Sea is clearly apparent. This transfer of ^{14}C to other carbon fractions occurs during uptake of ^{14}C enriched DIC by phytoplankton which is subsequently used in photosynthesis (Cook *et al.* 1995; Wolstenholme *et al.* 1999).

4) The increase in discharge activity in 1994/95 was clearly reflected as increased ^{14}C specific activities in both biota and carbon containing fractions of seawater (with the response of the DIC and POC being faster than that of the DOC and PIC fractions) in the Irish Sea (Wolstenholme 1999; Wolstenholme *et al.* 1999).

5) The inorganic carbon fraction of the sediment is substantially older than the organic carbon fraction of the sediment in the Irish Sea. and is seen to have a pre-Holocene component (Kershaw 1986; Kershaw *et al;* 1988; Cook *et al.* 1995; Wolstenholme *et al.* 1999).

6) The ranges of the organic carbon fraction shows unequivocal incorporation of Sellafield derived ^{14}C to the surface sediments with ^{14}C activities being enhanced above the ambient marine background (Cook *et al.* 1995; Wolstenholme *et al.* 1999).

7) Age reversals exhibited by the organic carbon fraction of the sediment in cores presented by Cook *et al.* (1995) and Wolstenholme (1999) were explained by dividing the sediment column into boxes of differing mixing intensities, with higher mixing intensities found at the surface than at depth in sediment column. Depth of mixing intensity was based on arguments developed by MacKenzie *et al.* (1999) using ^{137}Cs:^{241}Am activity ratios (Section 1.11.1).

8) Wolstenholme (1999) calculated that the total ^{14}C activity transferred to the sediments of the Sellafield "mud-patch" (290 km^2) was 1-2% of the total ^{14}C activity discharged from Sellafield since operations began in 1952.

While these studies have revealed much about the behaviour of Sellafield derived ^{14}C, a number of questions still remain. For example,(i) timing of responses in the carbon fractions of the Irish Sea to temporal changes in the discharge activities are not known, (ii) what is the budget for ^{14}C removed from the Irish Sea through the North Channel, (iii) if a larger area of seabed incorporating different sediment types were investigated, would the total activity incorporated into the Irish Sea sediments be bigger than those already found?.

In order to address some of the questions about the behaviour of Sellafield derived ^{14}C in the Irish Sea this study aimed to investigate the biochemical cycling of Sellafield derived ^{14}C in the in the water column, sediments and biota of the NE Irish Sea along with the temporal response of the carbon fractions to changes in the monthly discharge activity. This project also attempts to assess the rate of removal of this ^{14}C from the Irish Sea through the North Channel as well as the budget of ^{14}C present in Irish Sea sediments.

Answering all questions regarding behaviour and fate of ^{14}C in the Irish Sea is beyond the scope of this study so more specifically this project aimed to:

1 To establish the specific activities of ^{14}C in the various carbon containing fractions of the Irish Sea. That is the four carbon containing fractions of the water column (DIC, DOC, PIC and POC); the inorganic and organic carbon fractions of the sediments and to a limited extent the biota, using samples of mussel *(Mytilus edulis)* and seaweed *(Fucus sp)*.

2 To relate (if possible) temporal variations in the ^{14}C specific activities of these fractions to temporal variations in the ^{14}C activity of the Sellafield discharge. In order to do this sites that were close (Nethertown and the St. Bees Head site) and at a distance (Portpatrick) from the point of discharge were chosen for monthly sampling.

3 To establish geochemical cycling patterns of ^{14}C between these carbon fractions.

Other aims of the project were;

1) To estimate the ambient ^{14}C background in the marine environment due to natural ^{14}C production and atmospheric weapons testing. These results were then used to determine the contribution of Sellafield derived ^{14}C in each carbon fraction analysed.

2) To estimate a budget of Sellafield derived ^{14}C in the carbon fractions of the Irish Sea (based on ^{14}C activities found in the inorganic and organic carbon fractions of the sediments) and the flux of Sellafield derived ^{14}C from the Irish Sea through the North Channel (based on the activities of the DIC, DOC, PIC and POC measured at Portpatrick).

Chapter 2

METHODS AND MATERIALS

2.1 Location of sampling sites.

2.1.1 Portpatrick and Killantringan Bay

Portpatrick (54^0 51' N; 05^0 07' W) and Killantringan Bay (54^0 52' N; 05^0 09.5' W) (Figure 2.1) are located on the south west coast of Scotland. Seawater samples for the analysis of ^{14}C in the DIC, DOC, PIC, POC fractions and dissolved ^{137}Cs were collected from Portpatrick, while mussels and seaweed were collected from Killantringan Bay (a few miles from Portpatrick). These sites were chosen because;

1) Their North Channel location is relatively remote from the Sellafield discharge point.

2) Time series analysis will indicate the response of the four carbon fractions of seawater (DIC, DOC, PIC, and POC) and the flesh of the mussel *Mytilus edulis* to changes in the Sellafield discharge.

3) The North Channel is the main exit point for water from the Irish Sea. Measurements of ^{14}C activities above ambient background in the carbon fractions of the water column and dissolved ^{137}Cs activities at this location can be used to estimate the removal fluxes of these radionuclides from the Irish Sea.

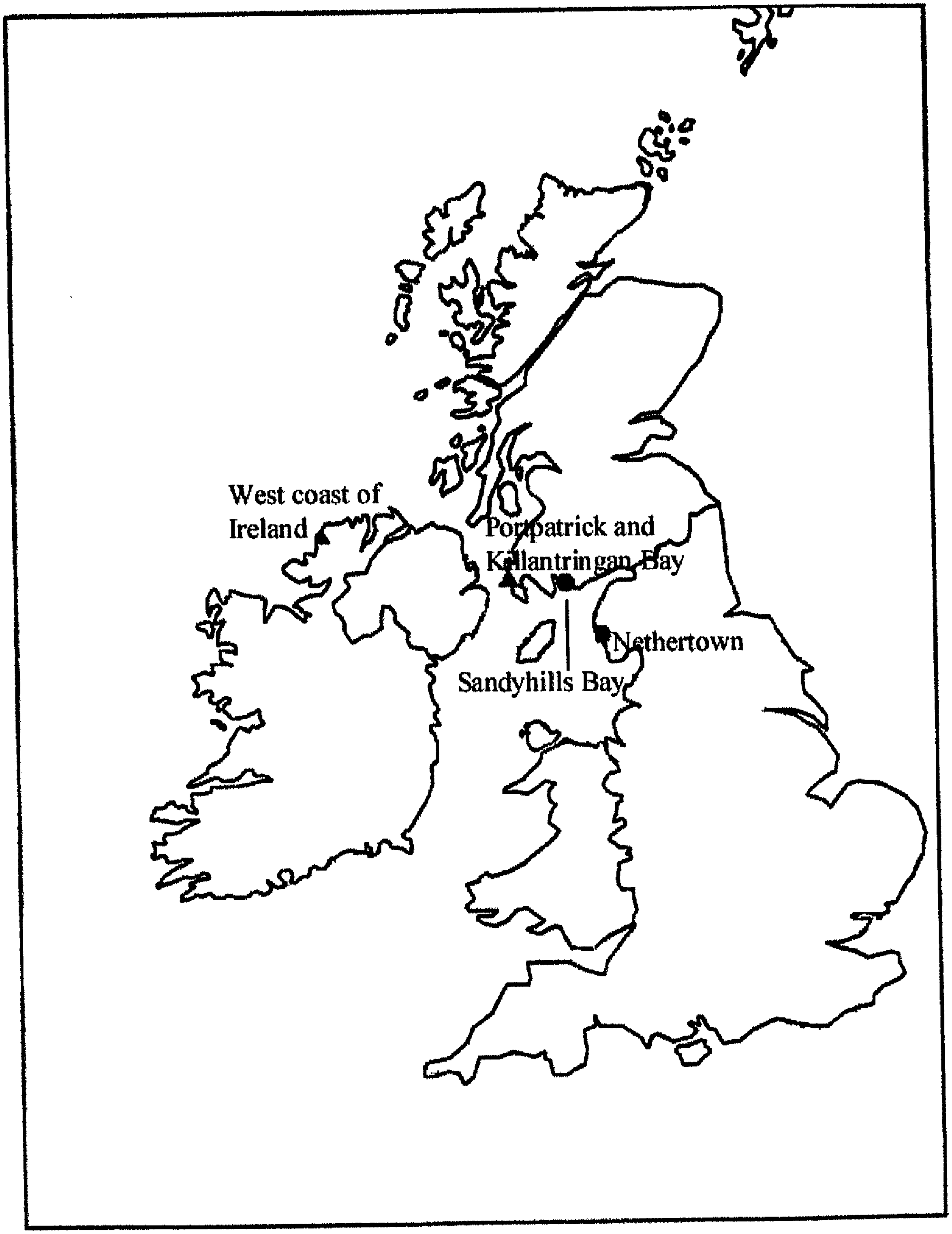
2.1.2 Nethertown.

Nethertown (54^0 27' N, 03^0 33' W) (Figure 2.1) is located on the North West English coast, approximately two kilometres north of Sellafield. Samples for the analysis of DIC, mussels and seaweed were collected from this site for the following reasons;

1) Its proximity to the point of discharge. At this site, the liquid effluent will not have undergone much dilution and samples collected here should show the maximum effect of the Sellafield discharge.

2) Time series analysis could show the response of the carbon containing samples to changes in the monthly discharge from Sellafield.

Figure 2.1 Map of sample sites



2.1.3. St. Bees Head.

The St. Bees Head site (54^0 31' N 03^0 41' W) (Figure 2.1) is located approximately 4 kilometres off the coast and approximately 10 kilometres north of Sellafield and was chosen for collection of water for ^{14}C analysis of the DIC, PIC, and POC fractions because of the unsuitability seawater from the Nethertown site for analysis of particulate material, due to the large amounts of resuspended sediment in seawater here. There is less resuspended sediment in the water column at the St. Bees Head site. The DIC was analysed for comparison with the DIC activities in seawater sampled during the same month at the Nethertown site. PIC and POC were analysed to examine the biogeochemical cycling of Sellafield derived ^{14}C in the water column and the (coarse time-scale) response of these fractions to changes in the activity of the Sellafield discharge.

2.1.4. Sandyhills Bay

Sandyhills bay is located on the south west coast of Scotland (54^0 53' N; 03^0 43' W) (Figure 2.1). This site was chosen to investigate the uptake of Sellafield derived ^{14}C in the carbonate component of a shell bank (coarse grained material) at distance from Sellafield.

2.1.5. Irish Sea sediments.

Sediment samples were collected from 13 locations in the NE Irish Sea (Figure 2.2. Table 2.1). The sample sites were chosen to give good coverage of the geographic area and of the different sediment types of the NE Irish Sea floor. In order to attempt to assess the budget of ^{14}C in NE Irish Sea sediments, Pederson cores (a modified version of the Kemp corer (Kemp *et al.* 1976)) were obtained from as many locations as possible. This apparatus was chosen because it minimises disturbance to the sediment-seawater interface, reduces core compaction and preserves the vertical integrity of the core. The apparatus uses suction to keep the sediment core in place and so is unsuitable for use in sandier sediments. In sandy areas, where collection of Pederson cores was impossible, samples were collected using a Van Veem grab.

Figure 2.2 Map of the NE Irish Sea bed showing locations of cores and grabs

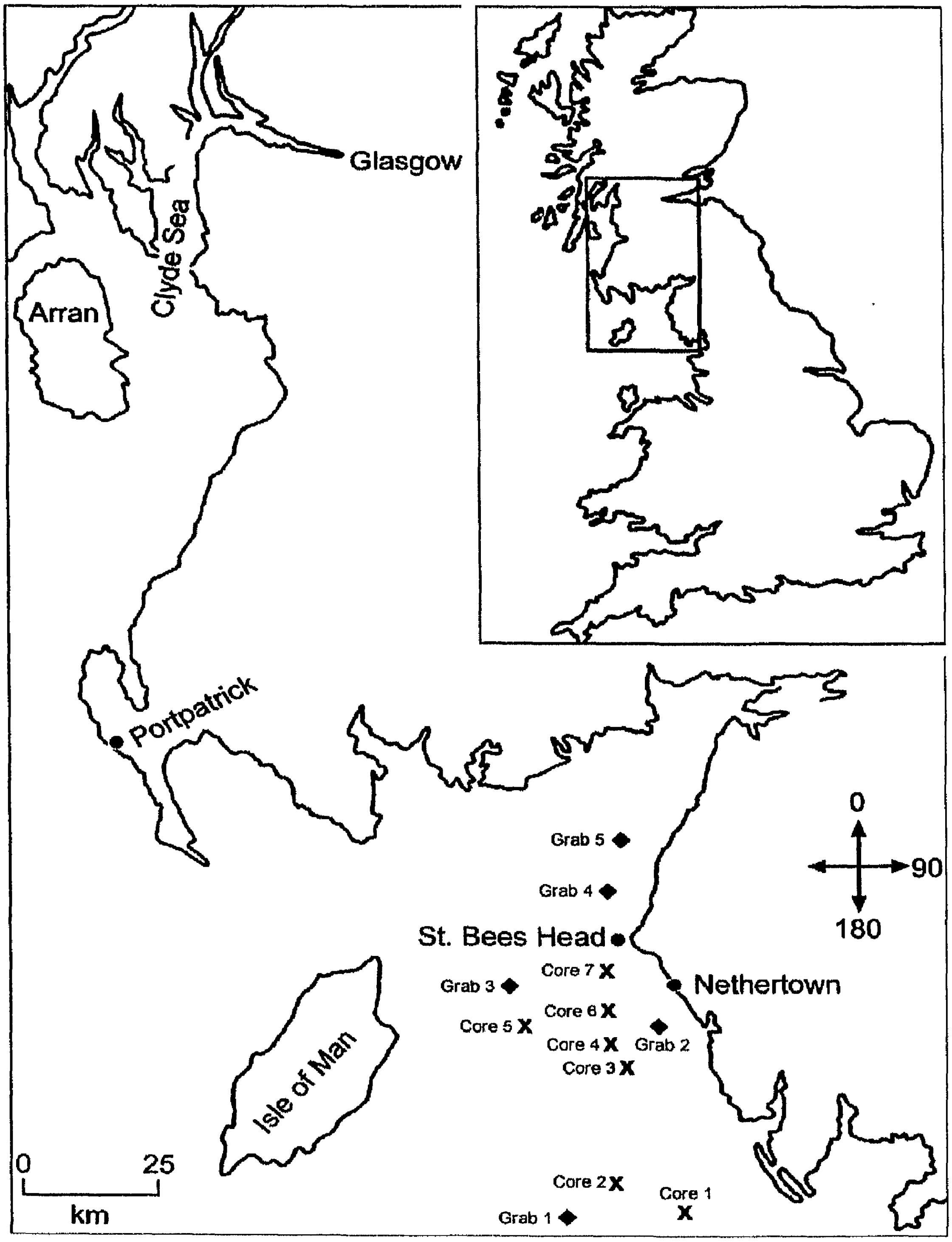


Table 2.1. Location of sediment cores and grab samples collected from the NE Irish Sea.

Sample Id	Latitude	Longitude	Method of collection	Date of sampling
Core 1 (PC186)	54^0 05' N	03^0 30 W	Pederson corer	10/6/99
Core 2 (PC85)	54^0 11' N	03^0 31' W	Pederson corer	2/6/98
Core 3 (PC87)	54^0 17' N	03^0 38' W	Pederson corer	3/6/98
Core 4 (PC89)	54^0 19' N	03^0 42' W	Pederson corer	3/6/98
Core 5 (PC185)	54^0 20' N	03^0 55' W	Pederson corer	10/6/99
Core 6 (PC92)	54^0 25' N	03^0 42' W	Pederson corer	3/6/98
Core 7 (PC86)	54^0 27' N	03^0 41' W	Pederson corer	2/6/98
Grab 1 (PC190)	54^0 03' N	03^{0}50' W	Van Veem grab	10/6/99
Grab 2 (PC187)	54^0 20' N	03^0 33' W	Van Veem grab	10/6/99
Grab 3 (PC189)	54^0 25' N	03^{0}58' W	Van Veem grab	10/6/99
Grab 2 (PC188)	54^0 37' N	03^0 46' W	Van Veem grab	10/6/99
Grab 5 (PC192)	54^0 42' N	03^0 43' W	Van Veem grab	10/6/99

2.1.6. Burtonport, west coast of Co. Donegal, Ireland.

In order to estimate the contribution from Sellafield to the ^{14}C activity of a sample, it is necessary to know the ambient "background" ^{14}C activity from natural production of ^{14}C and ^{14}C produced during atmospheric nuclear weapons testing that is present in the sample. The north west coast of Donegal (Figure 2.1) was chosen to represent the "ambient background" activity of carbon fractions in the North Atlantic coastal region because it is remote from the influence of Sellafield discharges (Bradley *et al.* 1991; McKay and Baxter 1986; Leonard *et al* 1998 Cook *et al.* 1998).

DIC, mussels, seaweed, crab, flatfish and round fish were sampled annually at this location from 1997 to 1999 inclusive, to investigate interannual variation in the ^{14}C activity of carbon fractions.

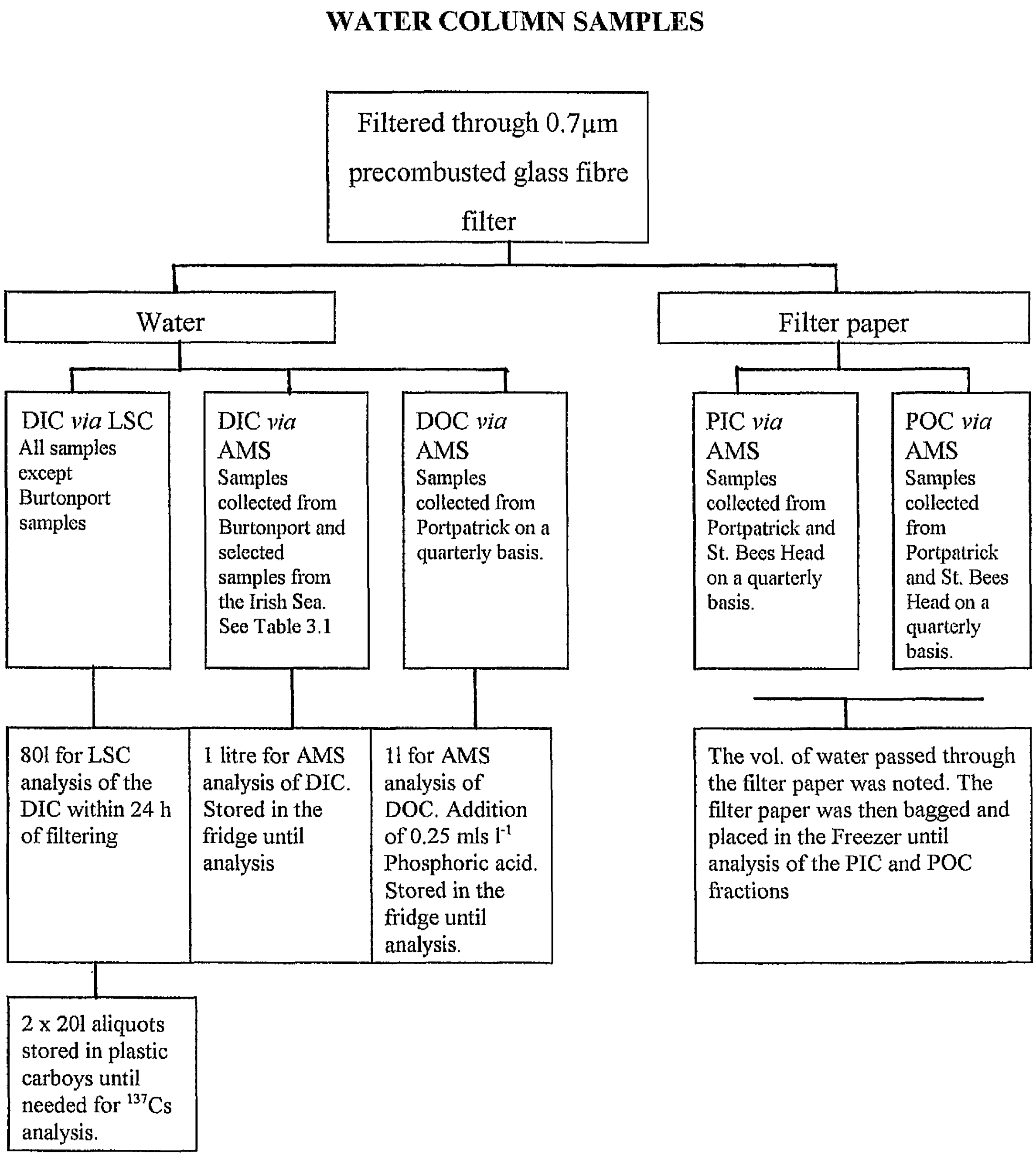
2.2. Sample collection, storage and pretreatment.

2.2.1. Water column.

Seawater samples were collected on a monthly basis from Portpatrick (August 1997 until July 1999 inclusive) and Nethertown (August 1997 until January 1999 inclusive) and on a quarterly basis from the St. Bees Head site (November 1997 until February 1999 inclusive). These sites represent the bulk of the sampling effort for the analysis of ^{14}C in the carbon fractions of the water column. The waters were all treated in the same manner during storage, pretreatment and analysis (Figure 2.3)

Samples were collected from a breakwater just beyond the harbour at Portpatrick and from the surf zone at Nethertown. Water from both sites was collected using a clean plastic bucket and then transferred into 10 litre polycarbonate carboys which had been cleaned by first soaking them in dilute nitric acid overnight followed by a thorough rinsing with distilled water. The carboys were rinsed three times with the sample water before filling to the brim to prevent exchange of CO_2 from the head space. 100 litres of water were collected from Nethertown and Portpatrick on all dates except November 1997, February 1998, May 1998, August 1998, November 1998 and February 1999 when 200 litres were collected from each site. Samples at the St. Bees Head site were collected by the crew of the MV Seascan by filling pre-cleaned 25 litre carboys using an onboard pump. The carboys were rinsed three times with sample water before filling them to the brim. 200 litres of water were collected from the St. Bees Head site on each sampling date.

Figure 2.3. Flow chart of pretreatments and methods of analysis for water column samples



Seawater was collected from the surf zone of the west coast of Co. Donegal in September in 1997 and 1998 and in February 2000. 100 l were collected in 1997 for radiometric analysis of the DIC fraction of seawater, 2-4 litres were collected in 1998 and 1999 for AMS analysis of the DIC fraction of Seawater. All samples were collected in pre-cleaned plastic containers as before.

Upon return to the laboratory, the samples were filtered through pre-combusted (500 ^{0}C for 1 hour) glass fibre filters of 0.7 μm pore diameter as soon as possible (within 6 hours to 3 days of collection). The filtering apparatus and filter papers were cleaned by pumping a dilute nitric acid solution throughout the apparatus for 10 - 15 minutes followed by rinsing with reverse osmosis water for 15 -20 minutes.

DIC

The samples were filtered through a pre-combusted glass fibre filter of 0.7 μm pore diameter. For radiometric ^{14}C analysis of the DIC fraction, 80 litres of seawater were analysed as soon as possible after filtering, typically within 1-2 days. For AMS ^{14}C analysis of the DIC fraction of seawater, pre-combusted 500 ml glass bottles were filled to the brim with filtered water. The samples were labelled and then stored in the dark in a fridge at $\leq$ 4 ^{0}C until required for analysis.

POC and PIC

Particles for analysis of ^{14}C activities in the PIC and POC fractions were collected on the 0.7 μm GF/F filter papers. The filters were double bagged, labelled with the volume of water filtered through the GF/F(±5%) and placed in a freezer at <- 4 ^{0}C until required for analysis.

DOC

Seawater for analysis of ^{14}C activities in the DOC fraction were filtered into precombusted 500 ml glass bottles. A couple of drops of concentrated phosphoric acid were added to each sample to poison the sample (prevent photosynthesis). The samples were then labelled and stored in the dark at <4° C until required for ^{14}C analysis by AMS.

Dissolved ^{137}Cs

^{137}Cs analysis was carried out 20 litre subsamples of the seawater from which the DIC had already been removed. After removal of the DIC, the samples, which were now acidified, were transferred to clean 25 litre carboys and stored for up to six months before analysis.

2.2.2. Sediment.

Sediment samples were collected by Pederson corer or Van Veem grab depending on the sediment type. Sediment samples were collected on two separate occasions. Cores 2, 3, 4, 6 and 7 were collected in June 1998, whilst Cores 1 and 5 and grabs 1-5 were collected in June 1999. All cores were collected from the MV Seascan. The shell bank sample was collected from the intertidal area of Sandyhills Bay in January 2000.

The cores were collected using core tubes of 8.5 cm internal diameter. The core tubes were cleaned by soaking in Decon 90 overnight, soaking in dilute nitric acid overnight and then rinsing thoroughly with reverse osmosis water. Separate core tubes were used for each core that was collected. The cores ranged in length from 60 cm to 95 cm. Cores were capped and strapped upright in the boat until it returned to the harbour (within a few hours of collection). Once the boat had docked, the cores were extruded by applying pressure to the base of the core. The sediment was sectioned in 2 cm increments from 0 cm-10 cm depth and in 5 cm increments from 10 cm depth to the base of the core. The outer 0.25 cm of each segment was discarded in order to minimise contamination of the samples by smearing. The core segments were placed in clean, pre-weighed and labelled polycarbonate jars which were placed in a freezer within 48 hours of collection.

The grabs were all collected on a cruise in June 1999 on the MV Seascan using a Van Veem grab. Subsamples of sediment were removed from the grab using a clean scoop and placed in clean pre-weighed and labelled polycarbonate jars. These were placed in a freezer within 24 hours of collection.

Prior to analysis, samples were removed from the freezer and allowed to defrost overnight. The wet weight of each defrosted segment of core was measured using an Oertling HC22 balance. The samples were then placed in an oven at 60°C until dry and then re-weighed.

The subsamples of the grabs were defrosted, placed in a clean 5 litre flask and homogenised before measuring the wet weight and drying in an oven set at 60°C.

Once dry, approximately 75% by weight of grabs PC187 and PC190 was wet sieved into the following size fractions. >500 µm; 500-63 µm and <63 µm. The sieves were cleaned thoroughly between samples. These size fraction samples were then placed in an oven at 60 °C. Once dry, the samples were homogenised by grinding with a pestle and mortar.

The individual core segments were ground using a mortar and pestle in order from the bottom segment to the top. The pestle and mortar were soaked for at least one hour in dilute nitric acid, followed by distilled water between samples to minimise contamination between core segments. The dried, ground sediment was then returned to its container for storage until required for analysis.

2.2.3. Biota

Mussel (*Mytilus edulis*)

Mussels were collected at low tide, on a monthly basis from Killantringan Bay and the beach at Nethertown from August 1997 until January 1999. The mussels at Killantringan Bay colonise the few out-cropping intertidal rocks on the beach. Both the colony and the size of the individual mussels are small, probably due to the high degree of exposure to wind and wave action on this beach. Due to this, care was taken over the number of individuals taken from the beach so as not to irreparably damage the colony. As a result, small sample sizes were often obtained from Killantringan Bay.

The mussel community at Nethertown is much stronger and approximately 400 g wet weight of flesh were collected on each date.

Mussels were also collected in September/October 1997, 1998 and 1999 from the west coast of Ireland from crevices in out-cropping rocks on the beach in front of Carrick Finn airport, Co. Donegal, located a few miles from Burtonport.

Mussels were placed in labelled bags and stored at <0 °C. Once required for analysis, they were removed from the freezer and placed in a large beaker of boiling water until the shells (valves) opened. The mussels were then drained and the flesh removed from the valves and the wet weight measured. The samples were then freeze dried, re-weighed and homogenised by crushing. In order to remove any contaminant shell or sedimentary material, a subsample from each sample was digested overnight in one molar HCl, filtered and rinsed in distilled water to remove the excess acid and then placed in an oven at 60 ^{0}C.

The mussel shells were cleaned by removing any epiphytes (e.g. barnacles). They were then placed in a furnace for 8 hrs at 500 ^{0}C to remove any organic carbon.

Seaweed (*Fucus* species)

Seaweed samples were collected at low tide from Killantringan Bay and Nethertown on a quarterly basis from February 1998 to February 1999 inclusive. The *Fucus* species at both sites were located close to where the mussel samples were collected.

Seaweed (*Fucus* species) was collected annually from the west coast of Ireland at the same time and location as the mussel samples.

All seaweed samples were gathered by hand, placed in plastic bags and stored in a cool box for the journey back to the laboratory after which they were stored at <0°C until needed for analysis. Prior to analysis seaweed was removed from the freezer and allowed to defrost overnight, after which it was washed with distilled water and the wet weight measured before drying in an oven at 60°C. Once dry, the seaweed was reweighed to obtain a dry weight. The dry sample was crushed and homogenised and a subsample acid washed in 1M HCl overnight, rinsed in distilled water and then placed in an oven at 60°C.

Fish and Crabs.

Flat fish and round fish were obtained by the fisheries manager in Burtonport from boats that had been fishing in a 30 mile radius of Burtonport harbour, while locally caught crab legs (*Cancer pagurus*) were obtained from the crab factory in Burtonport. Samples were collected in September/October 1997, 1998 and 1999.

The crab sample (whole or claws) was placed in boiling water for a few minutes, after which the claws were removed from the whole crabs and the white meat removed from the claws as only the white meat from the crab claws was analysed. The wet weight was measured at this point. The sample was freeze dried and a dry weight measured, after which they were crushed and homogenised.

All fish samples were first gutted and boiled in water for a few minutes. The skin and bones were removed and the wet weight of white flesh measured. The sample was then freeze-dried, re-weighed and crushed to give a homogenous sample.

2.3 Conversion of carbon containing material to CO_2 for radiometric analysis

2.3.1. Large scale hydrolysis of DIC

A closed system was set up (Figure 2.4) consisting of four 20 litre glass carboys, sealed with rubber bungs and connected to each other in series using flexible rubber tubing. Each carboy has an entry point in the rubber bung for addition of acid to the sample which can be sealed using Teflon screw taps. The first carboy **(c1)** in the series is attached to a carrier gas (oxygen) source through a flow metre and a pressure gauge. The last carbon **(c4)** in the series is connected to the vacuum line for the preparation and storage of CO_2, through a needle valve (N1, Figure 2.5).

Once the system has been leak tested to show that it is air-tight the DIC is hydrolysed by the addition of 250 mls of 4M HCl to each carboy. Oxygen gas thoroughly mixes the HCl into the sample water and in addition acts as a carrier gas.

The CO_2 evolved was passes through the needle valve into the vacuum line (Figure 2.5), and then transferred through two IMS/solid CO_2 traps **(T1, T2)** to remove any water vapour before being trapped cryogenically using liquid nitrogen **(T3, T4, T5)**. Oxygen flow rate and vacuum were monitored and kept constant for three hours. The oxygen was then turned off while the 20 litre carboys were pumped for a further 5 minutes using the low vacuum manifold.. The CO_2 evolved was then collected cryogenically and stored in bulbs overnight before conversion to benzene (*via* acetylene production) using the method described in Sections 2.5 and 2.6.

Figure 2.4 Large Scale hydrolysis of DIC

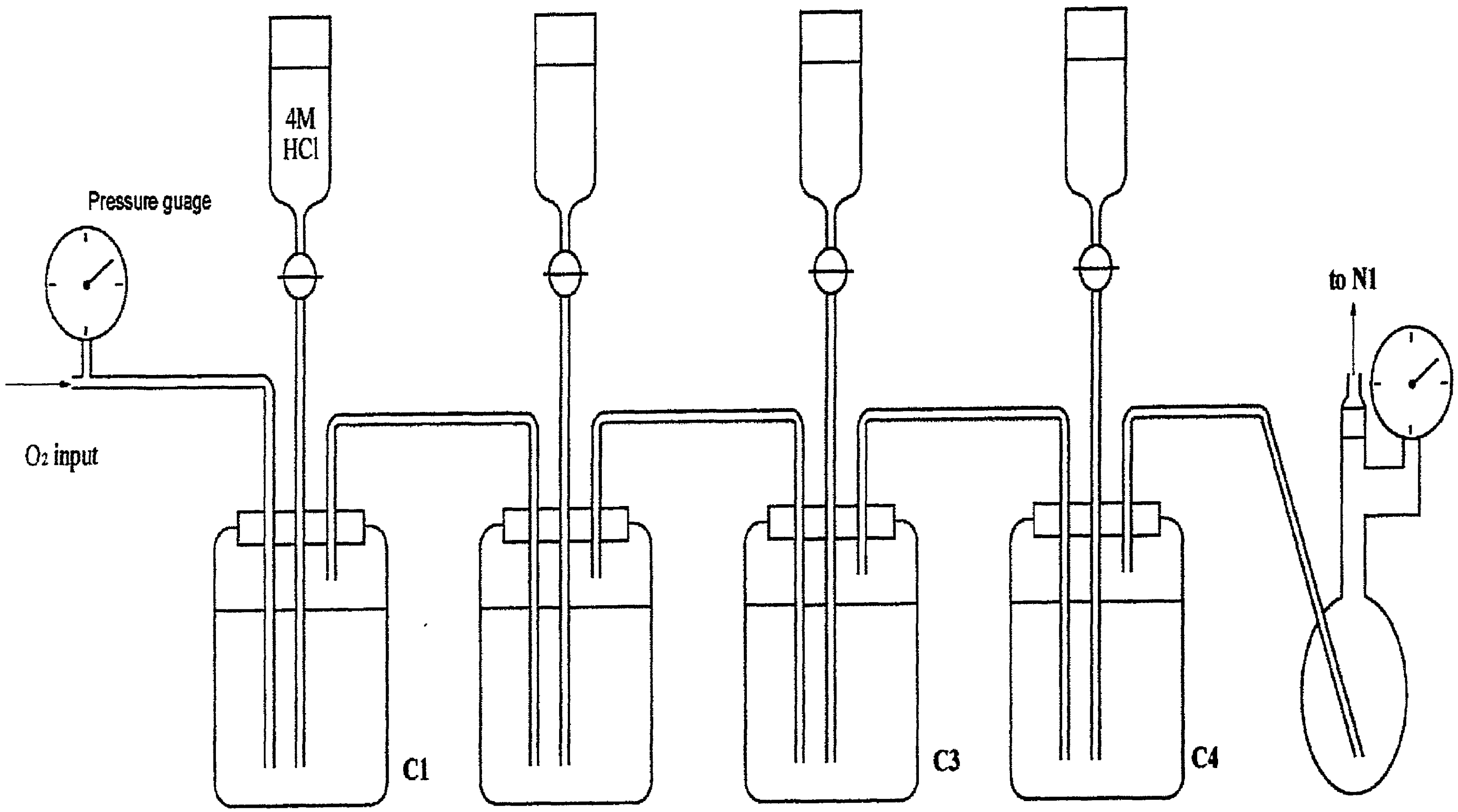
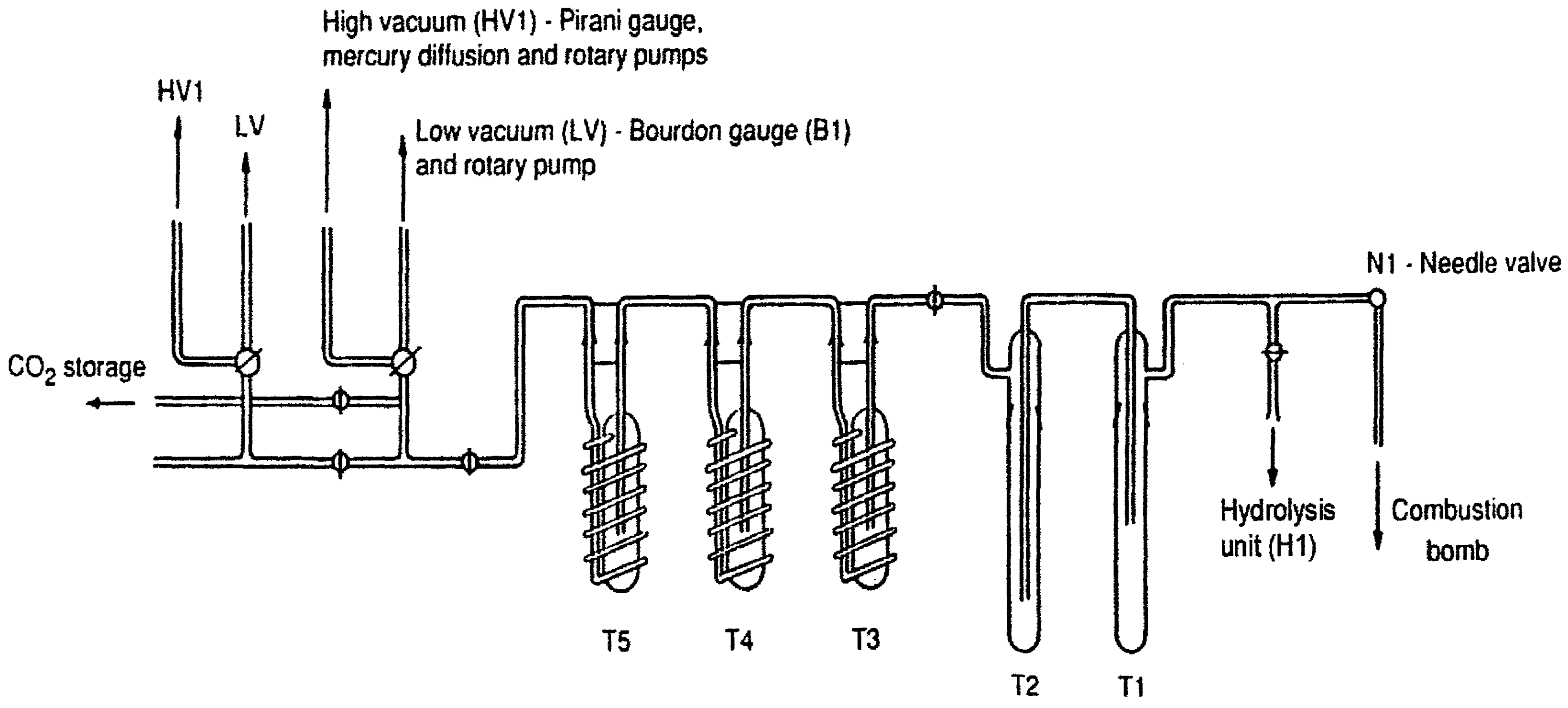


Figure 2.5 Vacuum manifold for preperation and storage of CO_2



2.3.2. Combustion of high organic content material (biota)

Material with a high organic carbon content (approximately 40% carbon) produces CO_2 when combusted in the presence of excess oxygen (Barker *et al.* 1969). All of the biological samples (except mussels collected from Killantringan Bay, December 1997 and September 1998 which were analysed by AMS) were treated in this fashion.

The weight of sample combusted varied depending on the weight of benzene required and the % organic carbon present in the sample. 10g of sample material was used for most combustion although the for some months, mussel samples from Killantringan was small and less than 10g were combusted.

The equation for the combustion of organic material to CO_2 is,

$$CHO_2 + O_2 \rightarrow CO_2 + H_2O \text{...eqn. 2.1}$$

Figure 2.6 illustrates the combustion bomb which is connected to the vacuum system *via* N1 (Figure 2.5). The sample was placed in a crucible along with nichrome wire in the combustion bomb which was evacuated and subsequently filled with excess oxygen. The reaction was started when an electrical current was applied to the wire. The CO_2 passed through two solid CO_2/IMS traps **T1, T2** (Figure 2.5) to remove water vapour produced during the combustion and then cryogenically trapped using liquid nitrogen. The CO_2 was collected and converted to benzene *via* acetylene production (Sections 2.5 and 2.6).

2.3.3 Large scale hydrolysis of carbonate containing material (sediment and shell material)

Hydrolysis reactions are used to generate CO_2 from carbonate containing samples using acid, in this case HCl. The general chemical reacion is as follows;

$$CO_3^{2-} + 2HCl \rightarrow CO_2 + H_2O + 2Cl^- \text{...............................eqn 2.2}$$

All shell material and most of the inorganic sediments were hydrolysed in this manner. The hydrolysis vessel (Figure 2.7) attached to the vacuum manifold *via* H1 (Figure 2.5). The samples (sediment or shells) were weighed accurately and placed in the hydrolysis vessel. The hydrolysis vessel was attached to the vacuum manifold at H1 (Figure 2.5), evacuated and leak tested. The inorganic carbon was hydrolysed by the addition of 400 mls of 4M HCl to the sample. The CO_2 produced entered the vacuum line *via* H1 and was passed through two solid

CO_2/traps to remove any water vapour. The CO_2 was then trapped cryogenically using liquid nitrogen. Once all the CO_2 had been collected it was stored overnight before conversion to benzene *via* acetylene production (Sections 2.5 and 2.6)

Figure 2.6 Combustion bomb

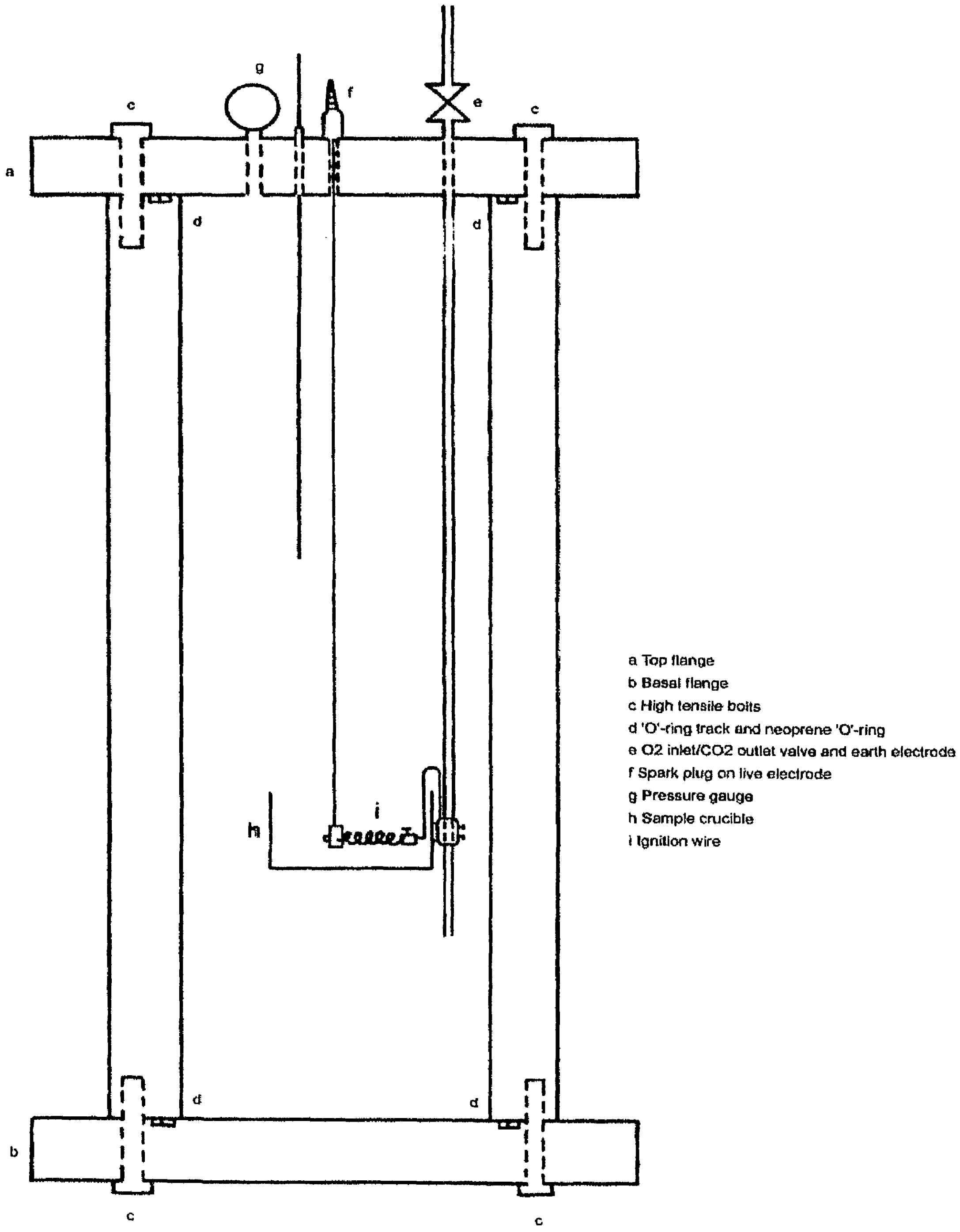
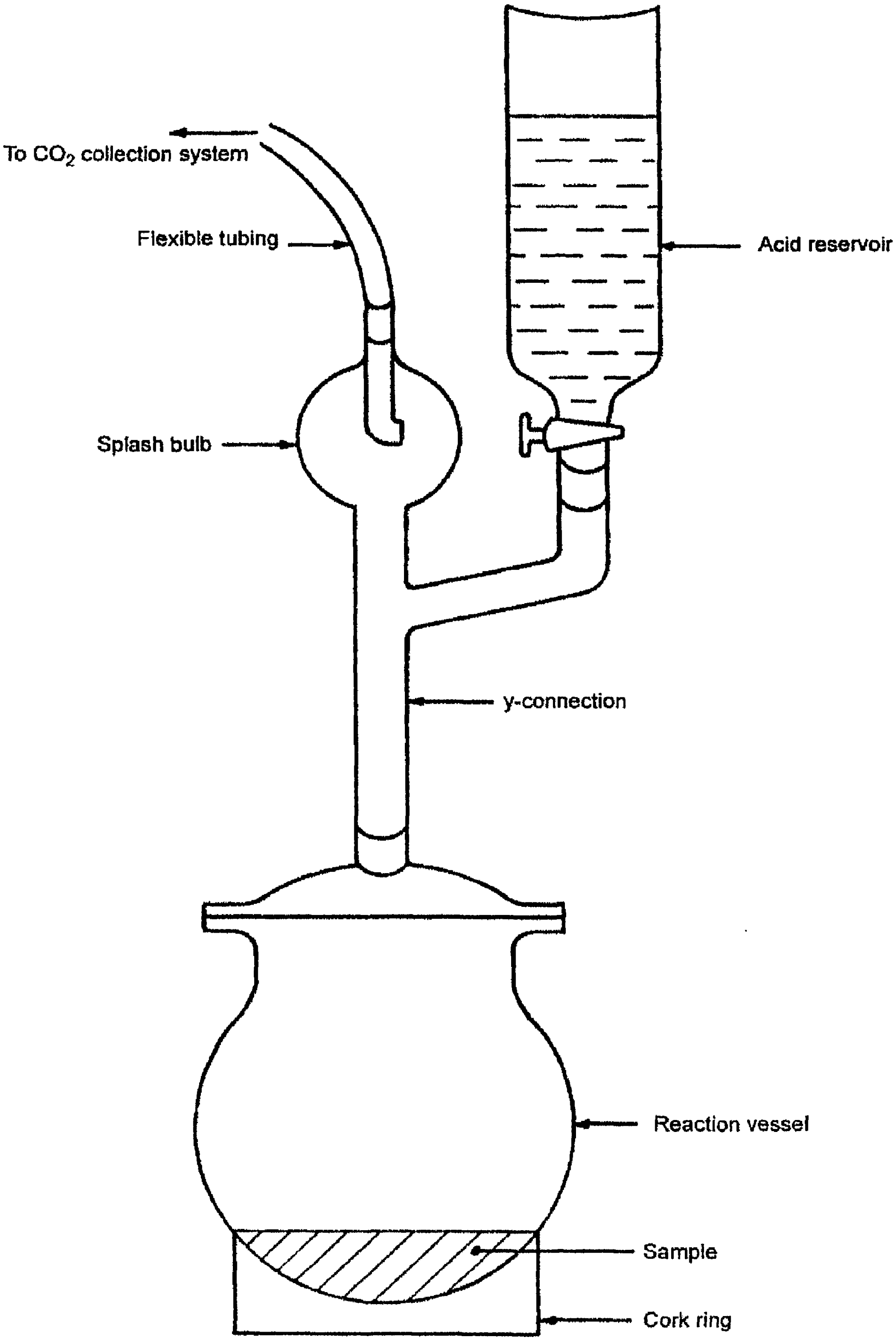


Figure 2.7 Hydrolysis vessel



2.3.4. Large scale combustion of material with low organic carbon (sediment)

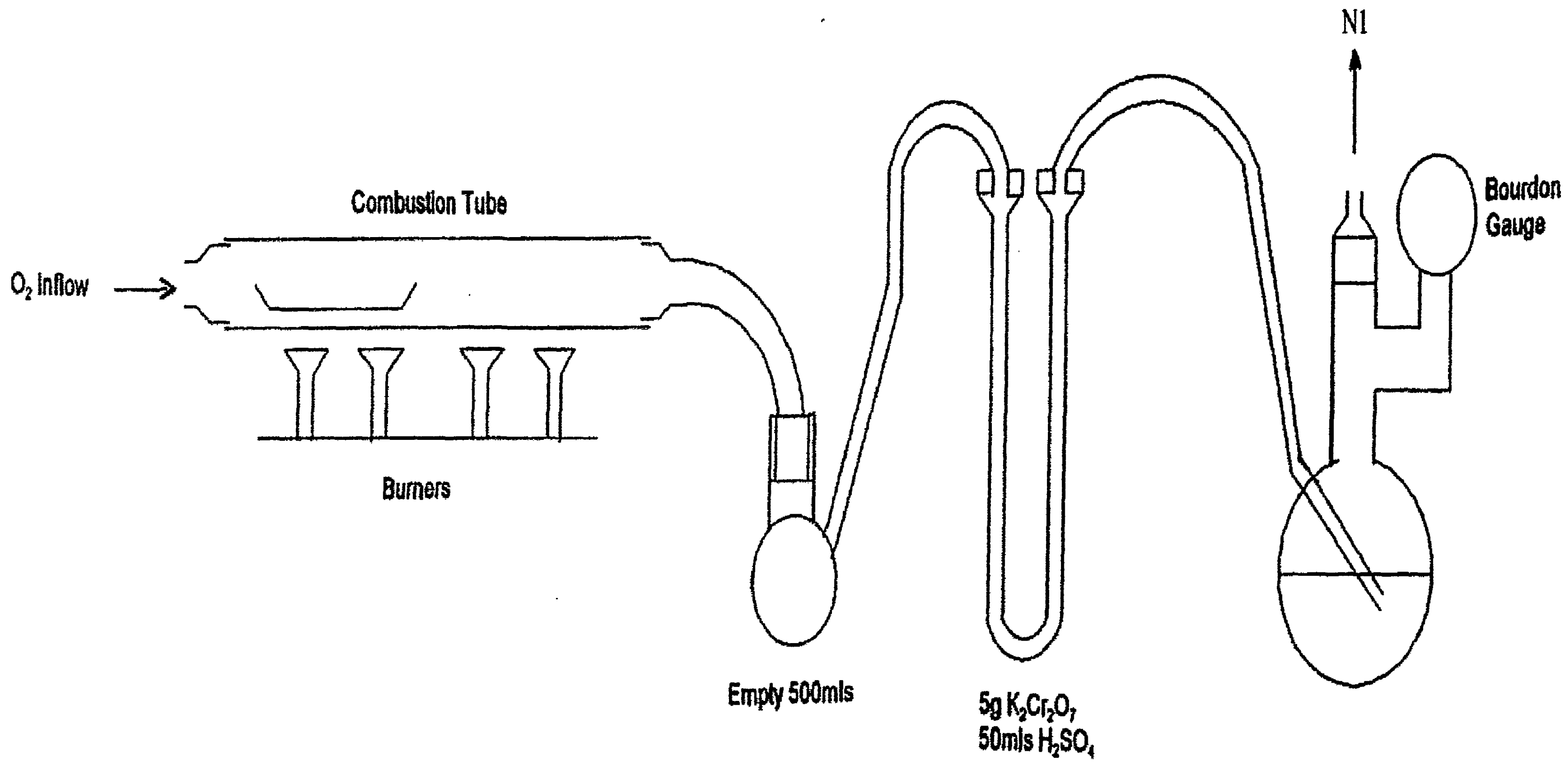
As with the combustion of material with a high organic carbon content, the organic carbon fraction of the sediment is combusted in excess oxygen *via* the same general equation,

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \text{..eqn. 2.1}$$

however, due to the low % carbon of these sediments they must be exposed to excess oxygen for a prolonged length of time. The system is described in Figure 2.8 and is attached to the vacuum line *via* N1 (Figure 2.5)

Once the inorganic carbon had been removed from the sediment the remaining material was filtered through a precombusted glass fibre filters (GF/A 1.6 μm pore diameter) using repeated distilled water rinses to remove any excess acid. The sediment was then placed in an oven set at 60 ^{0}C to dry. Once dry, the materiel was crushed and placed into precombusted quartz boats which in turn were placed in the quartz combustion tube Figure 2.8 with an O_2 pressure maintained at 500-700 mBar by means of a needle valve on the main line (Figure 2.5) while O_2 is fed at a rate of 1 dm^3 min^{-1}. The combustion was carried out by heating the sample by placing four Meker burners under the quartz combustion tube. A pressure of 500-700 mBar was maintained in the combustion tube during the combustion process. The resulting gas was passed through an empty flask, which helped remove water vapour and cooled the gas; a U-tube containing $K_2Cr_2O_7$ and H_2SO_4 which oxidised any CO present to CO_2 and removed any SO_3 and finally a water trap which removed soluble gaseous impurities and caught any H_2SO_4 which bubbled over. The product CO_2 was frozen down in the main vacuum line by passing the gas firstly through two solid CO_2/solid CO2 traps to remove water vapour (**T1, T2** Figure 2.5), followed by cryogenically trapping the evolved CO_2. The CO_2 was stored overnight before conversion to benzene *via* acetylene production.

Figure 2.8 Tube combustion system



2.4 Conversion of carbon containing material to CO_2 for graphite target preparation

2.4.1 Small scale extraction of CO_2 from inorganic carbon (sediment and PIC)

This method was used to extract CO_2 from inorganic sediment and PIC samples. Before analysis of PIC the filter papers containing particulate material was removed from the freezer and defrosted. The sample (filter paper or sediment) is then placed inside the large finger of the small scale hydrolysis apparatus (Figure 2.9). The smaller finger was then filled with acid (4M HCl). The apparatus was sealed and then connected to the "micro rig" *via* S1 (Figure 2.10) and evacuated to better than 1.3×10^{-2} mBar. When sufficient vacuum was attained, the reaction vessel was sealed, removed from the micro-rig vacuum line and the acid added to the sample by tilting the reaction vessel. After approximately 10 minutes the apparatus was placed back on the line. The CO_2 generated was passed through a solid CO_2/IMS trap (T1, Figure 2.10) which removed water, then the CO_2 was collected cryogenically in a liquid nitrogen spiral trap (T2, Figure 2.10). The CO_2 was pumped using the high vacuum manifold and then transferred to the calibrated finger using a liquid nitrogen trap where it was allowed to expand and the volume of CO_2 produced was measured. A 2 ml subsample was taken for graphite production as described in Section 2.7 while the rest is transferred into a mass spec. tube for stable isotope analysis (Section 2.8).

Figure 2.9 Small scale hydrolysis vessel

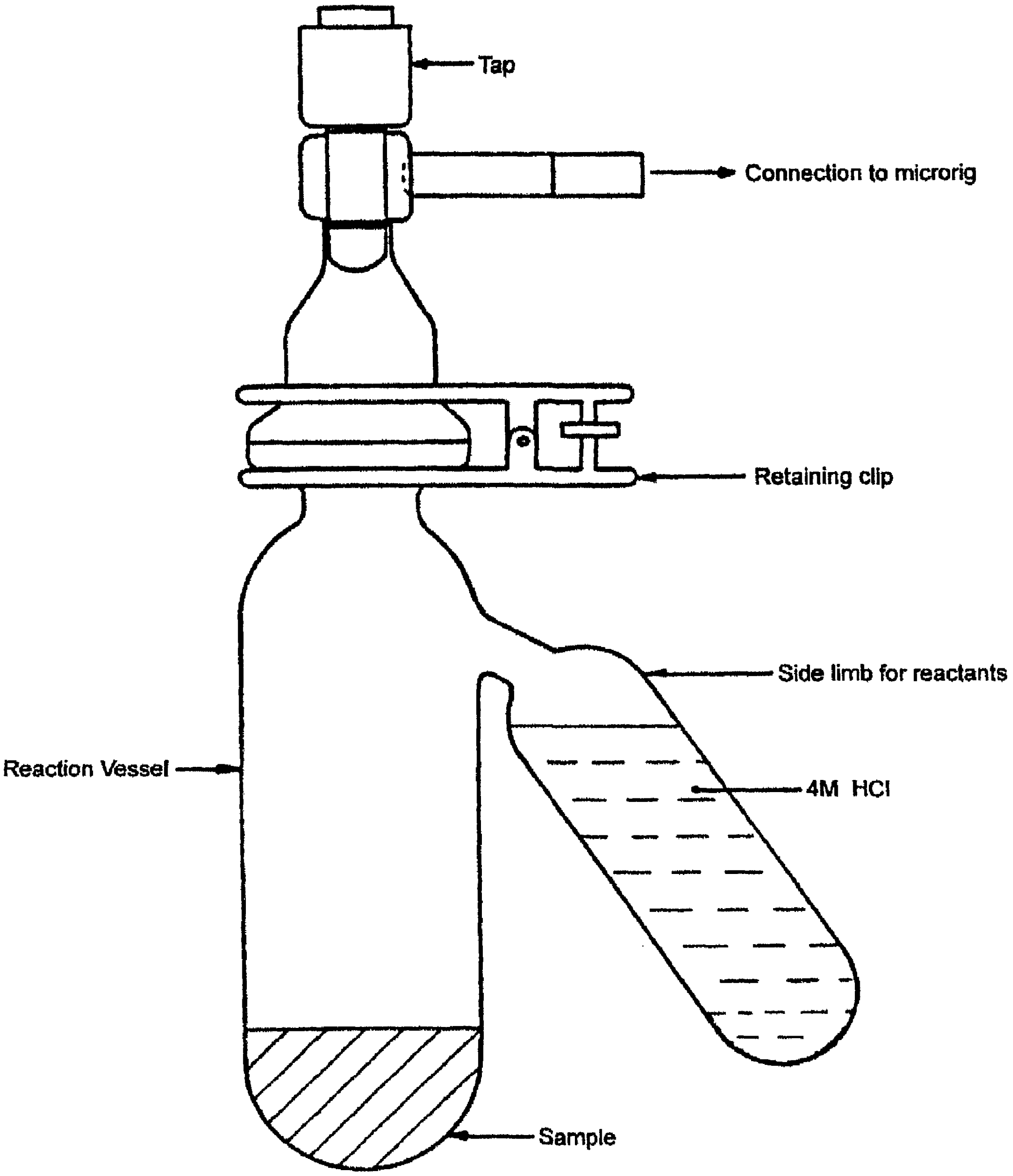
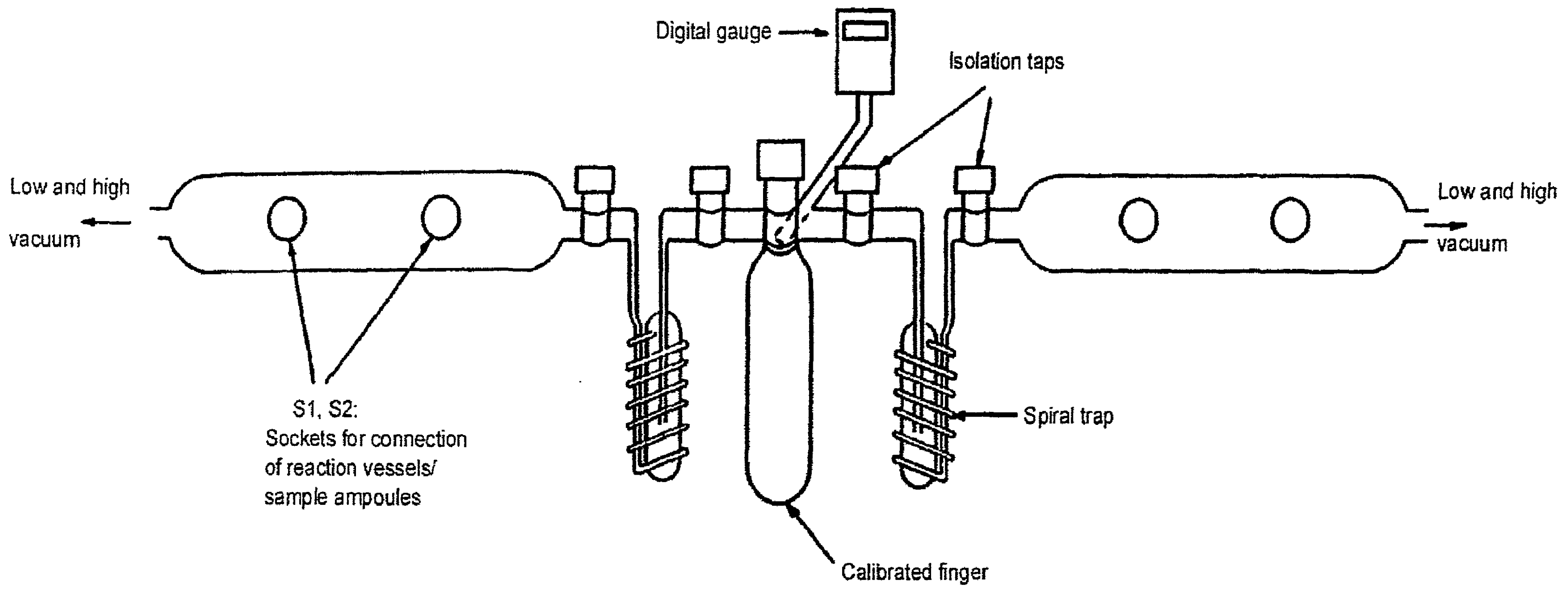


Figure 2.10 Micro rig vacuum line



2.4.2 Small scale combustion of materials containing organic carbon

This method was used for the combustion of organic materials in the sediments, POC and small mussel samples.

The same basic design was used for all sample tubes (Figure 2.11), but the size of the combustion tube depended on the sample size. All sample tubes were first loaded with silver wire and CuO and pre-combusted at 500 ^{0}C for 4 hours to remove any organic carbon contamination. The mussel samples were accurately weighed into pre-combusted 8 mm quartz inserts plugged at one end with quartz wool. The insert was placed into a 12 mm open ended quartz tube with 6 mm open ended stems.

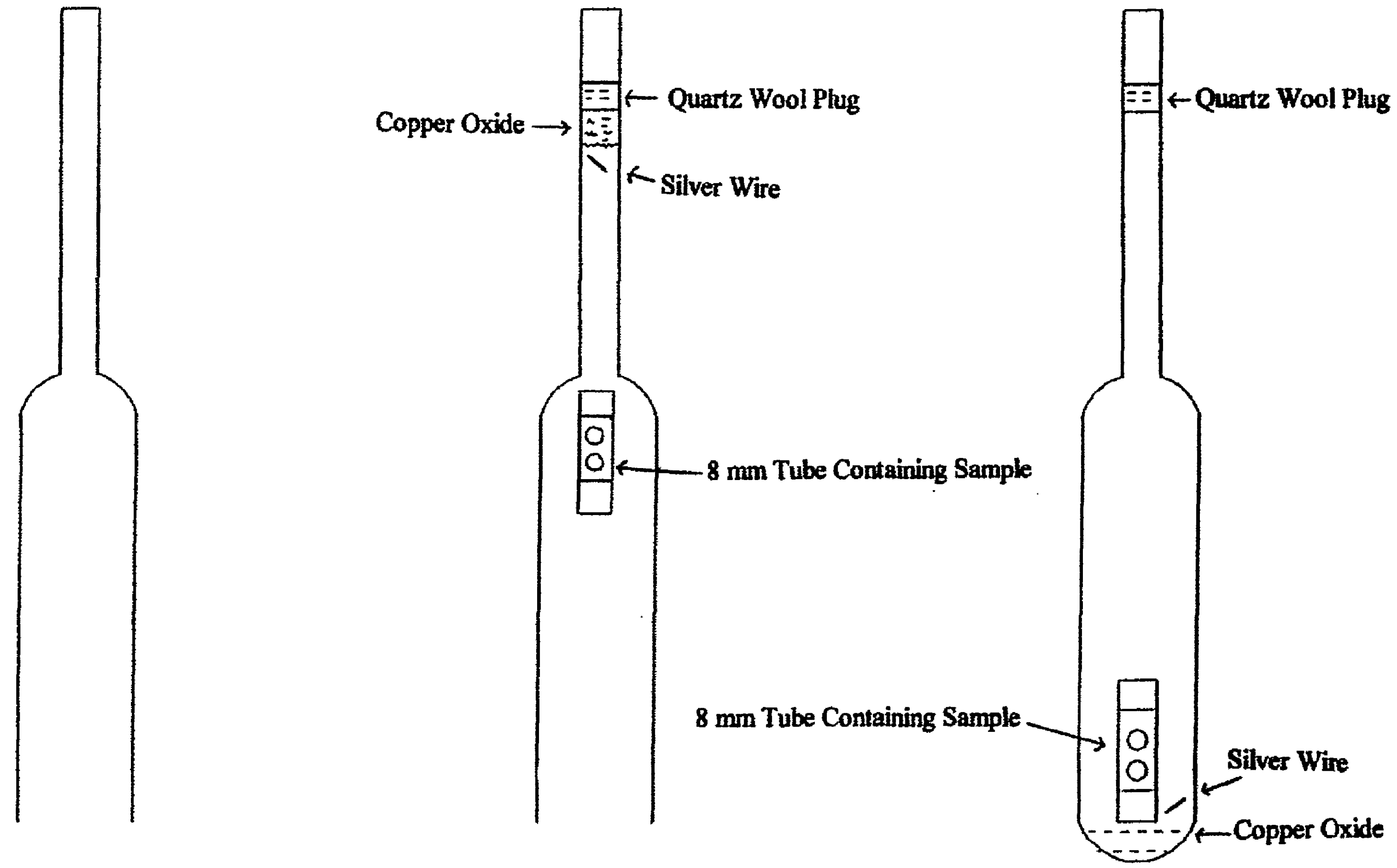
After removal of PIC, the residue from the hydrolysis was filtered through a pre-combusted glass fibre filter (GF/A 1.6µm pore diameter) using repeated distilled water rinses to remove any excess acid and then placed in the oven to dry. The dry filter papers were placed in 18 mm open ended quartz with 6 mm open stem tubes. Sediment samples were placed in 18 mm closed quartz tubes with 6 mm open stems.

Once the inorganic carbon had been removed from the sediment the remaining material was filtered through a precombusted glass fibre filter (GF/A 1.6µm pore diameter) using repeated distilled water rinses to remove any excess acid. The sediment was then placed in an oven set at 60^{0}C to dry. An accurately weighed amount of sediment was poured into a 18 mm closed quartz tube with 6 mm open stem.

An identifying number was etched on the outside of all combustion tube with a diamond tipped pen. The 12 mm and 18 mm open ended tubes were sealed. The 6 mm end was attached to the vacuum line and the pumped to 10^{-3} mBar, before being sealed.

The tubes were placed in a muffle furnace and heated overnight to a temperature of 850 ^{0}C for eight hours. They were then allowed to cool before being placed in a breaking unit (Figure 2.12) which in turn is attached to the micro-rig vacuum line (S1 Figure 2.10). The entire vacuum line was pumped to approximately 10^{-3} mBar. The breaker unit was also evacuated at this stage. The combustion tube was cracked open by closing the breaker stopcock. The gas produced was passed through a solid CO_2/IMS trap (T1, Figure 2.10) to removed any water produced. CO_2 was transferred into the calibrated finger using liquid nitrogen, the CO_2 was then allowed to expand and the volume of the gas measured. A 2 ml aliquot of CO_2 was

Figure 2.11 Quartz combustion tubes at various stages

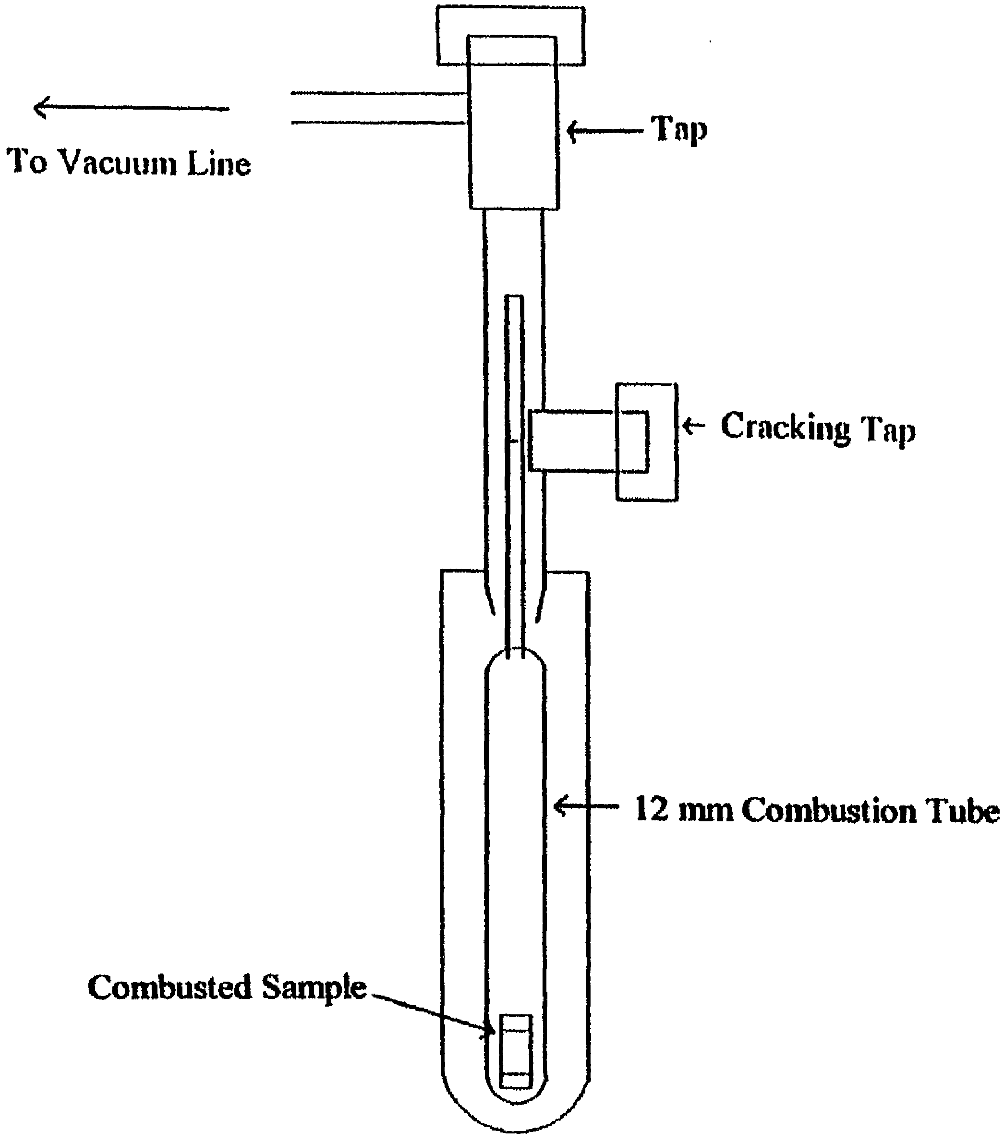


Open tube

Open Tube Containing Sample

Closed tube with organic sample

Figure 2.12 Combustion tube breaking unit

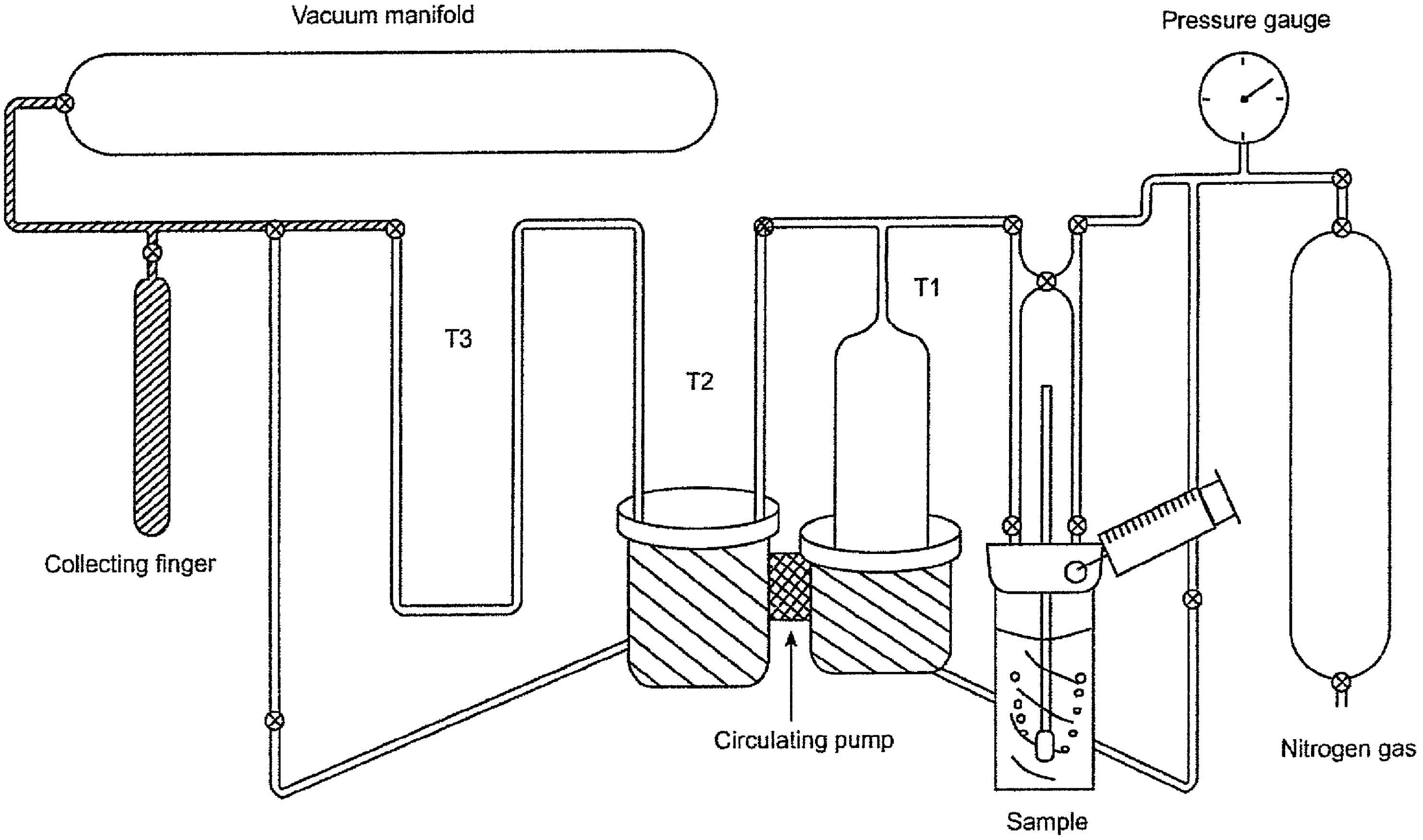


taken for graphite target preparation (Section 2.7) and the remaining gas used for obtaining a $\delta^{13}C$ value (‰ relative to PDB) (Section 2.8).

2.4.3 Small scale extraction of CO_2 from DIC.

The method was adapted from that described by M^c^Nichol *et al.* (1994). The glass salinity bottles were removed from the fridge and transferred to a glove box which had a positive pressure of N_2 gas so that the bottles were opened in a nitrogen filled atmosphere. 500 ml of filtered sample was measured out and transferred to section **a** (Figure 2.13). The lid **(b)** was placed on **(a)** and the sealed apparatus attached to the vacuum line. A finger containing nitrogen gas was attached to the vacuum line **(d)**, and once the vacuum line was pumped down, it was opened to allow the nitrogen carrier gas into the line to a pressure of approximately 0.4 bar. The pump circulated the nitrogen gas through the sample. Excess phosphoric acid was added to the sample in order to hydrolyse the DIC. Water vapour was trapped using a solid CO_2/IMS trap (T1) and CO_2 evolved from the sample was trapped cryogenically using liquid nitrogen surrounding two u-traps(T2 and T1). Nitrogen gas was circulated throughout the apparatus for 15 minutes. The CO_2 collected in the u-traps from the sample was then pumped to 1.3 x 10^{-2} mBar using the high vacuum manifold and then cryogenically transferred using liquid nitrogen to the collecting finger where the volume was measured. Two mls of CO_2 were transferred to a graphite finger for conversion to graphite (Section 2.7) while the rest of and the rest of the gas is used to obtain a $\delta^{13}C$ value (Section 2.8).

Figure 2.13 Small scale DIC hydrolysis appartus



2.4.4 Extraction of CO_2 from DOC for AMS analysis

2.4.4.1 Method development

The DOC pool is the second largest carbon pool in the oceans. However, it is difficult to analyse accurately with different values for DOC being obtained depending on the method used (Menzel and Vacaro 1964; Armstrong *et al.* 1966; Sharpe 1973; Sugimura and Suzuki 1988). For many methods the blank, which can be up to 33% of the sample volume is also a problem. Problems like this and others were discussed in an international workshop held in 1991 and the results of this workshop are available in Volume 41 of the journal Marine Chemistry.

For this study the method chosen was high temperature combustion (500 ^{0}C; Fry *et al.* 1996) of the dried salts from the sample. The concentration of DOC in seawater ranges from approximately 0.7 mg C l^{-1} for open ocean seawater to> 4.0 mg C l^{-1} for low salinity estuarine water (Carlson *et al.* 1994; Le Clercq *et al.* 1997; Fry *et al.* 1996; Raymond and Bauer 2001). The sample site (Portpatrick) is coastal, so a sample size of 500 ml was deemed adequate to provide enough carbon for a 1 mg graphite target. In order to minimise contamination it was decided to dry the sample in a 1litreflask, under vacuum and combust the resultant salts in this vessel. The resulting gasses were dried by passing through a CO_2/IMS trap (- 86 ^{0}C) and then underwent a secondary combustion at 500 ^{0}C with MnO_2 (removes SO_2) and CuO (removes HCl, and nitrous compounds) present in the gas Fry *et al.* (1996), to produce high purity CO_2. Initially, number of artificial seawater samples were made up by dissolving 12.5g ofNaCl and 4g $MgSO_4$ (pre-combusted for 1 hour at 500 ^{0}C) into 500 mls of reverse osmosis water (Whatman Milli-U10). To each 500 ml sample a known weight of a soluble organic compound, in this case Australian National University (ANU) sucrose ($\delta^{13}C = -10.8 \pm 0.1$ ‰: IAEA 1991b) was added. The work of Fry *et al.* (1996) suggests that the $MgSO_4$ will provide free oxygen for the oxidation of all DOC to CO_2. Initial experiments showed that yields of CO_2 were lower than expected, indicating that not enough free oxygen was provided by the $MgSO_4$ in the artificial seawater (Table 2.2). In order to minimise the possibility of additional carbon contamination we decided to add oxygen gas at the primary combustion stage. This approach consistently improved the recovery of CO_2 from the ANU sucrose to > 90 % (samples T21, 22, 30, 31 and 32). From the $\delta^{13}C$ value (‰ relative to PDB) it can be seen that the recovered gas has a similar $\delta^{13}C$ value to that of ANU sucrose indicating that either there

Table 2.2 Artificial seawater samples tests for DOC apparatus

Test sample	NaCl (g)	$MgSO_4$ (g)	ANU sucrose (mg)	oxygen (mls)	expected vol of CO_2 (mls)	recovered CO_2 vol. (mls)	% yield	$\delta^{13}C$ ‰ values
T28	12.5	4.0	38.7	none	30.4	9.5	31 %	- 10.6
T29	12.5	4.0	41.9	none	33.0	9.6	29 %	- 10.5
T21	12.5	4.0	35.4	10 mls	27.8	25.6	92 %	-10.6
T22	12.5	4.0	34.9	10 mls	28.2	26.8	95 %	- 10.5
T30	12.5	4.0	47.6	10 mls	30.6	31.9	104 %	- 10.3
T31	12.5	4.0	33.0	10 mls	26.0	24.7	95 %	- 10.5
T32	12.5	4.0	36.5	10 mls	28.7	26.3	92%	- 11.0

is little contamination of CO_2 or that any CO_2 contamination has a similar $\delta^{13}C$ value to the ANU sucrose.

Next, paired seawater samples were analysed. These samples were collected at the same time and filtered into two pre-combusted 5 litre flasks, one of which had 0.1295 g of ANU Sucrose added. The two flasks were stored at < 4 ^{0}C and 500 ml sub-samples were taken from each flask for paired analysis when required. As the samples were treated in the same fashion (except for the addition of ANU sucrose) the natural concentration of DOC should be the same in each sample. The recovery of CO_2 from the sucrose can be calculated from the total volume recovered minus concentration due to naturally present DOC divided by the volume of CO_2 expected from the sucrose added.

Samples 38 to 41 (Table 2.3) had very large greenish/yellow volumes of gas produced after the primary combustion stage, much of which was SO_2. A solid CO_2/pentane trap was introduced to remove this SO_2 for all samples after T41. For these four samples the secondary combustion stage did not totally clean up the gas from the primary combustion stage and there was a yellowish/green tinge to the gas after the secondary combustion stage which was cleaned up by passing the gas repeatedly through the solid CO_2/IMS and solid CO_2/pentane traps. In order to discover what was in the gas prior to the secondary combustion the VG Prism II was used to obtain a range of masses for the gas from the secondary combustion of T42. This revealed that there were traces of HCl, nitrates, sulphates and hydrocarbon fragments. In order to clean up the contaminants, some silver wire was added to the secondary combustion and the secondary combustion was carried out at 800 ^{0}C in a quartz tube in order to oxidise all the organic fragments. This cleaned up the gas so that graphite targets could be made. However, from the fact that there were traces of short chain hydrocarbons in the gas after the primary combustion implies that the temperature of the primary combustion was not high enough to oxidise all the DOC in the dried salts to CO or CO_2 and possibly, that some of the DOC was not oxidised at all. It would appear that for future analyses, quartz primary combustion tubes should be used as they will withstand the higher temperature combustion necessary for the total oxidation of DOC to CO_2. Unfortunately, the Portpatrick samples had already been dried in pyrex primary combustion tubes and so were combusted at 500 ^{0}C. From T46 it can be seen that addition of silver wire and increasing the secondary combustion stage produced clean CO_2. All the Portpatrick DOC sample gases were given a mass scan on the VG Prism II and proved to be clean CO_2.

Table 2.3 Seawater tests for the DOC system

Test sample	ANU sucrose (mg)	expected volume of CO2	Vol of CO2 recovered (mls)	% yield	$\delta^{13}C$ ‰ value	Results of prism mass scan
T38	None added	unknown	1.5 mls	/	-23.5	Not done
T39	13.0	VT38 + 10.2	6.6	50 %	- 12.6	Not done
T40	13.0	V41 + 10.2	3.44	21 %	- 16.0	Not done
T41	None added	unknown	1.3	/	- 23.1	Not done
T42	None added	unknown	1.8	/	Not done	traces of hydrocarbons
T43	13.0	T42+10.2	3.2	14 %	Not done	traces of hydrocarbon
T45	None added	unknown	1.7	/	Not done	traces of hydrocarbons
T46	None added	unknown	2.4	/	Not done	Just CO_2

Blanks were also run on the system using 10 mls of O_2 during the primary combustion with the secondary combustion at 500 ^{0}C. From Table 2.4 it can be seen that the blanks produced average of 0.32 mls of CO_2 for a 500 ml of artificial seawater sample, almost 20% of the average volume of CO_2 recovered from a 500 ml seawater sample (T38, T41, T42, T45 and T46).

However this blank was not subtracted from the volumes of CO_2 obtained from samples because it is unclear what main source of CO_2 to the blank was. For example, any CO_2 contributed by the reverse osmosis water, NaCl or $MgSO_4$ is not applicable as system blank. In conclusion it is clear that this method is in need of further refinement and testing. However, the ^{14}C specific activities for DOC samples presented in this study were analysed using the method described in Section 2.4.4.2. as the method stands it is clear that these results are provisional and improvements in the method are necessary before any further work is undertaken.

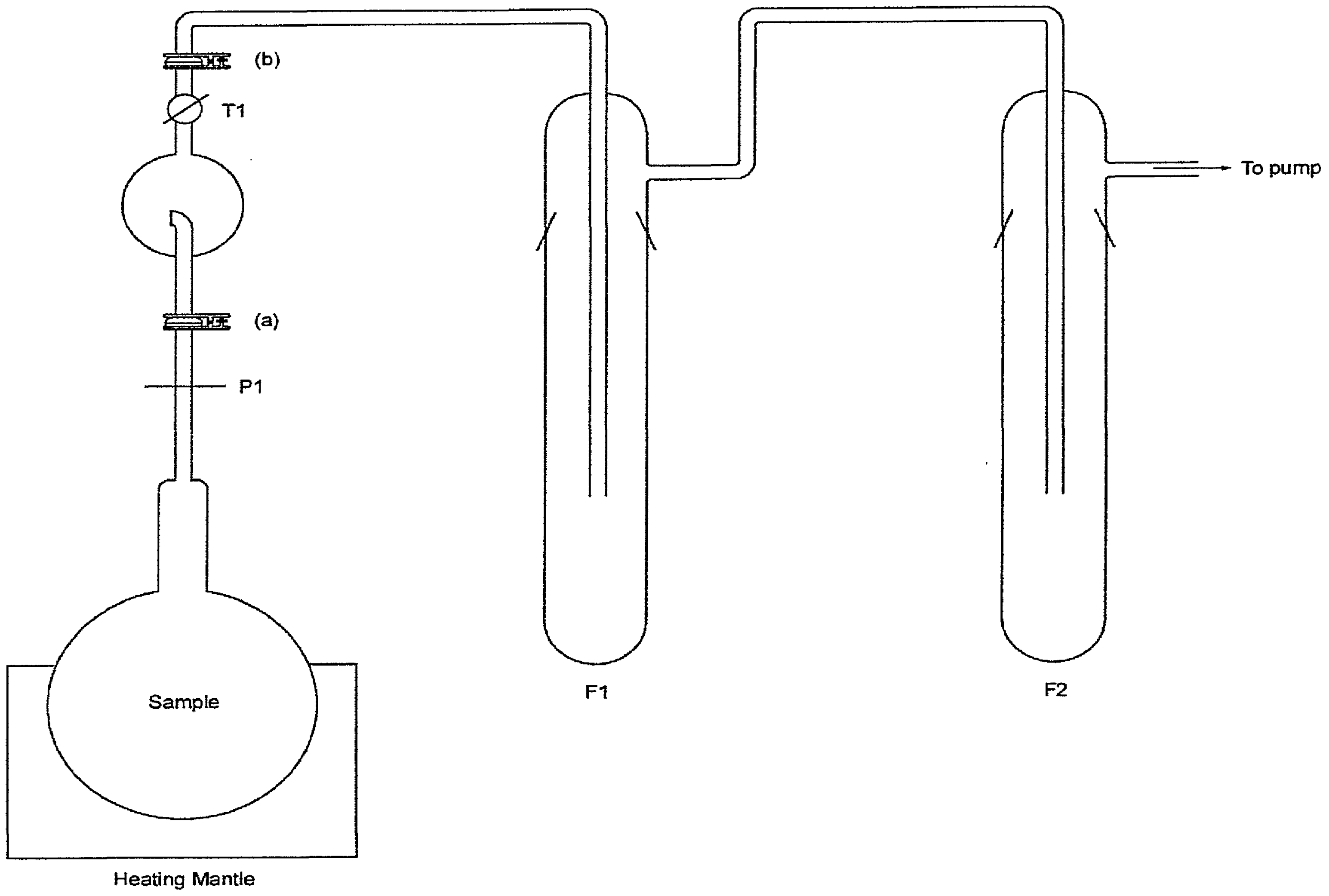
Table 2.4 Blanks run on the DOC system

Id Number	Composition of artificial seawater	Vol CO2 recovered	δ^{13}C ‰ (relative to PDB)
B1	12.5g NaCl 4g $MgSO_4$ 500 mls RO water	0.25 mls	N/A
B2	12.5 g NaCl 4 g $MgSO_4$ 500 mls RO water	0.33 mls	-128.47
B3	12.5 g NaCl 4 g $MgSO_4$ 500 mls RO water	0.38 mls	- 18.1

Section 2.4.4.2 Conversion of DOC in seawater samples to CO_2

(Refer to Figure 2.14). The sample is removed from the fridge, 500 mls were accurately measured out using a clean measuring cylinder and one ml of concentrated orthophosphoric acid was added. The sample was then placed in a pre-combusted round bottomed flask using a funnel *via* the **a1**. A splash head is added to **a1** and tap **T1** was closed. The round bottomed flask was then placed in the heating mantle and attached to the vacuum manifold **a1/b1**. Cooling finger **F2** was surrounded by liquid nitrogen and the pump was turned on. **T1** was

Figure 2.14 Extractions of DOC from seawater



opened slowly and the sample degassed. Once the sample was degassed the heating mantle was turned to 40 ^{0}C. The sample was pumped until dry, ensuring that cooling fingers **F1** and **F2** were always surrounded by liquid nitrogen.

Once the sample is dry **T1** is closed and the round bottomed flask transferred to the micro-rig (Figure 2.10) where approximately 0.1 litre of high purity oxygen was added to the sample. The round bottomed flask was sealed at point **p1** using an oxy-acetylene torch. The round bottomed flask was then placed in a furnace at 500^0 C overnight.

Once the round bottomed flask had cooled it was removed from the furnace and placed in a breaking unit and attached to the micro rig (Figure 2.10). The round bottomed flask was opened and the gas passed through a spiral trap surrounded by solid CO_2/IMS (to remove water) and **s2** which was surrounded with solid CO_2/pentane which removes SO_2. The remaining gas was cryogenically trapped with liquid N_2 in a collecting finger. The CO_2 was allowed to expand and the volume of the gas recorded.

The gas was then transferred to a pre-combusted quartz combustion tube which contained 0.5 g of CuO and 0.1 g of MnO_2. This combustion tube was sealed and placed in the furnace at 800 ^{0}C for two hours.

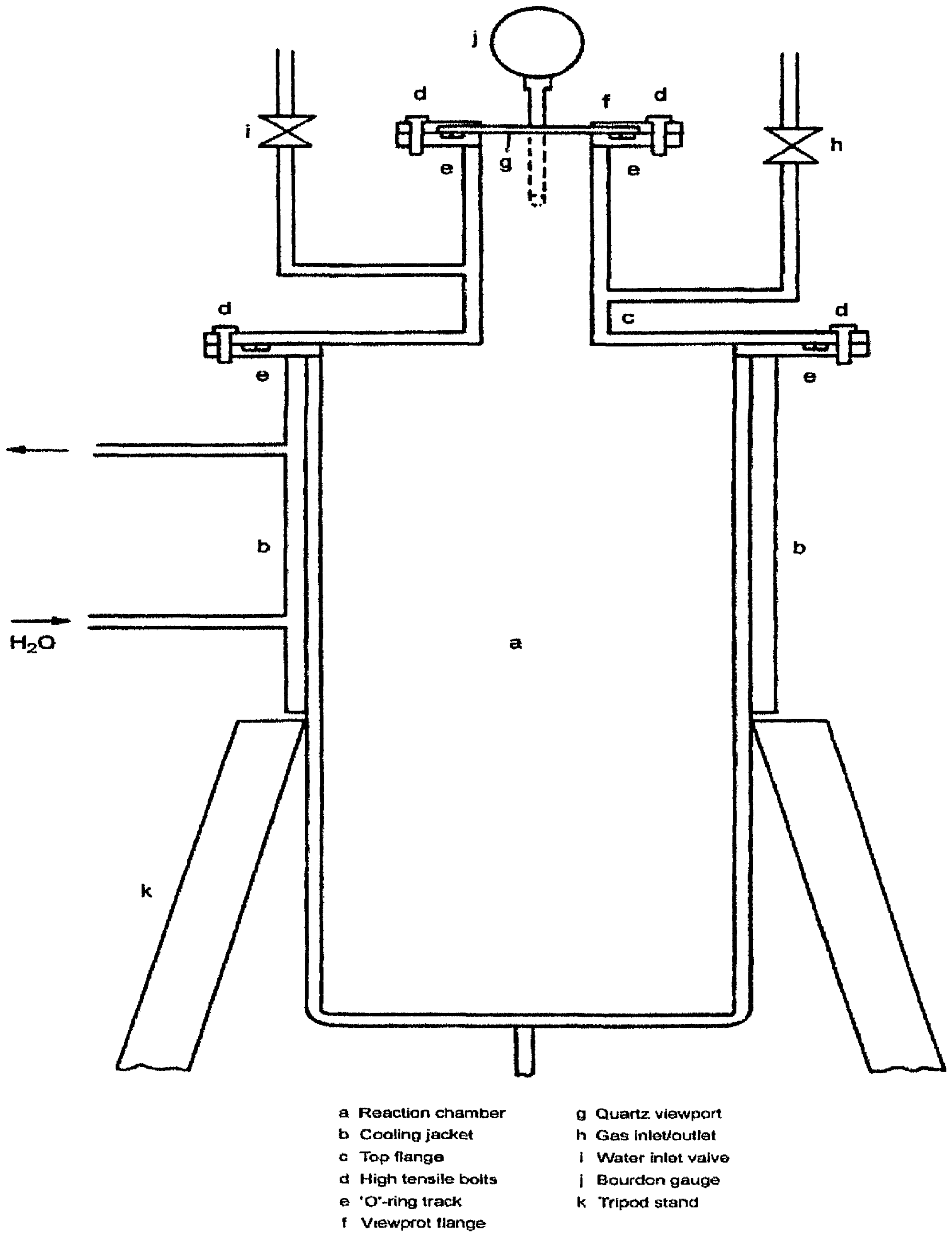
Once the combustion tube had cooled it was removed from the furnace and placed in a breaking unit and attached to the micro rig. The combustion tube was opened and the gas passed through two spiral traps, one of which was surrounded by solid CO_2/pentane and the other by solid CO_2/IMS. The CO_2 was cryogenically trapped in the calibrated finger using liquid nitrogen. Once the CO_2 had been collected it was allowed to expand and the volume of the gas was measured and recorded. A 2 ml aliquot was taken for the preparation of a graphite target and the remaining gas used for obtaining a δ^{13}C value (‰ relative to PDB).

2.5 Conversion of CO_2 to C_2H_2

2.5.1 Conversion of CO_2 to Li_2C_2

Based on earlier work by Arrol (1947), Barker (1953) developed a viable two stage method for the conversion of CO_2 to C_2H_2 *via* an intermediary of Li_2C_2. Both reactions were carried out in a stainless steel reaction vessel (Figure 2.15), connected to the CO_2 storage system vacuum line (Figure 2.5), and was designed in two parts to allow rapid isolation from the atmosphere,

Figure 2.15 Lithium bomb



preventing oxidation of the Li, in addition to easy cleaning between samples. The lower part is where the reaction occurs, with the upper part being water cooled to condense any lithium vapour. The second (or top) half of the reaction vessel contains the gas inlet/outlet valve, pressure gauge, water inlet valve and a quartz glass viewport which allows monitoring of the reaction. Two burners connected to a gas supply are used to heat the vessel.

The chemical equation for the production of Li_2C_2 is:

$$2CO_2 + 10Li \rightarrow Li_2C_2 + 4Li_2O \text{...eqn 2.4}$$

Prior to the formation of LiC, Li metal was added to the reaction vessel *via* the viewport (2.5g per litre CO_2), the pot was sealed, connected to the low vacuum manifold and evacuated. Once the cooling jacket water had been turned on, the burners were lit and the reaction vessel heated until the Li was molten and produced a shiny mirrored surface.

The pump was then be turned to the high vacuum manifold and the vessel pumped until the vacuum approached 1.3 x 10^{-2} mBar. Prior to CO_2 addition, a small sample was taken for mass spectrometric analysis and the remaining sample was slowly added to the reaction vessel through the gas inlet valve, ensuring that the internal pressure did not exceed 400 mBar, as this reduced the C_2H_2 yield. On addition of the sample, the Li metal discoloured and became black as the carbide was formed while the exothermic nature of the reaction resulted in a rise in temperature to approximately 800 °C.

Throughout this process, some carbon can be lost due to the following side reactions,

$$4Li + 2CO_2 \rightarrow Li_2CO_3 + C + Li_2C \text{....................................eqn 2.5}$$

$$Li_2O + CO_2 \leftrightharpoons LiCO_3 \text{..eqn 2.6}$$

However, at temperatures above 600 °C, Li_2CO_3 decomposes significantly due to the reversible nature of the reaction. At temperatures above 900 °C, this reconverted CO_2 forms Li_2C_2 *via* Eq. 2.5 and the elemental carbon formed in Eq. 2.5 undergoes $2C + 2Li \rightarrow Li_2C_2$ to again from Li_2C_2 (Gupta and Polach 1985).

When all the CO_2 had been adsorbed onto the lithium, the reaction vessel was isolated from the vacuum line and heated for a further 45 minutes, after which time the burners are switched off and the vessel connected to the C_2H_2 collection system and pumped through the low vacuum manifold until cooled to room temperature.

2.5.2. Hydrolysis of Li_2C_2 to C_2H_2

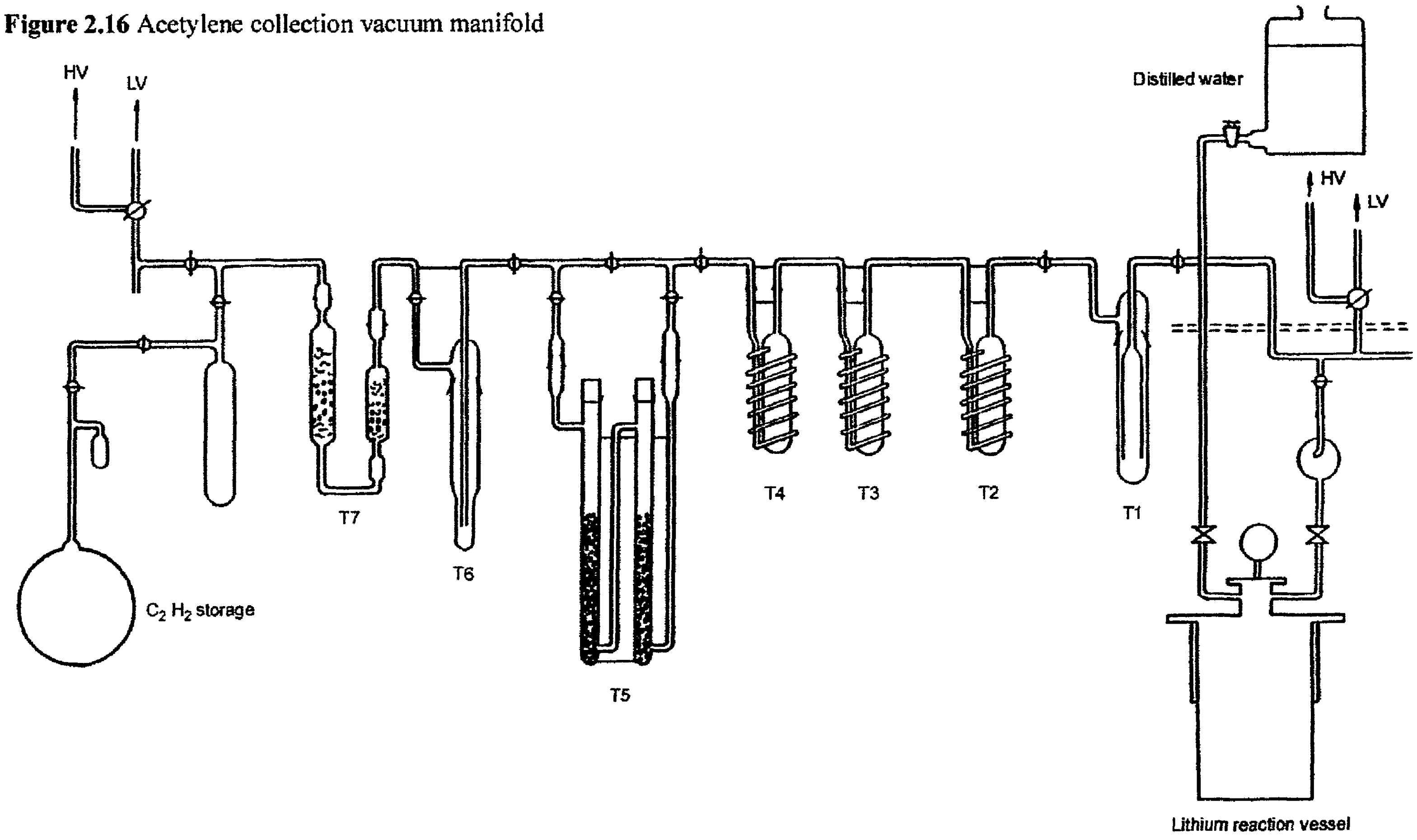
Once the carbide had cooled, the second stage of the C_2H_2 production was carried out . The chemical equation for this reaction is:

$$Li_2C_2 + 2H_2O \rightarrow C_2H_2 + 2LiOH \ldots\ldots\ldots\ldots \text{eqn 2.7}$$

As before, for the CO_2 collection, the C_2H_2 collection system (Figure 2.16) has three spiral traps (**T2**, **T3** and **T4**), but only one water trap (**T1**). The system was connected to a low vacuum manifold with a rotary pump, and a high vacuum manifold with an air-cooled oil diffusion pump backed by a rotary pump (a mercury pump may cause the formation of explosive acetylides). C_2H_2 was produced from Li_2C_2 by the controlled addition of distilled water. The pressure in the reaction vessel was allowed to build up to approximately 950 mBar before being released, passing through the IMS/solid CO_2 slush trap into the three liquid N_2 cooled traps until the internal pressure was approximately 400 mBar This process was repeated until no increase in pressure occurred on addition of water. The residual pressure in the reaction vessel was released until the mixture began to "boil". The reaction vessel and water trap are then isolated from the sample which was pumped *via* the low vacuum manifold and then isolated.

The C_2H_2 was subjected to a rigorous clean-up before it was converted to C_6H_6. Once the sample had been pumped by the low vacuum manifold, the IMS/solid CO_2 slush trap was placed on the third spiral trap and the sample allowed to sublime at room temperature. The sample was collected cryogenically using liquid nitrogen, after if had passed through a scrubbing column of H_3PO_4 and glass beads(**T5**), another IMS/solid CO_2 slush trap (**T6**) and finally a column containing P_2O_5 coated glass beads (**T7**). The H_3PO_4 column removed any ammonia present in the sample, while the solid CO_2/solid CO_2 slush and P_2O_5 column removed any final traces of moisture. When all the C_2H_2 had frozen down in the collection finger, it was pumped *via* the high vacuum manifold until the vacuum was better than 1.3×10^{-2} mBar, before being transferred cryogenically using liquid nitrogen to the C_2H_2 storage bulbs.

Figure 2.16 Acetylene collection vacuum manifold



2.6 Conversion of C_2H_2 to C_6H_6

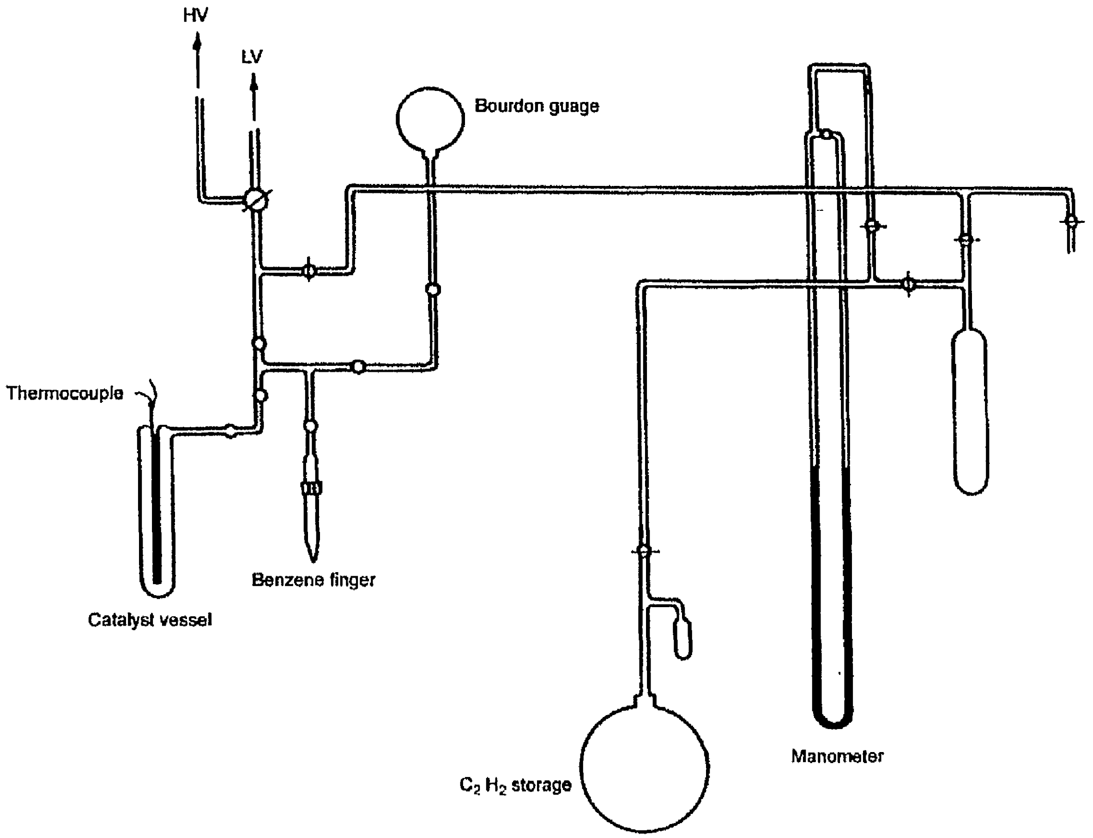
The final step in sample processing was the conversion of C_2H_2 to C_6H_6 which involved a cyclotrimerisation reaction *ie,*

$$3\ C_2H_2 \rightarrow C_6H_6 \qquad \text{eqn 2.8}$$

In the early 1960's, this reaction was carried out by pyrolysis of C_2H_2 at 650 °C (Tamers 1960) and by using diborane activated catalysts (Noakes *et al.* 1963). Post-1965, however, most radiocarbon laboratories employing liquid scintillation techniques have used transition metal activated silica-alumina catalysts (Pietig and Scharoensell 1966; Noakes *et al.* 1965; Tamers 1960) and in this study, a chromium activated silica-alumina pelletised catalyst was used.

The C_6H_6 section of the glass vacuum line is detailed in Figure 2.17 and consisted of a removable catalyst tube surrounded by a furnace, a thermocouple, a removable cold finger for C_6H_6 collection, a Bourdon gauge and connections to both the C_2H_2 storage system and the low and high vacuum manifolds *via* grease-less stopcocks to prevent grease from contaminating the sample C_6H_6. The catalyst tube was filled with new catalyst for every synthesis to reduce the risk of carry-over from previous samples, although theoretically the chromium (III) and (IV) can be reactivated back to the (VI) form (by heating in air to 450°C). Once the catalyst tube was filled and connected to the line it was pumped *via* the low vacuum manifold while the surrounding furnace heated the catalyst to 350 °C, ensuring the removal of any moisture and gases present. This temperature was maintained for 30 minutes before the furnace was turned off and the catalyst allowed to cool while being pumped by the high vacuum manifold to 1.3×10^{-2} mBar. C_2H_2 was introduced to the catalyst when the temperature reached 120 °C. Further aliquots of C_2H_2 are introduced until the temperature approached 160 °C (due to the exothermic nature of the reaction). When the temperature rise ceased, the C_6H_6 was transferred cryogenically into the benzene collection finger using liquid nitrogen, thus freeing active sites on the catalyst. When the catalyse had cooled to 120 °C, more C_2H_2 was added and the process repeated until the complete C_2H_2 sample was converted to C_6H_6. When all the C_2H_2 was on the catalyst, the furnace was heated to 160 °C and the C_6H_6 which was produced was allowed to pass over into the collection finger. The sample in the collection finger was then removed from the vacuum line, capped and stored in a refrigerator for a minimum of three weeks to allow any radon to decay.

Figure 2.17 Benzene preparation vacuum line



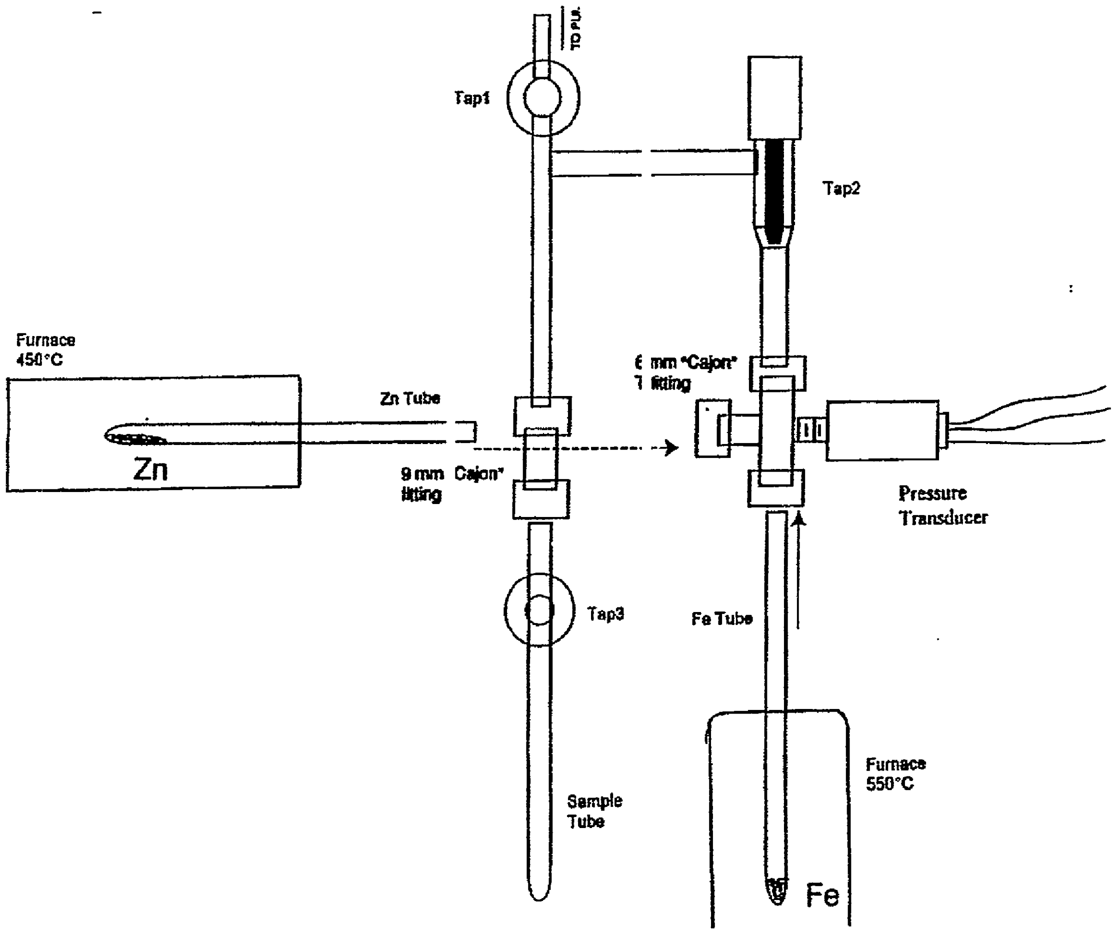
2.7 Conversion of CO_2 to Graphite.

Graphite targets were prepared from CO_2 using the method of Slota *et al.* (1987). The graphite preparation line (Figure 2.18) was pumped in advance to clean the reaction vessels before loading the next set of samples and then the furnaces were switched on. The zinc powder requires a furnace temperature of 450 °C while the iron requires a furnace temperature of 550 °C. The equation below illustrates the chemical reactions involved in the preparation of graphite;

$$Fe^{2+} + Zn + CO_2 \rightleftharpoons Fe^{2+} + ZnO + CO \rightleftharpoons Fe^{2+}C + 2ZnO + O \ldots\ldots\ldots\ldots \text{eqn } 2.9$$

A ratio of 2:1 iron :carbon is required for graphite production. Apart from the DOC samples, where the sample size was small, 1 mg graphite targets were prepared and sent to the University of Arizona AMS facility for analysis.

Figure 2.18 Grapherite preparation line



2.8 Isotopic Fractionation Measurement

Isotopes of the same element, such as ^{12}C, ^{13}C and ^{14}C have slightly different thermodynamic properties which can result in changes in the isotopic ratio of the element during chemical and physical processes in both the laboratory and the environment. As an example of environmental isotopic fractionation, Craig (1953) found a 2 ‰ depletion in the ^{13}C:^{12}C ratio of terrestrial plants relative to that of their carbon source *ie.* the atmosphere. As the mass difference is double for ^{14}C:^{12}C, relative to ^{13}C:^{12}C, Craig (1954) assumed an isotopic fractionation difference of the same magnitude (*ie.* a 4 ‰ depletion of ^{14}C).The extent of isotopic fractionation for ^{14}C cannot be measured directly from ^{14}C:^{12}C ratios using a conventional mass spectrometer, hence, ^{13}C:^{12}C ratios are determined and used to calculate a fractionation factor by assuming a doubling of the deviation for ^{14}C. The sample of CO_2 for mass spectrometric analysis is collected prior to lithium carbide formation, with the assumption that no further fractionation is induced during the conversion to acetylene and benzene (Campbell 1977). Carbon stable isotope ratios are reported in the $\delta^{13}C$ ‰ notation relative to PDB, where PDB is a cretaceous belemnite, *Belemnita americana*, from the Peedee formation in South Carolina, USA and is the primary standard for $\delta^{13}C$ fractionation determinations. The isotopic composition of the samples were measured on a VG SIRA or PRISM instrument by comparing the m/z 45/44 and 46/44 ratios for sample CO_2 with those of a working, secondary standard CO_2 calibrated against NBS 22 oil ($\delta^{13}C = -29.61$ ‰ PDB) and NBS 19 marble ($\delta^{13}C = +1.93$ ‰ PDB), and making the usual instrumental correction factors (Craig 1957). The deviation of the sample ^{13}C:^{12}C ratio relative to the standard ^{13}C:^{12}C ratio was calculated from the equation:-

$$\delta^{13}C = [{}^{13}C{:}{}^{12}C_{sample}/{}^{13}C{:}{}^{12}C_{standard} - 1] \times 1000‰ \text{.........eqn 2.10}$$

Correcting measured ^{14}C activities for this isotopic effect, prior to age calculation, has been recommended by Stuiver and Polach (1977) and conventionally results in all radiocarbon samples being corrected to a $\delta^{13}C$ of -25 ‰, which is the average $\delta^{13}C$ value of 1890 wood. The equation

$$\text{fractionation factor} = [1-2(\delta^{13}C + 25/1000)] \text{..........................eqn 2.11}$$

produces a fractionation factor (F.F.) Which can be applied directly to the sample activity to give an isotope fractionation corrected activity. However this work aims to compare the specific activity of the samples to the "ambient background" specific activity, irrespective of the $\delta^{13}C$ ‰ (PDB) value of the sample in order to calculate the contribution of Sellafield derived ^{14}C to the specific activity of the samples. Therefore, a fractionation factor is not applied to the specific activities presented in this work. $\delta^{13}C$ ‰ (PDB) values for samples were obtained, where possible, as this value can provide information about the source of the sample carbon. In addition, if in the future, the results were to be presented as absolute percent modern (pM) or ages (y BP) a F.F. would have to be applied in the conversion from specific activity.

2.9. Liquid Scintillation Counting

The basic theory behind liquid scintillation counting has been described in detail in the works of (Birks 1964; 1965; Birks and Poullis 1972; Knoll 1979; Gupta and Polach 1985) and will only be discussed generally in this section with relation to this work.

2.9.1 Theory

Liquid scintillation counting requires the sample to be in direct contact with a solvent capable of absorbing the energy released during the emission of a beta particle. The beta particle will dissipate its energy by collisions with this solvent resulting in excitation of the solvent molecules. These excited solvent molecules are not readily detected hence a scintillation solution contains not only a solvent, but, also a solute, which is termed the scintillator. Once excited the solvent molecules can transfer energy to other solvent molecules or to a solute molecule. Energy passed to the solute molecule disturbs the orbital electron cloud of the solute raising it to a state of excitation, and on its return to the ground state, a photon of light is released. The total number of photons from the excited scintillator molecules constitutes the scintillation in which the intensity of light is proportional to the initial energy of the beta particle. For ^{14}C, the scintillation intensity will range from 0-156 ke V. The detection of this light is carried out by two photomultiplier tubes (PMTs, whose surfaces act as photocathodes) which transduce the detected photons into electrical pulses.

Modern liquid scintillation spectrometers consist of two photomultiplier tubes (PMTs) diametrically opposite each other and a centrally mounted optimising reflector. The inner faces of the PMTs are uniformly coated with a photosensitive material which converts the absorbed photons of light into electrical energy by the release of photoelectrons. PMTs are linear devices, therefore, the amplitude of the electrical pulse generated is directly proportional to the number of photons detected. Monitoring the occurrence of electrical pulses in a given time period gives an indication of the number of scintillations, and hence, beta emissions, which are taking place in the sample.

2.9.2 Counter and Scintillation cocktail.

In this study, the "scintillation cocktail" used was 12 g of butyl-PDB (2(4'-tret-butylphenyl)-5-(4''-biphenylyl)-1,2,3-oxadiazole)), as the primary scintillant, and 6 g of bis-MSB (1,4-di(2-methylstyryl)-benzene), as the secondary scintillant, dissolved in one litre of toluene.

Quenching

The counting efficiency of the solvent-solute system can be affected by both chemical and colour quenching. The first of these absorbs beta energy before photons of light are produced. In comparison, colour quenching occurs as the photons are passing through the medium resulting in changes in the wavelength of the light reaching the PMTs, thereby reducing the response.

All samples are quenched to some extent, resulting in a decrease in the number of photons per keV reaching the PMTs and, hence, the pulse amplitude is reduced for the same energy of particle. This results in a shift of the whole spectrum to lower energies.

The method used in Packard counters to monitor the extent of quenching in each individual sample is the external standard technique which uses the movement of the external standard spectrum as an indicator of quenching. An external source of gamma radiation is placed adjacent to the sample for 15 seconds before sample counting commences. This produces electrons in the scintillation solution due to the Compton collision process. These electrons cause scintillations which can be detected and used to produce an external standard spectrum. The contribution from the sample count rate is deducted by counting for a similar time period in the absence of the external standard to provide an indication of quenching dependent only on the external standard spectrum. Analysis of the external standard spectrum produces an index which can be related to the measuring efficiency in the region of interest. The index is termed the SIE (Spectral Index of the External standard). The association between the SIE and the measured efficiency on the sample region is obtained by measuring a series of standards of known activity which have all been quenched to varying degrees with acetone (a known quenching agent) and the regression equation used to calculate a quench factor for the sample relative to a baseline value.

The presence of quenching agents shifts the external standard spectra to lower energy levels as it does for actual samples. Thus, the Compton spectrum is generated in the scintillation solution and monitors the occurrence of quenching. The external standard method cannot determine effects of inhomogeneity in the sample although this is not a concern when benzene is the sample. As the index, SIE , is based on the Compton electron distribution, it is relatively unaffected by the sample volume or the type of vial used.

2.9.3 Backgrounds

During the course of this study there were three vacuum lines in use for the preparation of benzene for LSC counting. As the DIC and biota from Portpatrick and Nethertown and St Bees Head were expected to have ^{14}C activities in excess of modern activity (226 Bq kg^{-1} C), these samples were prepared on the high activity benzene preparation line (Line 1). In comparison the inorganic and organic fractions of the sediment were expected to be in the range of 10,000 and 2,000 y BP and so were prepared on the low activity lines (Lines 2 and 3).

To ensure that scintillation events not attributable to ^{14}C in the sample are taken into account a background count rate is monitored. This is done by preparing samples of scintillation grade benzene or synthesising samples which are known to contain no ^{14}C activity (*eg.* marble chips and Kauri Wood) in the same manner as real samples and counting them in batches together with the samples. These background samples are monitored for any change in their count rate as an indicator of counter stability and are also used as a means of monitoring the vacuum line for carry-over and memory effects.

12 backgrounds were run during the course of this study, 8 on Line 1 and 4 backgrounds on Lines 2 and 3. For nine of the twelve samples the background counts per minute (cpm) was within ± 2σ of the average scintillation grade benzene (SGB) cpm for the same counting batch. B579, B584, and B679 were not within ± 2σ of the average cpm SGB, being approximately 0.3, 0.2 and 0.2 cpm higher than the corresponding SGB count rates of 4.376 ± 0.054, 4.018 ± 0.043 and 2.069 cpm respectively. These excess counts would contribute very little to the activity of the samples which had count rates ranging from 8 to 2750 cpm, although the majority of the samples were above the ambient background count rate of approximately 20 cpm.

While there is some discrepancy (3 of 12 background samples without error) between the background samples and SGB it appears to be random and is negligible in comparison to the actual sample activities measured during this study.

2.9.4 Modern reference Standards

All radiocarbon results are calculated relative to an international primary reference standard which is 1890 wood, assumed to have a natural ^{14}C specific activity of 226 Bq kg^{-1} C and is equivalent to 100% modern (pM). In the laboratory, a secondary standard, Oxalic acid II is supplied by the National Institute of Standards and Technology which, when multiplied by 0.07459, equals the activity (corrected to $\delta^{13}C = -25‰$) of the primary standard. Four modern standards are normally counted in the sample batches to enable accurate calculation of the sample specific activities.

2.9.5 Known Age Samples

As part of the quality assurance procedures, a number of known age samples (Samples with consensus values from the Third International Radiocarbon Intercalibration (TIRI), barley mash Buiston Crannog Wood as well as an in-house standard) were analysed along with the samples and compared to the published consensus values and average value for the in-house standard. Results of the TIRI Barley mash, TIRI Buiston Crannog wood and in-house standard are presented in Table 2.5. There was no inorganic material (DIC, shell or sediment) available with a known ^{14}C age/activity, so known age samples were chosen to reflect the ^{14}C content of the sample material. TIRI Barley Mash has a consensus value of 116.35 pMC (Scott *et al.* 1998) and was chosen as the known age material to be analysed along with the high activity material (DIC, biota, shell material). TIRI Buston Crannog wood has a consensus value of 1,605 ± 8 yBP (Scott *et al.* 1998) and the in-house standard wood which has an age of 4,535 ± 60 yBP, were chosen to be run with the low activity (sedimentary) material.

Of the barley mash samples run on Line 1 only BM75 was outwith 2σ error of the consensus value.

It is clear that the TIRI Barley Mash is close to the consensus value and also that the TIRI Buiston Crannog wood results are within 1σ error of the consensus value, indicating that there is no carryover between samples on lines 2 and 3 and giving confidence to the accuracy and precision for sample ^{14}C specific activities presented in this work.

Table 2.5 Results for known age samples prepared in the same manner as the sample material.

QA type	pMC or age yBP ± 1σ	$\delta^{13}C$ (‰ relative to PDB)	line
Barley mash (116.35 ± 0.01 pMC)			
BM72	116.8 ± 0.6	- 27.2	1
BM73	117.5 ± 0.7	-27.0	1
BM75	118.6 ±0.5	- 27.4	1
BM77	116.4 ± 0.6	- 26.9	1
BM82	117.0 ± 0.7	- 27.0	1
BM83	117.2 ± 1.2	- 27.0	1
BM88	116.7 ± 0.8	- 26.8	1
BM90	116.6 ±0.6	-26.7	1
BM91	116.2 ± 0.7	-26.9	2
in house standard 4,535 ± 60 yBP			
W31	4510 ± 60 yBP		2
W32	4490 ± 60		2
Buiston Crannog Wood (1,605 ± 8 y BP)			
BCW21	1550 ± 50		3
BCW24	1550 ± 50		3

2.9.6 Specific Activity Calculations

When calculating a ^{14}C specific activity (Bq kg^{-1} C) a fractionation factor was not applied to the sample count rate. This study was concerned with the activity of the sample and not the environment in which it was formed. For example, the activity of the DIC fraction of seawater has a $\delta^{13}C$ activity of approximately 0 ± 1‰ (relative to PDB) due to preferential uptake of the heavier isotope from the atmosphere however, the ^{14}C activity of the DIC in the vicinity of Sellafield not subject to this mechanism process but on dispersion and dilution of the discharged effluent in the water column. Calculation of the sample specific activities reported in this work derived from LSC counting, were calculated using a spread sheet but the basics of the calculation are detailed below.

For calculation of the sample specific activity the following information must be known

1) Background count rate ± 1σ
2) Modern (oxalic) count rate ± 1σ
3) Quench factor ± 1σ
4) Average sample cpm ± 1σ

The average background count rate of the system is determined using the count rates observed in background samples counted with each batch. Unlike the background calculation the individual modern count rates are corrected for quenching and fractionation and divided by the weight of sample benzene to give net activity in cpm g^{-1}. A weighted mean of these modern count rates gives the average modern count rate ± 1σ. The overall equation for calculation of specific activity (Bq kg^{-1} C) is:

$$\text{Specific activity} = \frac{\text{Q.F x NET COUNT RATE x 226}}{\text{SAMPLE WEIGHT x MODERN COUNT RATE}} \quad \text{eqn 2.12}$$

and involves the following steps:
1). Net sample count rate (NCR) =sample count rate -background count rate
2) Multiply (NCR) by the quench factor
3) Divide by the weight of sample benzene
4) Divide by the average modern count rate
5) Multiply by 100
6) Multiply by 2.26

Results from the AMS facility University of Arizona, were reported as fraction modern [net sample cpm g^{-1} ÷ net modern cpm g^{-1}]. This is converted to Absolute percent modern (pMC) by correcting the modern (oxalic acid) activity for decay from the year of sample collection back to 1950. The isotopic ratio measured by the AMS is the $^{14}C/^{13}C$ ratio, unlike the $^{13}C/^{12}C$ isotopic ratio measures by a MS. Therefore the fractionation factor applied by the University of Arizona must be corrected to relate the ^{14}C to the ^{12}C of the sample to give a fractionation factor which is then removed and the number multiplied by 226 to give the sample specific activity in Bq kg^{-1}C

2.10 Intercomparison of methods for the extraction of CO_2 from the DIC fraction of seawater

During this study the DIC fraction of seawater was converted to both benzene and graphite and then analysed both by LSC and AMS methods respectively. For example, the DIC fraction of seawater from Burtonport in 1997 was converted to benzene and analysed by LSC. However, due to transport logistics the DIC from the west coast of Co. Donegal, Ireland, for 1998 and 1999 were analysed by AMS as a much smaller volume of water was needed. Therefore, it was important to know if the two methods were comparable as the results from the west coast of Ireland were to be used to calculate the ambient ^{14}C background value which would be subtracted from all the other DIC activities in order to calculate the contribution of ^{14}C from Sellafield.

In order to compare these two methods, some of the quarterly samples from Portpatrick and the St. Bees Head site were analysed both by LSC and AMS. In addition, in order to incorporate some quality control for the LSC method, duplicate samples were analysed in November 1997, February 1998, May 1998, August 1998, November 1998 and February 1999 from both Portpatrick and the St. Bees Head site. Results are presented in Table 2.6.
Apart from the sample collected in November 1998 at Portpatrick, the ^{14}C activities (Bq kg^{-1} C) are within error of each other and show reasonably good agreement between both within the LSC program and between the LSC and AMS program. From the sample collected in November 1998 neither the results from the LSC or AMS programs were similar. There is no obvious reason for this dissimilarity, but it is interesting to note that the result from the AMS program is between those from the LSC program.
In the samples collected from the St. Bees Head site the samples collected in November 1997, February 1998, November 1998 and February 1999 were within 2σ error of each other while those collected in May 1998 and August 1998 were not. As with the November 1998 sample at Portpatrick the AMS values were the middle values. There is no obvious reason of why there are different activities for these months. The explanation may perhaps be that, during the summer months when the weather is less stormy, the Sellafield discharge takes longer to be completely mixed with the rest of the water column such that significant differences can be found between 25lcarboys that are collected within a half an hour and a few tens of metres

of each other at the sampling site.

Overall, this exercise shows that there is good agreement between the AMS and LSC programs and the results are directly comparable. The inconsistencies exhibited between activities for samples collected in May and August 1998 warrant further investigation, which was beyond the scope of this project. If it is true that the Sellafield discharge is not mixed in the NE Irish Sea it would cast doubt on any ^{14}C results taken from this area and then applied to a larger area.

Table 2.6 Analysis of the ^{14}C specific activity (Bq kg^{-1} C ± 1σ) in the DIC fraction of seawater at St Bees Head and Portpatrick by LSC and AMS.

Date	LSC 1 (Bq kg^{-1} C)	LSC 2 (Bq kg^{-1} C)	AMS (Bq kg^{-1} C)
St Bees Head			
November 1997	4585 ± 29	4543 ± 16	
February 1998	1368 ± 5	1361 ± 6	
May 1998	1799 ± 7	1937 ± 7	1841 ± 8
August 1998	1138 ± 4	1186 ± 4	1157 ±4
November 1998	491 ± 3	480 ± 3	-
February 1999	452 ± 3	453 ± 3	453 ± 3
Portpatrick			
November 1997	361 ± 3	367 ± 3	-
February 1998	417 ± 3	415 ± 4	-
May 1998	375 ± 3	374 ± 2	376 ± 3
August 1998	381 ± 2	376 ±2	374 ± 2
November 1998	458 ±2	353 ± 2	376 ± 2
February 1999	332 ± 3	337 ± 3	-

2.11 Gamma spectroscopy analysis of Sellafield derived radionuclides in seawater and sediment

Gamma spectroscopy was performed using ether a Canberra or Tennelec HPGE gamma photon detector. The Canberra detector had a relative efficiency of 25 % and resolution of 2.0 keV (FWHM) at 1.33 MeV while the Tennelec detector had a relative efficiency of 30 % and resolution of 1.95 keV (FWHM) at 1.33MeV. Both detectors were housed in graded Pb-Cd-Cu shields to reduce background. Spectra were recorded using an EG&G Ortec ADCAM unit and were analysed using the Ortec software package "GammaVision".

2.11.1 Extraction of dissolved ^{137}Cs from seawater

The dissolved ^{137}Cs was extracted from seawater samples following the method of MacKenzie *et al.* (1979). Acidified seawater (Figure 2.3) was filtered through a 0.2 μm cellulose nitrate filter paper. A column of length 5 cm and area of 1 cm^2 of KCFC (potassium hexacyanacobalt (II) ferrate (II)) ion exchange resin was made up by packing the required volume of conditioned KCFC (100 ^{0}C for 3 hours) into a 10 cm length of Tygon R-3606 plastic tubing. 20 litres of filtered seawater was passed through the KCFC column, which was then removed and dried at 60 ^{0}C. Excess tubing was removed leaving the section of tubing containing the KCFC. To maintain a constant geometry for gamma spectroscopy, a wooden plug was inserted into the top of the KCFC column, taking care not to lose any granules, and the column was sealed by wrapping in cling film. The column was inserted into a specially constructed plastic holder which fitted exactly over the gamma detector and so ensured reproducible placement of the columns on the detector.

A combined extraction and detection efficiency of 2.4 % was determined by passing seawater (from which dissolved ^{137}Cs had previously been removed) containing a known activity of ^{137}Cs through the column. Samples were counted for 24 hours on the Canberra detector.

2.11.2 γ-spectroscopy of sediment samples

In the case of sediments direct gamma spectroscopy analysis was used determination of specific activities of ^{137}Cs and ^{241}Am without any chemical processing.

Depending on the dry weight of the sample available, either 30 or 80 g was used for gamma spectroscopy analysis. Samples, PC85a, PC86b, PC87b, PC87c, PC89c, PC185a and PC186a were analysed using 30g, while 80g were used for the rest of the samples. The 80 g samples were contained in plastic petri dishes with a diameter of 11 cm, while the 30 g samples were contained in 4 cm diameter plastic containers. Detection efficiencies for ^{137}Cs and ^{241}Am were determined using 30 and 80g sediment samples which were compatible in chemical composition and density with the samples being analysed. These samples were spiked with known activities of ^{127}Cs and ^{241}Am and their gamma spectra recorded to allow calculation of the detection efficiencies. From previous work it is known that both the ^{137}Cs and ^{241}Am specific activities are variable with depth in Irish Sea sediments, so samples were counted for an appropriate length of time to obtain 10,000 net counts in the ^{137}Cs and ^{241}Am photopeaks..

Section 2.12 Analysis of sediment for ^{238}Pu and $^{239/240}$Pu

Alpha particles have highly efficient interaction with electrons, resulting in very high specific ionisation (ion pairs per unit path length) and linear energy transfer (energy deposition per unit path length). This means that self absorption (*ie* absorption of alpha particle energy within sources) represents a major problem in alpha spectroscopy analysis and places severe restrictions on source thicknesses. In practice, the thickness of sources for alpha spectroscopy analysis should not exceed 10 mg cm^{-2} so rigorous chemical separation of plutonium from the sediment matrix is required. Moreover, any air between the source and the detector will result in absorption of alpha particle energies, with resultant spectral degradation. Therefore, alpha spectroscopy must be carried out under vacuum.

Section 2.11.1 Extraction of plutonium radionuclides from sediment

The plutonium analytical procedure is labour intensive and the time constraints of this project meant that only a limited number of plutonium analyses could be performed. 10 - 20 g sub-samples of sediment from selected depths of cores PC85, PC86 and PC89 were ashed (500 ^{0}C overnight) and analysed using the method of Wong (1971). Once the sample had cooled it was transferred to a 500 ml beaker where carbonate material was removed using 9M HCl. Once effervescence had stopped 0.073 Bq of ^{242}Pu was added to the sample to act as a yield tracer.

The samples were taken to near dryness on a hotplate after which they were digested with 20 ml of 9M HNO_3. Thereafter, the sample was taken to near dryness then digested with 20 ml of concentrated H_2O_2 before again being taken to near dryness. A further digestion was carried out with a mixture of 50 % (v/v) 12M HCl and 15M HNO_3 (aqua regia) in order to totally dissolve the authigenic components of the sample. The sample was then taken to near dryness after which 20 ml of 9M HCl was added and the sample left overnight to dissolve the plutonium isotopes. The sample was then centrifuged at 3,000 rpm for five minutes after which the solution was decanted and retained. 9M HCl was added to the centrifuge tubes which were shaken to dis-aggregate the sediment and mix it with the acid. The solution was again removed by centrifugation and combined with the first leaching solution. A final leaching of the sediment was carried out using the same procedure, but in this case using distilled water. Once more the solution was combined with the previous leaching solutions. Plutonium was then co-precipitated from the combined acid leaching solution by careful addition of concentrated ammonia solution until production of a persistent dense brown precipitate of ferric hydroxide occurred in the pH range 8.0 to 9.0. The Fe naturally present in the sample was sufficient for this purpose. The precipitate was separated from the solution, which contained many of the matrix elements of the sample by centrifugation. The precipitate was washed twice with distilled water before re-dissolution in 15M HNO_3, after which the solution was taken to dryness on a hotplate. This step was repeated at least three times in order to ensure the oxidation of plutonium from the + 3 oxidation state to the + 4 oxidation state. The sample was then re-dissolved in about 50 ml 9M HCl prior to the ion exchange separation procedure.

A 6 cm x 10 cm anion exchange column was prepared using Bio Rad AG1-X8 anion exchange resin of 100 - 200 mesh. The column was pre-conditioned using 1.2M HCl followed by 9M HCl prior to addition of the sample. In 9M HCl, all plutonium is essentially held on the resin as $(Pu\ Cl_5)^-$ $(Pu\ Cl_6)^{2-}$ (Cleveland 1970a; 1970b, and 1979) along with anionic compounds of iron and uranium, whilst radium, thorium and americium pass through the column with the sample solution. The column was then washed with 50 ml 9M HCl after which the plutonium was eluted using six, 15 ml washes using a 9M HCl plus 1M ammonium iodide solution. This process involves the I^- reducing the plutonium to the + 3 oxidation state which cannot form anionic complexes in hydrochloric acid and is washed from the column. The solution containing the eluted plutonium was evaporated to dryness and the iodine was removed by oxidation by addition of nitric acid and again taking the sample to dryness. This step was repeated until all the I^- was removed after which the sample was re-dissolved in 8M HNO_3. A second anion exchange separation was performed, using a column of Bio-Rad AG1X8 resin of the same dimensions a before, but preconditioned with 8M HNO_3. Under these conditions plutonium was adsorbed onto the resin as an anionic complex with NO_3^-, while the iron and uranium passed through without adsorption. The column was then washed twice with two 20 ml portions of 8M HNO_3 followed by a 9M HCl wash the plutonium was eluted using six, 15 ml washes using a 9M HCl plus 1M ammonium iodide solution. The sample was dried and the I^- removed as before.

The plutonium isotopes were re-dissolved in about 8 drops of 12M HCl before addition of a 40 ml of 3.75% (w/v) NH_4Cl solution, from which the plutonium was electrodeposited onto a 2.5 cm diameter stainless steel disc. Electro-deposition was carried out using an electrolysis cell which consists of a cylindrical perspex body, 6 cm in diameter and 10 cm in depth, together with a brass base. A perspex support holds a platinum wire anode in the centre of the cell, while the stainless steel disc itself acts as the cathode, being firmly fixed in the centre of the base and sealed from the plating solution by use of a Teflon coated rubber o-ring fitted between the planchette and the cell body. The copper base acts as a sink for the heat produced during the plating process and is also fitted with a locating pin for an electrical contact from the electrolysis voltage supply unit (Hallberg *et al.* 1960). Electroplating was carried out for one hour at 3 amps and approximately 10 - 15 volts. The planchette was washed with reverse osmosis water and dried before counting on a EG&G Ortec 576 dual alpha spectrometer.

The detectors used were 450 mm^2 Si surface barrier detectors of resolution (FWHM) 20 keV. The output signal from the amplifier of the 576 spectrometer unit was fed to a 16 input Canberra model 1520, mixer/router and spectra were recorded using the Canberra "system 100" software package. Spectra were analysed manually. Counting times varied from 10 to 24 hours to give suitable counting statistics. Appropriate corrections were applied for detector background when necessary.

Chapter Three

RESULTS AND DISCUSSION

3.1 ^{14}C ambient background activities due to natural production and atmospheric nuclear weapons testing

In order to estimate the contribution of ^{14}C from Sellafield to any marine organism or biogoechemical fraction of seawater or sediment, it is imperative to know the ambient background ^{14}C activity, due to natural production, atmospheric nuclear weapons testing and any other anthropogenic contribution (*eg* use of ^{14}C as a tracer in industrial processes), made to the carbon fractions in question (*eg* DIC, mussel flesh, organic fraction of the sediment, *etc.*).

3.1.1 West coast of Ireland

Ambient background for DIC activities is relatively uniform over the North Atlantic (Broecker *et al.*, 1985). More recently, work by Cook *et al.* (1998) on the background ^{14}C activity of the near-shore marine environment around the British Isles in 1995 showed that the DIC fraction of seawater and biota from the west coast of Co. Donegal, Ireland are not significantly influenced by the liquid radioactive waste discharges from Sellafield and are mainly influenced by North Atlantic waters. As the North Atlantic is the source of water to both the west coast of Ireland and the Irish Sea (*via* the St George's Channel) (Bowden 1950), this site is suitable for the estimation of the ambient ^{14}C background in the UK coastal marine environment and was adopted for this purpose in the present work. Samples were collected annually from this area from 1997 to 1999. The sample types were seawater (for DIC analysis), mussels (*Mytilus edulis*), seaweed (*Fucus* sp), crab (*Cancer pagurus*), roundfish (haddock) and flatfish (plaice). The location, method of sampling and analytical methods are discussed in Chapter 2. The results of the analyses are presented in Table 3.1 and Figure 3.1.

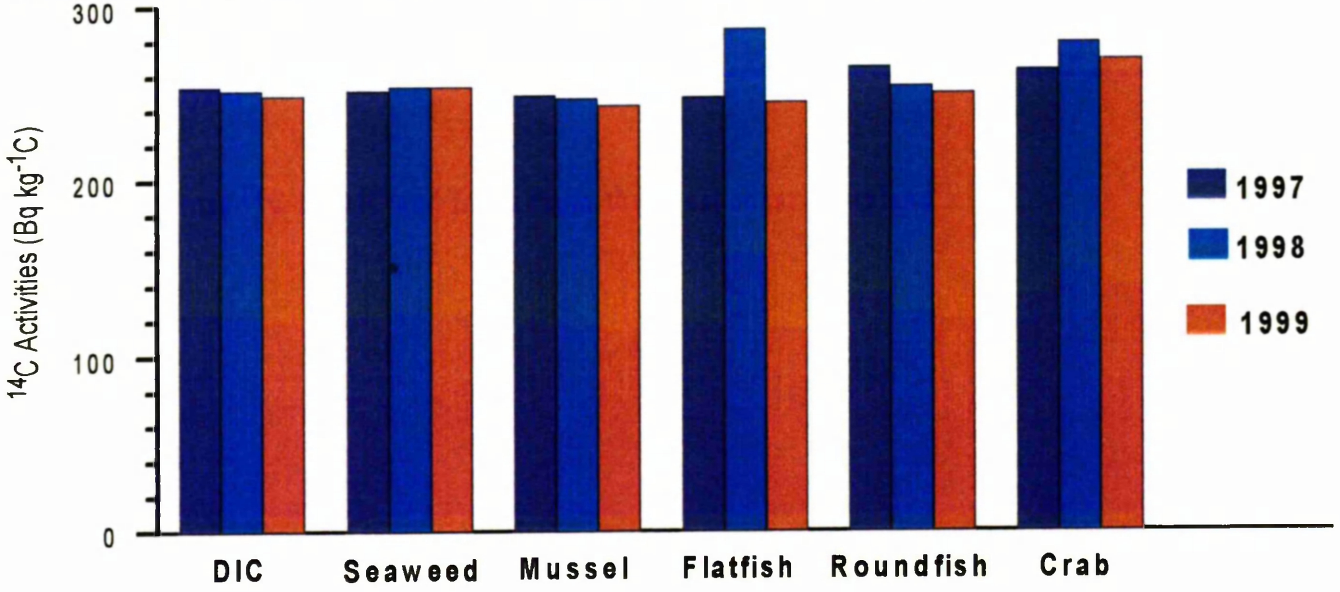
The activities over the entire suite of samples ranged between 244 ± 1 Bq kg^{-1} C in 1999 and 287 ± 3 Bq kg^{-1} C in 1998. The average activity across the different sample types was 256 ± 3 Bq kg^{-1}, with the mean value for each sample type presented in Table 3.1. Within the DIC,

Figure 3.1 Gross ^{14}C activities in DIC and biota from the West Coast of Ireland (Bq kg^{-1} C ± 1σ) 1997 -1999

Year	DIC	Seaweed	Mussel flesh	Mussel valve	Flatfish	Roundfish	Crustacea
1997	254 ± 2	252 ± 1	249 ± 2	NS	248 ± 1	(266 ± 3)	263 ± 1
1998	252 ± 1	254 ± 1	247 ± 1	NS	(287 ± 1)	254 ± 1	279 ± 2
1999	249 ± 2	254 ± 1	243 ± 1	256 ± 1	245 ± 1	250 ± 1	269 ± 1
Weighted mean	252 ± 1	253 ± 1	246 ± 2	-	246 ± 2	252 ± 2	267 ± 5

NS No sample analysed

Figure 3.1 Gross ^{14}C in DIC and Biota from the West coast of Ireland



mussel and seaweed sample types, however, the results are within 2σ error of each other and in the case of the DIC and mussels, the results were also within error of the ^{14}C specific activities reported by Cook *et al.* (1998). A larger data set would be needed to show any long-term variations in the ^{14}C specific activity of any individual carbon fraction.

The specific activity of the mussel shells collected in 1999 is higher than that of the corresponding mussel flesh. The shell is composed of annually deposited layers of calcium carbonate embedded in an organic matrix (Barnes 1987). The calcium carbonate is extracted from the DIC and so reflects its stable isotope signature and ^{14}C activity. The overall activity of the shell is an integrated reflection of the activity of the DIC during the lifetime of the organism(s), while the mussel flesh has a high rate of carbon turnover reflecting the ^{14}C activity of its food source over a period of a few months. While it appears that there is a difference in activity between the mussel shell and flesh during the lifetime of the animals it must be remembered that the calculation of activity did not take into account the differences in δ^{13} values between the mussel shell and flesh (fractionation factor) of approximately - 19 and 0 ‰ (relative to PDB), respectively. Applying the fractionation factor to the mussel and DIC activities presented in Table 3.1 gives activities of 243.0 and 243.2 Bq kg^{-1} C, showing that the difference in un-fractionated activity is due to different metabolic pathways for carbon uptake.

The activity of the crab (*Cancer pagurus)* samples for all three years was higher than that of the other samples (collected in the same year) with the exception of the roundfish sample in 1997 and the flatfish sample in 1998. The crab samples were all obtained from the Burtonport Fishermans Co-operative crab processing plant, which is supplied by local fishermen who fish within approximately 32 km (20 mile) radius of the processing plant. This higher activity is highly unlikely to be due to an enhancement (contamination) of the local ^{14}C activity, as the other samples have, on average, lower ^{14}C activities. The ^{14}C activities (Bq kg^{-1} C) presented here for crab meat agree well with those presented by Cook *et al.* (1998) for crab from the west coast of Co. Donegal, which was higher in activity (at 263 ± 2 Bq kg^{-1} C) than the best estimate of marine background activity of 247 ± 1.0 Bq kg^{-1} C, calculated by the authors for 1995.

Unlike the DIC, mussel and seaweed samples, the ^{14}C activities for the flatfish (plaice) and roundfish (haddock) samples from 1997 to 1999 are not within error of each other. The boats that were collecting these samples were fishing within approximately 81 km (50 miles) of the west coast of Donegal. These differences in activity could be due to a number of factors including 1) fishing different stocks with different ranges, 2) non representative sampling (2 fish per species) of the fish population and 3) possible inclusion of fish caught at a greater distance than 81 km (50 miles).

From this study there is evidence that different species have different ^{14}C activities, (*eg* the crab activities in comparison with the mussel/seaweed samples). Interannual variations in ^{14}C activity were also observed within some species/animal type (*eg* flatfish and roundfish). On the basis of the observed differing activities for different species collected at the same location it was decided that it was more appropriate to assign each individual species and carbon fraction (*eg* DIC) an ambient background value rather than take an average value for all sample types.

The DIC and sedentary organisms (mussels and seaweed) all give similar inter-species results and exhibit consistent results between different years, it can therefore be concluded that these values are representative of the marine background. The non-sedentary species *ie*, the flatfish, roundfish and crab did not give similar interspecies results, or in the case of the roundfish and flatfish, consistent interannual results. In this study, a weighted mean of the three years was used in determining the background figure for DIC, mussels, seaweed and crab sample types. From Table 3.1 it can be seen that for flatfish and roundfish, some of the activities are similar to the activity for marine background deduced from the DIC and sedentary organisms, while some are significantly above this value. In order to calculate a background activity for flatfish and roundfish, the higher activities (266 ± 3 and 287 ± 1 Bq $kg^{-1}C$, respectively) were excluded and a weighted mean value calculated from the remaining two figures as the background activity for these sample types. The background for the crab sample type was calculated as a weighted mean from results for each of the three years of sampling.

3.1.2 DOC, PIC and POC

While the background DIC activity is relatively uniform over the North Atlantic (Broecker *et al.*, 1985), the ambient background values for the other three biogeochemical fractions of seawater are more difficult to estimate as they are more dependent on local variables such as contributions from terrestrial run-off, sediment re-suspension, the levels of primary and secondary production, *etc*. Therefore, ^{14}C activities for the PIC, POC and DOC fractions in Atlantic waters are not necessarily applicable to the Irish Sea. It was concluded that the best available estimates for Irish Sea PIC, POC and DOC ^{14}C backgrounds were from those samples collected in 1989 at the St. George's Channel and the North Channel and reported by Begg

(1992). These values used for PIC, POC and DOC background activities were 144 ± 10, 125 ± 6 and 176 ± 4 Bq kg^{-1} C, respectively. Some Sellafield ^{14}C activity would have been incorporated into these samples but, for the purposes of the present study, this was estimated to be negligible as Sellafield ^{14}C discharges at that time were much lower than current discharges. In addition, these samples were collected some distance from Sellafield and the DIC values at these locations were close to the background activity at this time. For this reason the calculated excess ^{14}C values contributed by Sellafield will be minimal for the DOC, PIC and POC fractions.

3.1.3 Inorganic and organic sediment fractions

Sellafield derived ^{14}C has been incorporated into both the inorganic and organic fractions of the sediment of the NE Irish Sea (Cook *et al.* 1995; Wolstenholme 1999) since discharges began in 1952. However, sediment collected from the NE Irish Sea prior to 1952 could not be obtained for analysis, therefore, it is not possible to determine exactly the ^{14}C activity or age of the sediments prior to the commencement of Sellafield discharges (Section 1.6.7). Accumulating sediments provide an archive of past environmental conditions and could potentially be used to derive an estimate of the pre-Sellafield ^{14}C activity of the sediment. However, Irish Sea sediments are subject to intensive mixing and are inherently unsuitable for this purpose. Accumulating saltmarsh sediments have been shown to provide a record of the time integrated Sellafield discharges as a consequence of onshore transport of sediment from the well mixed off-shore deposits (Stanners and Aston 1981; Aston and Stanners 1982; Hamilton and Clarke 1984; Mackenzie *et al.* 1987; Mackenzie and Scott 1993). On this basis, a saltmarsh core from the Solway Firth, analysed by Wolstenholme (1999), was used to estimate the pre-Sellafield background. There is some ambiguity about this estimate of the pre- Sellafield activity so, following the procedure of Wolstenholme *et al.* (1999), two alternative estimates were used for the ambient background of the sediment.

In the saltmarsh core, the ^{14}C activity of the inorganic carbon fraction increased from infinite age (^{14}C activity is below detection limit) with respect to ^{14}C in sections that did not contain detectable levels of ^{241}Am to 16,110 ± 320 y BP in upper sections of the core that were contaminated with Sellafield derived ^{241}Am. This core indicates that the pre-Sellafield age of NE Irish Sea sediments could be of infinite age. The approach taken by Wolstenholme *et al.* (1999) assumed two possible ambient background ages. The first assumed that the sediments were of infinite age prior to ^{14}C discharges from Sellafield *ie.* 0 Bq kg^{-1}C (and therefore likely to underestimate the pre-Sellafield activity of the sediment), while the second assumed that the background is represented by the inorganic ^{14}C activities in the low intensity mixing zones of each core. This approach gives average values of 45 Bq kg^{-1}C for the inorganic carbon fraction and 131 Bq kg^{-1}C for the organic fraction using the data from the low intensity mixing zones from cores collected and analysed during this study.

The background for the organic fraction of the sediments of 131 Bq kg^{-1}C is the same as hte value of 131 Bq kg^{-1}C calculated by Dr. G. Cook (Pers Comm) by assuming constant production of ^{14}C in the upper atmosphere and transfer to the surface oceans, constant primary production and deposition of organic material in the sediments during the Holocene, allowing for decay of ^{14}C during this time. The alternative approach of deriving the background from deeper sections of saltmarsh sediments (Wolstenholme 1999) suggests that the pre-Sellafield activity o or the organic carbon fraction of the sediments is approximately 98 Bq kg^{-1}C (56 - 60 cm).

3.2 ^{14}C and ^{137}Cs activities in seawater and removal through the North Channel.

Analyses of dissolved ^{137}Cs and ^{14}C activities in the DIC of seawater from the NE Irish Sea and the North Channel were carried out on a monthly basis for two sites, Nethertown and Portpatrick, respectively. Results are presented in Table 3.2 and 3.6, respectively, as dissolved ^{137}Cs activities (mBq l^{-1}), gross (measured) ^{14}C activities (Bq kg^{-1} C) and net ^{14}C enhancements (Bq kg^{-1} C) above the estimated ambient background for DIC of 252 ± 3 Bq kg^{-1} C. Analysis of the biogeochemical carbon fractions was carried out on samples collected on a quarterly basis at St. Bees Head (DIC, PIC and POC) and Portpatrick (DIC, DOC, PIC and POC). Results for the gross ^{14}C activities (Bq kg^{-1} C) and ^{14}C activities (Bq kg^{-1} C) above the calculated ambient backgrounds for St. Bees Head and Portpatrick are presented in Table 3.3 and 3.7 respectively.

3.2.1 ^{14}C activity in the DIC and dissolved ^{137}Cs in seawater from Nethertown

DIC

The net ^{14}C activities in the DIC during the period of research ranged between 344 ± 4 and 8,057 ± 25 Bq kg^{-1} C (Table 3.2). Graphing the net ^{14}C activities and the monthly ^{14}C discharge data from Sellafield (Figure 3.2), shows that there is little similarity between the trends in the monthly activities in the DIC at Nethertown and the monthly ^{14}C discharge trends. From Figure 3.2 it can be seen that the highest net ^{14}C activities in the DIC occurred in March and June 1998 (8,057 ± 25 and 5,807 ± 27 Bq kg^{-1} C respectively). The corresponding discharges for those months were low (540 and 242 GBq respectively) in comparison with the peak discharge activity in November 1997 (1750 GBq), four months prior to the peak in net ^{14}C activities.

Figure 3.2 Monthly ^{14}C discharges from Sellafield and net ^{14}C activities in the DIC fraction of seawater at Nethertown

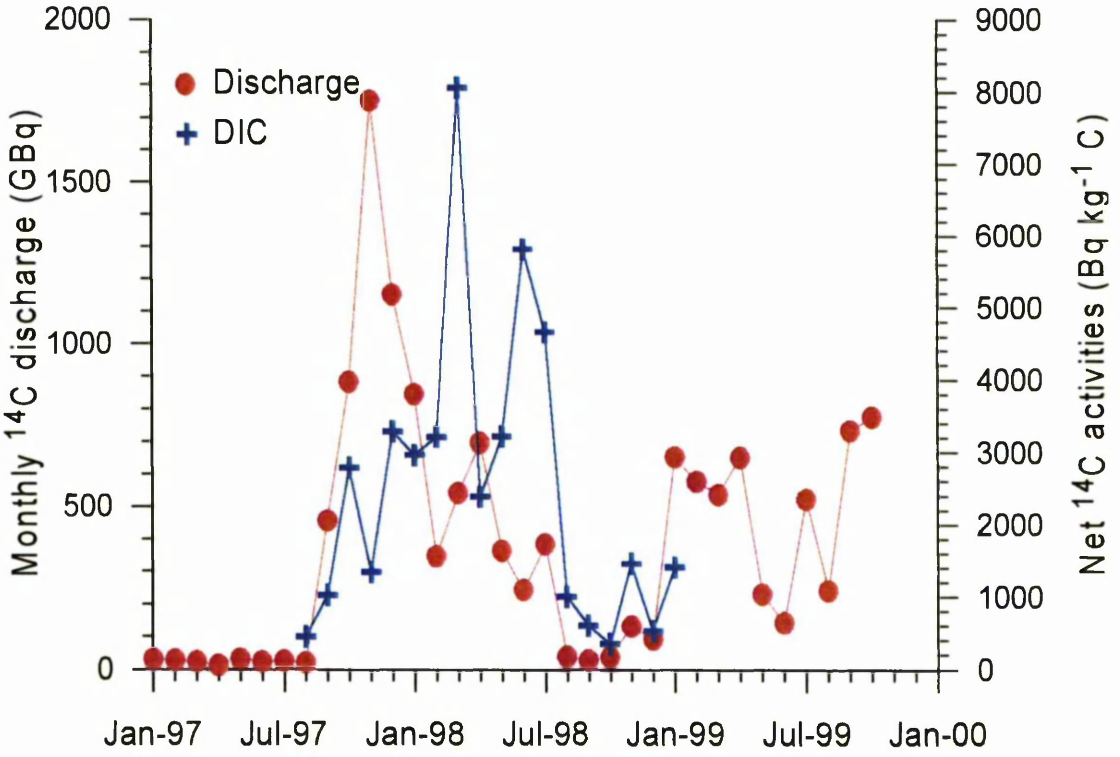


Table 3.2 Dissolved ^{137}Cs activities (mBq l^{-1} ± 1σ), gross ^{14}C activities (Bq kg^{-1} C ± 1σ) in the DIC fraction, net ^{14}C activities (Bq kg^{-1} C ± 1σ) (*ie.* above ambient background of 252 ± 3 Bq kg^{-1} C ± 1σ) and δ^{13}C ‰ (relative to PDB) values in the DIC fraction for seawater samples collected at Nethertown (Latitude 54^0 27'.3' N Longitude 03^0 33.3' W).

Collection Date	Dissolved ^{137}Cs (mBq l^{-1} ± 1σ)	Gross DIC ^{14}C (Bq kg^{-1} C ± 1σ)	Net DIC ^{14}C (Bq kg^{-1} C ± 1σ)	δ^{13}C ‰ (relative to PDB)
Aug. '97	426 ± 1	692 ± 4	440 ± 5	+ 0.5
Sept. '97	467 ± 2	1264 ± 6	1012 ± 7	- 0.3
Oct. '97	287 ± 1	3031 ± 9	2779 ± 9	+ 0.2
Nov. '97	300 ± 1	1587 ± 7	1335 ± 7	- 0.0
Dec. '97	326 ± 1	3535 ± 9	3283 ± 9	+ 0.2
Jan. '98	207 ± 2	3208 ± 9	2956 ± 10	+ 0.1
Feb. '98	224 ± 1	3460 ± 15	3208 ± 15	+ 0.2
Mar. '98	761 ±1	8309±25	8057 ± 25	N/A
Apr. '98	272 ± 1	2631 ± 9	2379 ± 9	+ 0.3
May '98	139 ±2	3464 ± 11	3212±11	- 0.5
June '98	240 ± 1	6059 ±27	5807 ± 27	+ 0.5
July '98	221 ± 1	4908 ± 15	4656 ± 15	+ 0.3
Aug. '98	256 ± 3	1250 ± 5	998 ± 5	+ 0.3
Sept. '98	165 ±2	850 ± 4	598 ± 5	+ 0.4
Oct. '98	172 ± 1	596 ± 3	344 ± 4	- 0.5
Nov. '98	209 ± 2	1705 ± 6	1453 ± 7	+ 0.2
Dec. '98	245 ± 3	772 ± 3	520 ± 4	- 0.7
Jan. '99	214 ± 2	1652 ± 7	1400 ± 7	- 0.4

There was also a peak in discharges in April 1998 (although smaller than the November 1997 peak in discharges) three months prior to the peak in net ^{14}C activities in July 1998. This pattern could indicate either (a) a three - four month lag time in discharges and arrival of ^{14}C at Nethertown or (b) the distribution of ^{14}C is highly heterogeneous immediately after discharges and the measured activities represent packets of very recently contaminated seawater. Nethertown is only a few miles from the point of discharge and taking into account the well established fact that the predominant flow of water in the Irish Sea is northwards, the most likely interpretation of the data is that there is a (spatial and temporal) heterogeneous distribution of waste in the vicinity of the pipeline and the Nethertown site. The results from Nethertown indicate that this site is unsuitable for assessing the overall activity of the DIC in the NE Irish Sea as water from this location is not well mixed with respect to the Sellafield discharge.

$\delta^{13}C$ values (‰ relative to PDB) for the DIC fraction of the water column at Nethertown are presented in Table 3.2 and range between - 0.7 and + 0.5 ‰. These values are within the range for marine DIC (- 1.0 to + 1.0 ‰ relative to PDB) and suggest that there was no significant terrestrial influence on the DIC fraction of seawater during the sampling period.

Dissolved ^{137}Cs

The dissolved ^{137}Cs activities in seawater at Nethertown ranged from 139 ± 2 to 761 ±1 mBq l^{-1} between August 1997 and February 1999 (Table 3.2). From Figure 3.3 it can be seen that there is little similarity between the measured activities of dissolved ^{137}Cs at Nethertown and the monthly discharges of ^{137}Cs from Sellafield. As with the DIC, peaks in the measured dissolved ^{137}Cs activities do not match peaks in the ^{137}Cs discharge activities, supporting the conclusion that seawater at Nethertown is not well mixed with respect to the Sellafield discharges. From Figure 3.4(A) it can be seen that there are some similarities between trends in the dissolved ^{137}Cs activities and the net ^{14}C activities of the DIC in seawater. Both have peak activities in March 1998 and smaller peaks in June/July 1998 (although this is more pronounced for the DIC). Figure 3.4(B) also shows similarities between the ^{14}C and ^{137}Cs discharge activities, with a peak in discharge in activity for both radionuclides occurring in November 1998. The ^{14}C discharge peak in November 1998 is much larger relative to other ^{14}C discharges than the ^{137}Cs discharge peak to other ^{137}Cs discharges during the study. This is not reflected in the peak in net ^{14}C and ^{137}Cs activities in seawater for November 1998 as both show the similar relative increases in activity relative to those of the previous months.

Figure 3.3 Monthly ^{137}Cs discharges from Sellafield and dissolved ^{137}Cs activities in seawater at Nethertown

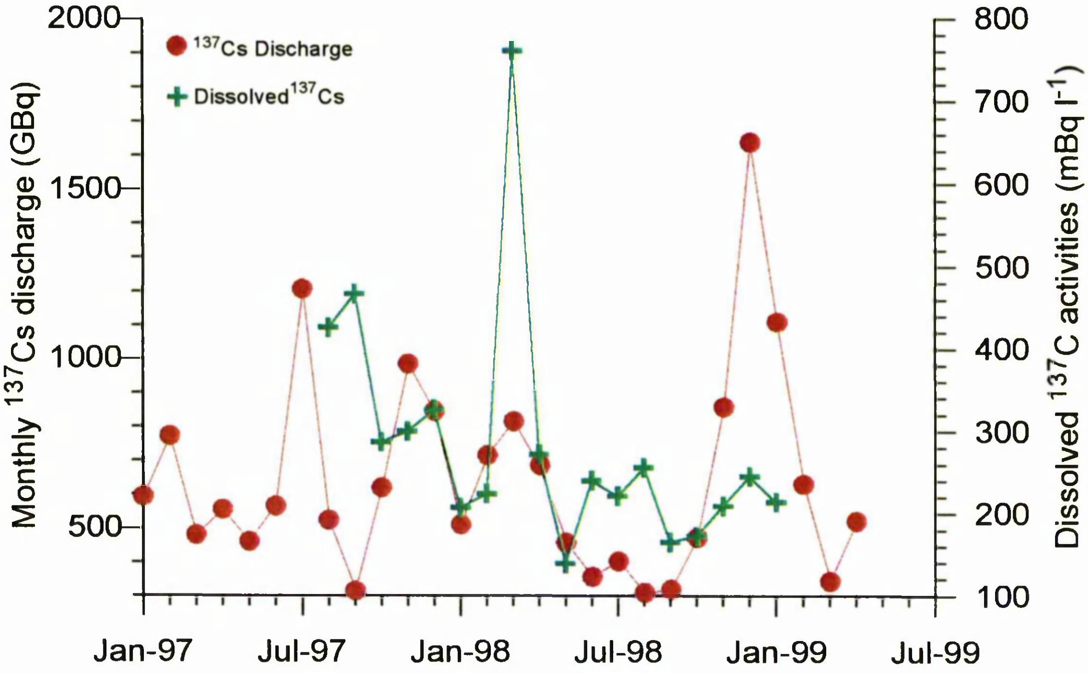
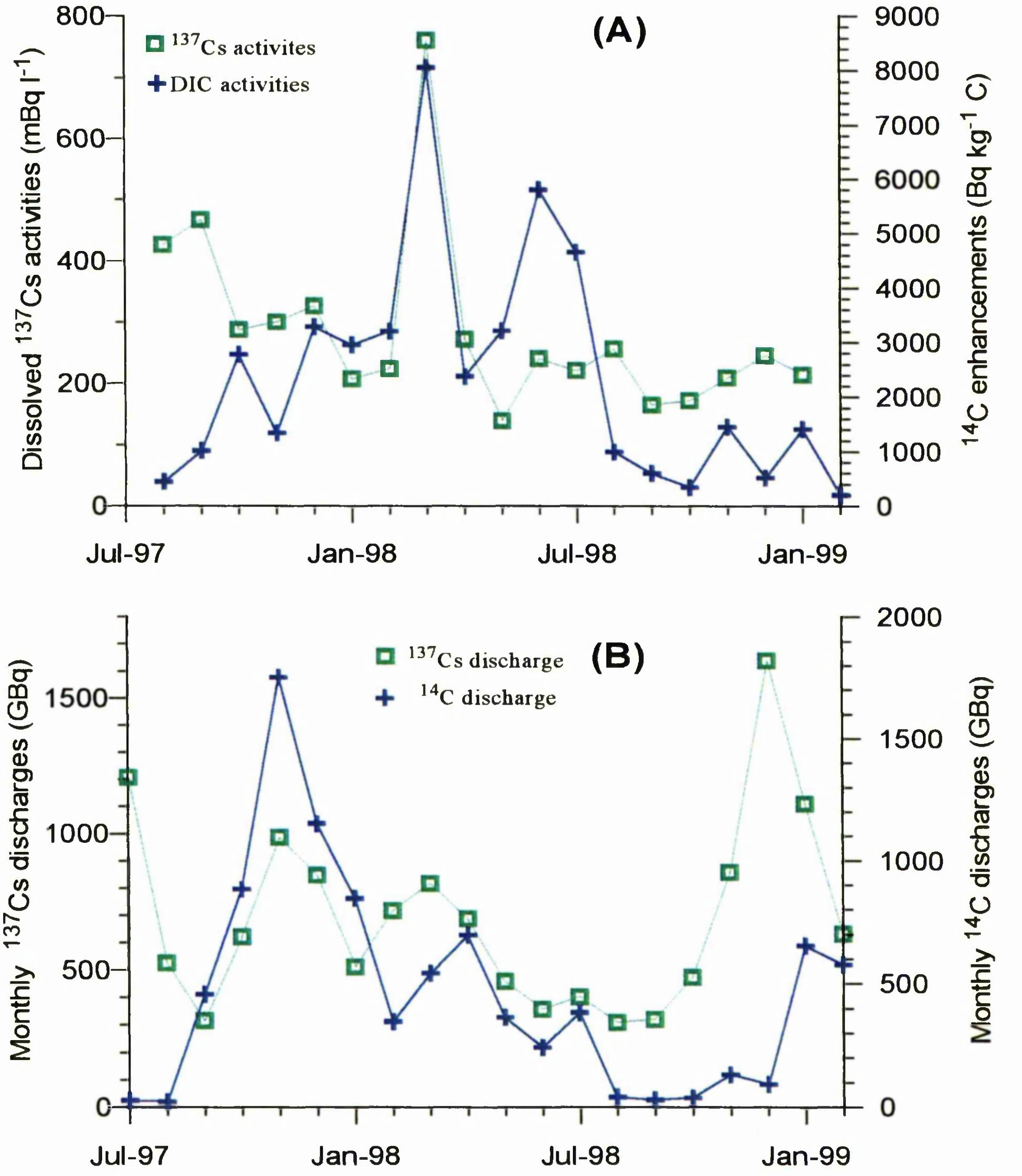


Figure 3.4 (A) Monthly dissolved ^{137}Cs activities and ^{14}C enhancements above ambient background in the DIC fraction in seawater at Nethertown and (B) monthly ^{137}Cs and ^{14}C discharges from Sellafield.



3.2.2 ^{14}C activity in the DIC, PIC and POC fractions of seawater at St. Bees Head

Biogeochemical fractions

The ^{14}C activities of the DIC, PIC and POC are presented in Table 3.3 as gross (measured) ^{14}C activities and net ^{14}C activities above the estimated ambient background value for each biogeochemical fraction (Section 3.1). The values for the DIC activities are an average of the duplicate samples measured for each month (Section 2.12). The net activities ranged between 201 ± 2 and 4,301 ± 18 Bq kg^{-1} C ± 1σ for the DIC, 72 ± 10 and 860 ± 11 Bq kg^{-1} C ± 1σ for the PIC and 171 ± 6 and 3,741 ± 13 Bq kg^{-1} C ± 1σ for the POC. The DIC and POC fractions appear to be close to equilibrium and temporal variations in both show a strong qualitative resemblance to those of the monthly discharges, although this may be an artifact of the sampling time-scale and better temporal resolution (*eg* on a monthly basis) may not show such close resemblance to the monthly discharges (Figure 3.5).

In each case, the activity of the DIC is higher than the activity of the other two carbon fractions. Normalising the gross activities of the PIC and POC by dividing by the gross activity of the DIC for the same month, provides an indication of the transfer of ^{14}C from the DIC to other carbon fractions. The gross activities were used to allow comparison with the results of Cook *et al.* (1995) and Wolstenholme (1999) who did not correct the activity of the carbon fractions for the ambient background activity during the year of sampling. Normalised activities from this work and the work of Cook *et al.* (1995) (samples collected at the Sellafield site) and Wolstenholme (1999) are presented in Table 3.4. The work of Wolstenholme (1999) specifies that samples were collected within a "zone" but does not specify whether or not the same site within each zone was sampled repeatedly or whether the samples were collected at random locations within the zone. Both zones are therefore presented here as there is no indication as to which zone is closest to St Bees Head, the site investigated during this study. As the sites of collection are not the same for all three studies, only the broadest comparisons can be made between them.

With the exception of March 1995 (Wolstenholme 1999) which is an anomalous result as the DIC was transiently extremely enhanced, the normalised values for the PIC ranged between 0.1 and 0.6 for all three studies. In general, the normalised values are lower for the studies of Cook *et al.* (1995) and Wolstenholme (1999) and only show values which are above consistently 0.3 (within the same sample set) between May 1998 and February 1999. Due to the limited nature

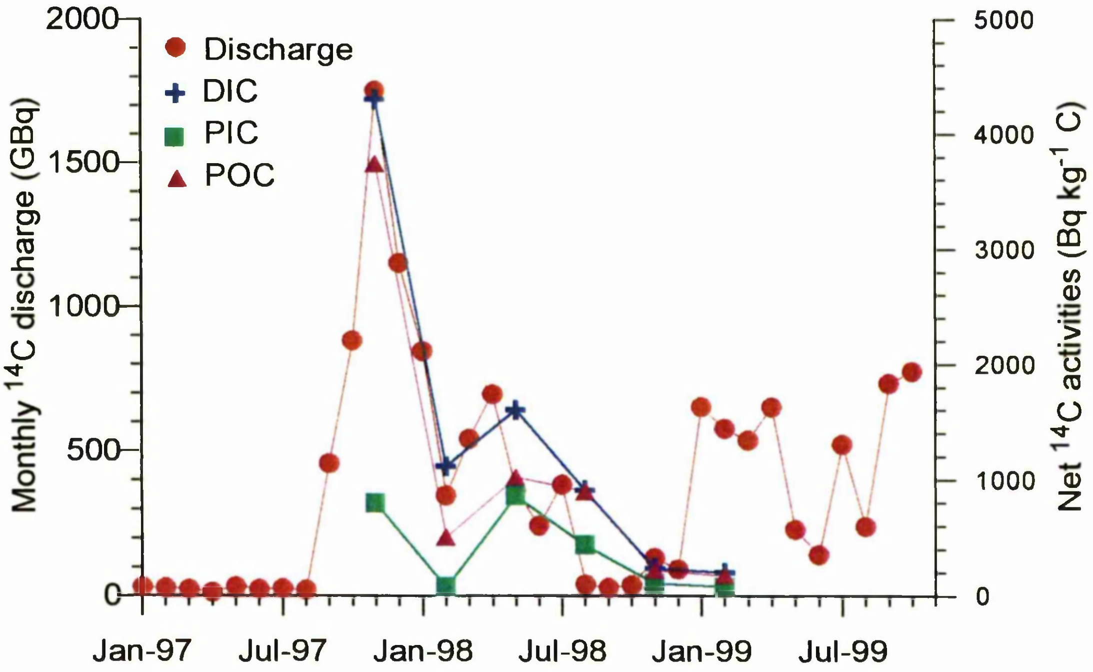
Table 3.3 Gross ^{14}C activities (Bq kg^{-1} C ± 1σ) and net ^{14}C activities (*ie.* above ambient background) in the DIC, DOC, PIC and POC fractions of seawater (all Bq kg^{-1} C ± 1σ) collected on a quarterly basis at St Bees Head (Latitude 54^0 27" N Longitude 03^0 33' W). Background activities are 252 ± 3, 176 ± 4, 144 ± 10, 125 ± 6 and 253 ± 2 Bq kg^{-1} C ± 1σ, respectively.

Date	Gross DIC	Net DIC	Gross PIC	Net PIC	Gross POC	Net POC
Nov. 97	4553 ± 18	4301 ± 18	913 ± 4	796 ± 11	3616 ± 12	3741 ± 13
Feb. 98	1365 ± 4	1113 ± 4	216 ± 1	72 ± 10	631 ± 3	506 ± 7
May 98	1853 ± 43	1601 ± 43	1004 ± 4	860 ± 11	1146 ± 4	1021± 7
Aug.98	1160 ± 14	908 ± 14	579 ± 3	579 ± 10	1024 ± 4	899 ± 7
Nov. 98	486 ± 5	234 ± 5	247 ± 4	103± 11	343 ± 2	218 ± 6
Feb 99	453 ± 2	201 ± 2	219 ± 2	75 ± 10	296 ± 1	171 ± 6

of the sample set between May 1998 and February 1999 it is difficult to see any reason for the normalised value for the PIC to change, but it is possibly due to either oxidation of small amount of organic matter by the 4M HCl used during the PIC hydrolysis procedure or to a change in the equilibrium of the system.

For the POC the normalised values range between 0.03 and 1. The value of 0.03 is due to the very high activity of the DIC in March 1995 reported by Wolstenholme (1999) and is anomalous. The data seem to exhibit a trend of lower values during winter months, when rates of primary production are also lower.

Figure 3.5 Monthly ^{14}C discharges from Sellafield and quarterly net DIC, PIC and POC activities above ambient background in seawater at St Bees Head.



The average normalised values for the POC during this study are slightly higher than the average values of the previous studies, but reasons for this are difficult to explain from the data and could simply be a function of sample site.

Table 3.4 Normalised results for the biogeochemical fractions of the water column at St. Bees Head from this study and from Cook *et al.* (1995) and Wolstenholme (1999).

Date of Collection	DIC	PIC	POC
Cook *et al.* (1995) samples collected at the Sellafield site			
December 1989	1	0.2	0.3
February 1991	1	0.3	0.4
June 1993	1	0.4	1
Wolstenholme (1999) Sellafield site			
February 1995	1	0.6	0.3
July 1995	1	0.3	0.4
November 1995	1	0.1	0.3
March 1996	1	0.2	0.5
June 1996	1	0.1	0.5
November 1996	1	0.1	0.4
Wolstenholme (1999) Sellafield North site			
March 1995	1	0.01	0.03
July 1995	1	N/A	0.5
November 1995	1	0.1	0.4
March 1996	1	0.2	0.5
June 1996	1	0.2	0.9
November 1996	1	0.2	0.5
This study. St Bees Head site			
November 1997	1	0.2	0.8
February 1998	1	0.2	0.5
May 1998	1	0.5	0.6
August 1998	1	0.5	0.9
November 1998	1	0.5	0.7
February 1999	1	0.5	0.7

The $\delta^{13}C$ values (‰ relative to PDB) are presented in Table 3.5. The $\delta^{13}C$ values for the DIC range between - 0.1 and + 0.8‰. These values are within the range for marine DIC (- 1.0 to + 1.0 ‰ relative to PDB) and suggest that there is no significant terrestrial influence on the DIC fraction of seawater during the sampling period. The $\delta^{13}C$ values for the PIC range between - 8.2 and + 0.7 ‰ (relative to PDB). These values fall outside the range of - 1.0 and + 1.0 ‰ for marine inorganic carbon, indicating that either there is a secondary source of PIC to the system either through river runoff or sediment resuspension (sediment resuspension can be ruled out as previous studies (and this study Section 3.4) have shown that the inorganic fraction of sediments in the NE Irish Sea is of marine origin) (Kershaw 1986; Kershaw *et al.* 1988; Begg 1992; Wolstenholme 1999) or that carbon with a more negative $\delta^{13}C$ value was added during the analysis (*eg*. oxidation of some organic material during the hydrolysis reaction or a leak in the system during the hydrolysis which would add atmospheric CO_2).

The $\delta^{13}C$ values for POC range between - 19.1 and - 23.5. Organic mater produced in the marine environment, typically has a $\delta^{13}C$ value of between - 18.0 and - 22.0 ‰ while that of terrestrially produced organic matter is between - 24.0 and - 32.0 ‰. The $\delta^{13}C$ values in this study indicate that at times the main source of organic material to the POC is marine produced, while at other times there is some terrestrial influence on the POC fraction.

Table 3.5 $\delta^{13}C$ values (‰ relative to PDB) for the biogeochemical fractions of the water column at St Bees Head from this study.

Date of Collection	DIC	PIC	POC
November 1997	+ 0.4	- 3.7	- 22.0
February 1998	+ 0.8	0.0	- 23.1
May 1998	+ 0.0	- 6.6	- 19.4
August 1998	+ 0.7	- 8.2	- 19.1
November 1998	+ 0.4	- 3.4	- 23.1
February 1999	- 0.1	+ 0.7	- 23.5

3.2.3 ^{14}C activity in the DIC, dissolved ^{137}Cs and ^{14}C activity in the biogeochemical fractions of seawater at Portpatrick.

DIC

The net ^{14}C activities of the DIC fraction of seawater at Portpatrick were lower than those at Nethertown and St. Bees Head, ranging between 67 ± 4 and 271 ± 4 Bq kg^{-1} C from August 1997 to July 1999 (Table 3.6). To compare the results with other authors, gross activities must be used as previous studies have all reported ^{14}C activity of the DIC as gross ^{14}C activities. The Portpatrick DIC gross ^{14}C activities were higher than those reported by Begg *et al.* (1991), but similar to those found by Cook *et al.* (1998), reflecting the fact that Begg *et al.* (1991) analysed samples collected prior to the increase in ^{14}C discharges from Sellafield, while those analysed by Cook *et al.* (1998) were collected after the increase.

Plotting the net ^{14}C activities in DIC at Portpatrick and the monthly ^{14}C discharges from Sellafield (Figure 3.6), reveals a qualitative resemblance between temporal variations in the two data sets. The ^{14}C discharges from Sellafield were consistently less than 100 GBq per month until September 1997, after which there was a sharp peak at 1,750 GBq in November 1997. Similarly, the net ^{14}C activities of the DIC at Portpatrick exhibited small variations between 111 ± 4 and 120 ± 4 Bq kg^{-1} C between August and November 1997, after which they increased rapidly to a sharp peak (271 ± 5 Bq kg^{-1} C) in January 1998. Assuming these variations in the two sets of data are related, gives an apparent transit time of two months between the peak discharges of ^{14}C from Sellafield and the appearance of a peak in net ^{14}C activity in the DIC at Portpatrick. Subsequent peaks in the ^{14}C discharges from Sellafield in April 1998, July 1998 and February-April 1999 were all less than half the activity of the November 1997 peak discharge and, correspondingly, temporal variations in the activity of the DIC at Portpatrick were smaller over this time period. Nevertheless, some similarities between discharge trends and DIC ^{14}C activity trends are apparent. For example, between August and December 1998 the ^{14}C discharge activities were less than 140 GBq per month and this period of low discharges appears to be reflected in the low DIC activities at Portpatrick between February and April 1998, which ranged between 81 ± 4 and 83 ± 4 Bq kg^{-1} C. These values are comparable to the low activities of the DIC between August and December 1997 (111 to 120 Bq kg^{-1}C) which also followed a long period of low discharges.

Table 3.6 Dissolved ^{137}Cs activities (mBq l^{-1} ±1σ), gross ^{14}C activities in the DIC fraction (Bq kg^{-1} C ± 1σ), net ^{14}C activities (Bq kg^{-1} C ± 1σ) (*ie.* above ambient background of 252 ± 3 Bq kg^{-1} C) and δ^{13}C ‰ (relative to PDB) values in the DIC fraction for seawater samples collected at Portpatrick (Latitude 54^{0} 51' N, Longitude 05^{0} 07' W).

Collection Date	Dissolved ^{137}Cs (mBq l^{-1} ±1σ)	Gross DIC ^{14}C (Bq kg^{-1} C ± 1σ)	Net DIC ^{14}C (Bq kg^{-1} C ± 1σ)	δ^{13}C ‰ (relative to PDB)
Aug. '97	48 ± 1	372 ± 3	120 ± 4	+ 0.8
Sept. '97	44 ± 2	369 ± 3	117 ± 4	+ 0.4
Oct. '97	46 ± 2	368 ± 3	116 ± 4	+ 0.5
Nov. '97	44 ± 2	363 ± 2	111 ± 4	+ 0.7
Dec. '97	53 ± 2	423 ± 3	171 ± 4	+ 0.8
Jan. '98	50 ± 2	523 ± 3	271 ± 5	+ 0.9
Feb. '98	37 ± 2	416 ± 2	164± 4	+ 0.6
Mar. '98	36 ± 2	402 ± 2	150 ± 4	+ 1.1
Apr. '98	28 ± 2	361 ± 2	109 ± 4	N/A
May '98	29 ± 3	375 ± 1	123 ± 4	- 0.1
June '98	27 ± 2	382 ± 5	130± 6	+ 1.3
July '98	30 ± 2	388 ± 4	136 ± 5	+ 2.0
Aug. '98	33 ± 1	378 ± 3	126± 4	+ 1.1
Sept. '98	39 ± 1	374 ± 2	122 ± 4	+ 0.6
Oct. '98	31 ± 1	353 ± 5	101± 6	+ 0.7
Nov. '98	34 ± 1	376 ± 2	124 ± 4	+ 0.4
Dec. '98	51 ± 1	388 ± 2	136 ± 4	+ 0.6
Jan. '99	47 ± 1	367 ± 3	115 ± 4	+ 0.5
Feb. '99	36 ± 2	335 ± 3	83 ±4	+ 0.4
Mar. '99	33 ± 1	338 ± 3	86 ± 4	+ 1.5
Apr. '99	22 ± 1	333 ± 3	81 ± 4	+ 0.6
May '99	20 ± 2	416 ± 4	164 ± 5	N/A
June '99	21 ± 1	319 ± 3	67 ± 4	+ 1.7
July '99	29 ± 1	373 ± 5	121 ± 6	+ 1.9

Figure 3.6 Monthly ^{14}C discharges from Sellafield and net ^{14}C activities in the DIC fraction of seawater at Portpatrick

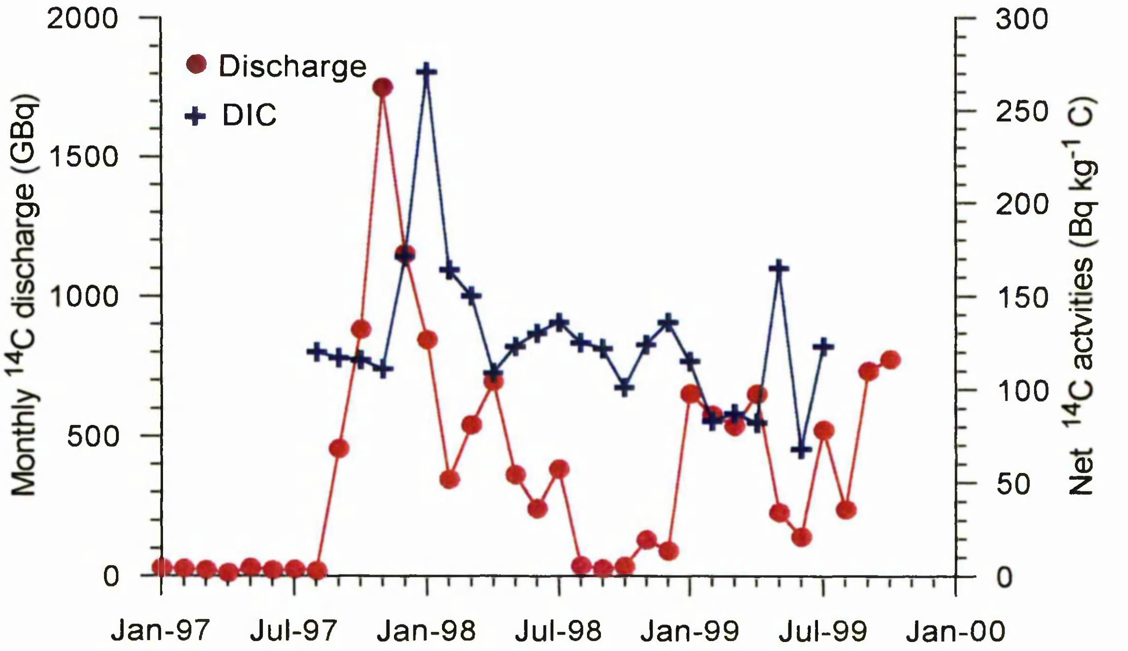


Figure 3.7 shows the plot of monthly ^{14}C discharges along with Portpatrick DIC ^{14}C activity with assumed transit times from Sellafield to the North Channel of 1, 2 and 3 months. From this, it is apparent that for the first nine months of the study (August 1997 to April 1998 inclusive) a two month transit time best matches variations in the net activity of the DIC at Portpatrick to variations in the discharged activity (June 1997 to February 1998 inclusive). From May 1998 onwards however, a two month transit time does not give a good match between the DIC ^{14}C data and the discharge pattern, suggesting that the transit time from Sellafield to the North Channel was not constant during the course of this study. This observation is consistent with the variable nature of the current regimes in the Irish Sea and North Channel (Jefferies *et al.* 1973, 1982; Brown and Gmitrowicz 1995; Knight and Howarth 1999).

With the assumption of variable transit times, the pattern of peaks and troughs in activity of the DIC was matched by eye to those in the discharges shown in Figure 3.8a, giving a relatively good match between the two sets of data. The implied transit times derived from this approach vary between two and five months as shown in Figure 3.10b. It is difficult to know if there any variations in the transit time from January 1997 to August 1997 as the variations in the transit times from Jan. 1997 to Aug. 1997 as the variations in discharge activities and net activities in the DIC at Portpatrick are small. Overall, using this method gives shorter transit times during the winter months (2-3 months) and longer transit times during the summer months (approximately 5 months) suggesting seasonal variations.

Figure 3.7 Net ^{14}C activities in the DIC assuming (a) one month transit time, (b) two months transit time and (c) three months transit time.

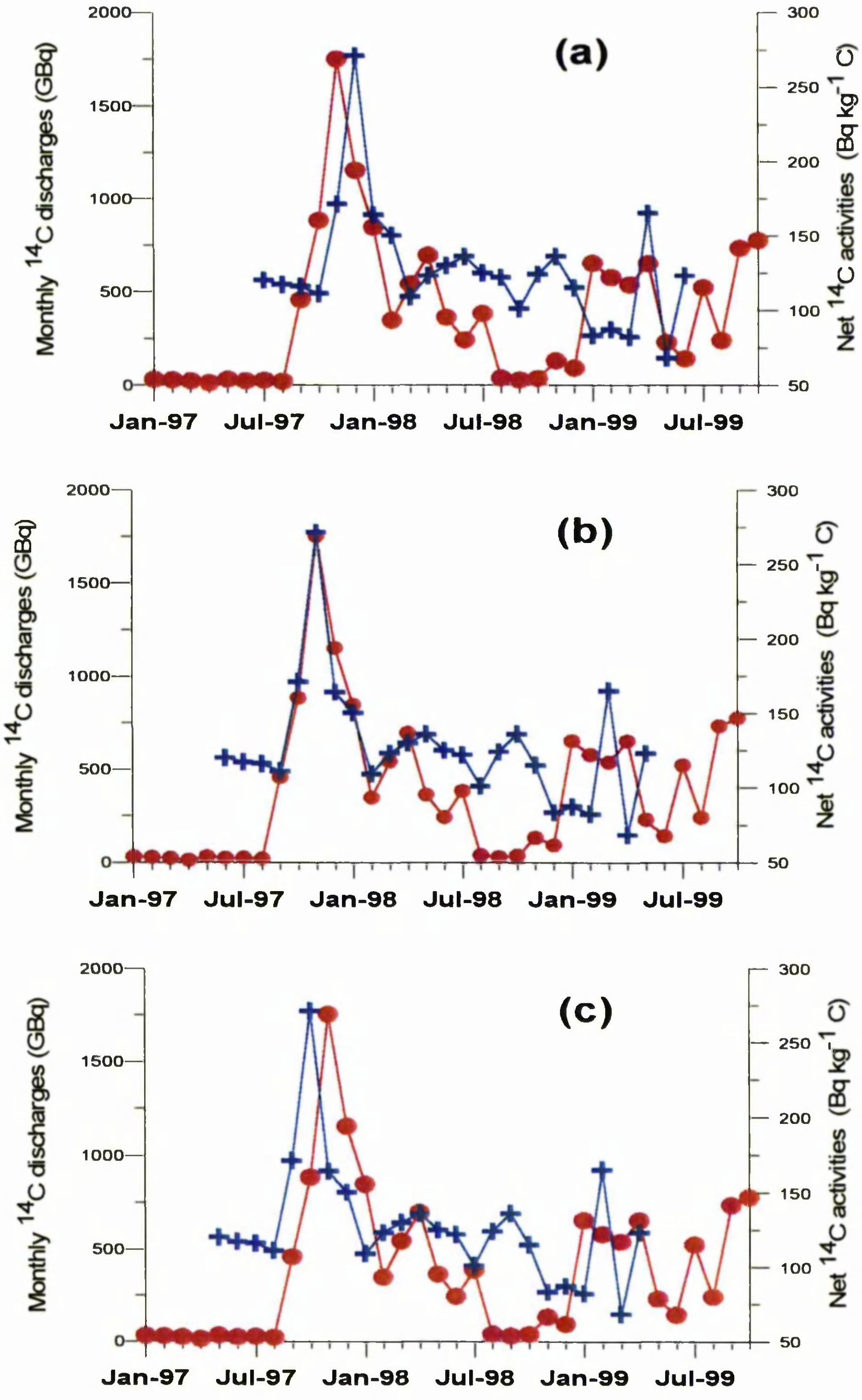
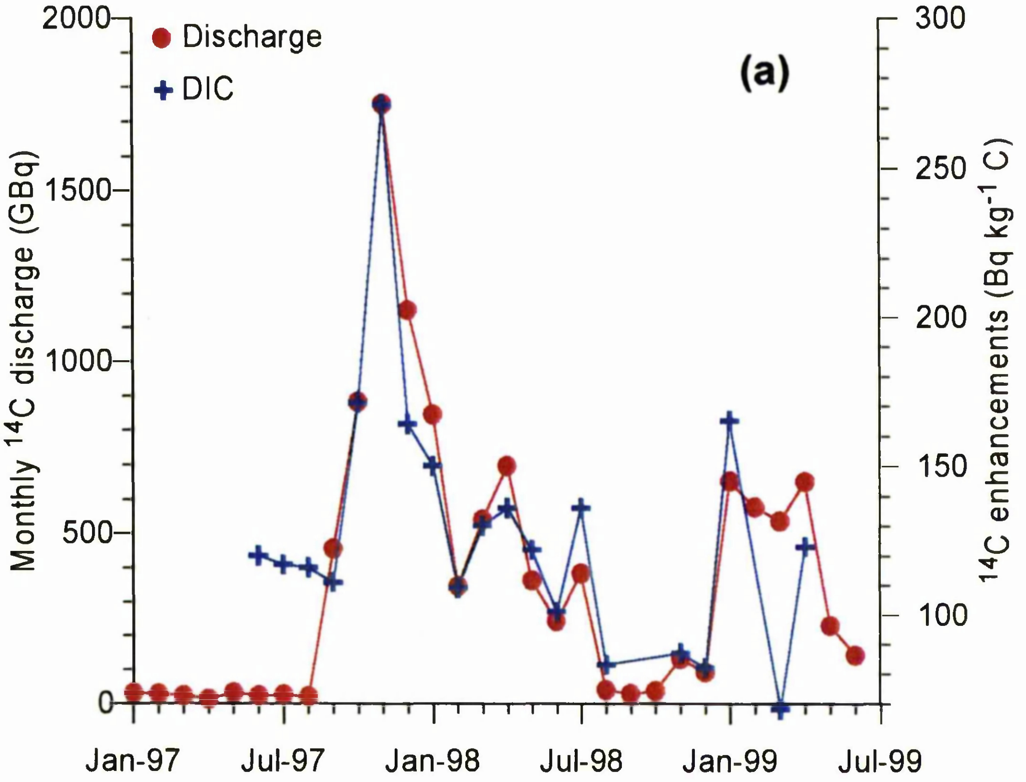
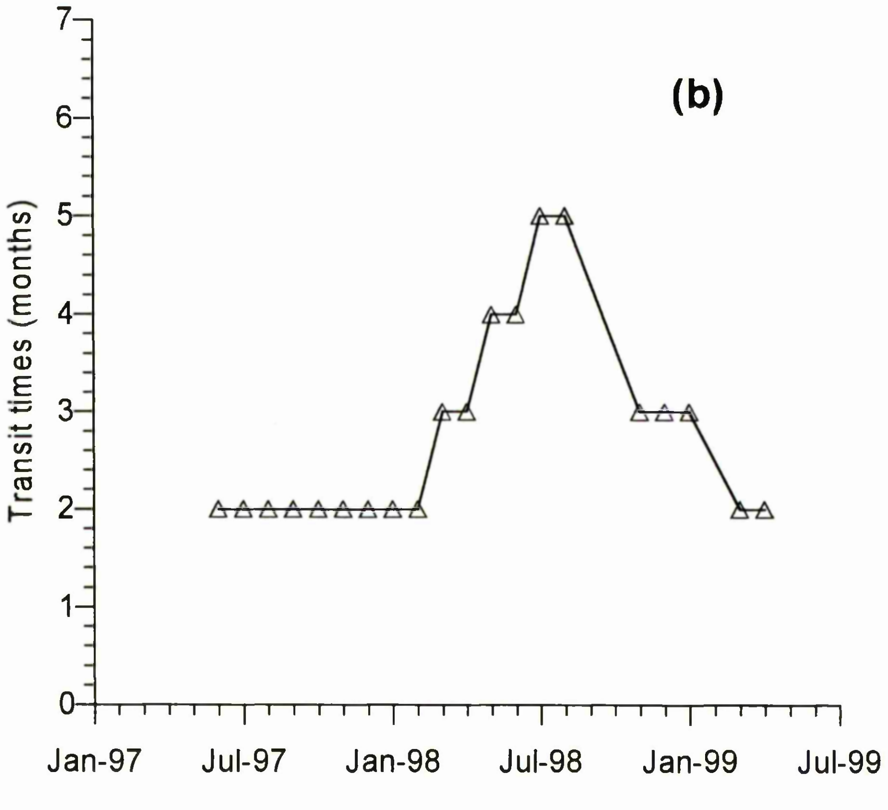


Figure 3.8 (a) net activities matched by eye to the discharge activities assuming variable transit times and (b) transit times calculated from Figure 3.8(a).





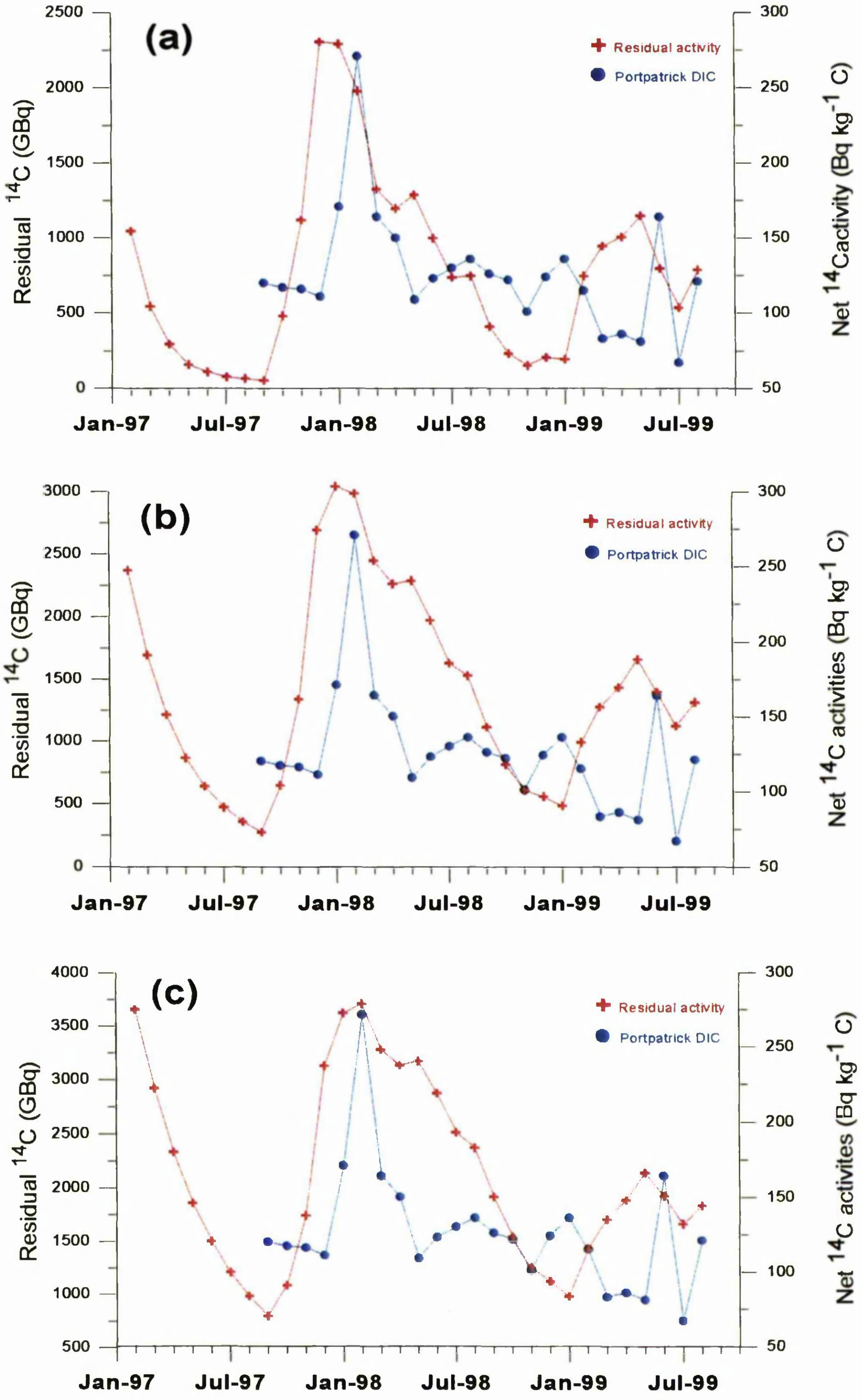
An alternative approach to estimate variations in ^{14}C activities of water leaving the Irish Sea on the basis of known monthly discharges (from January 1992 to August 1999) is to assume that the seawater system (in this case the NE Irish Sea) is well mixed and that any particular discharge is removed from the system according to first order kinetics. The removal of any particular discharge can therefore be characterised by a halving time $D_{½}$ (analogous to the half-life in radioactive decay) and a mean residence time $1/D_{½}$. For a continuous sequence of, T, monthly discharges, the inventory of ^{14}C in the NE Irish Sea water (assuming no other significant removal processes) will be given by:

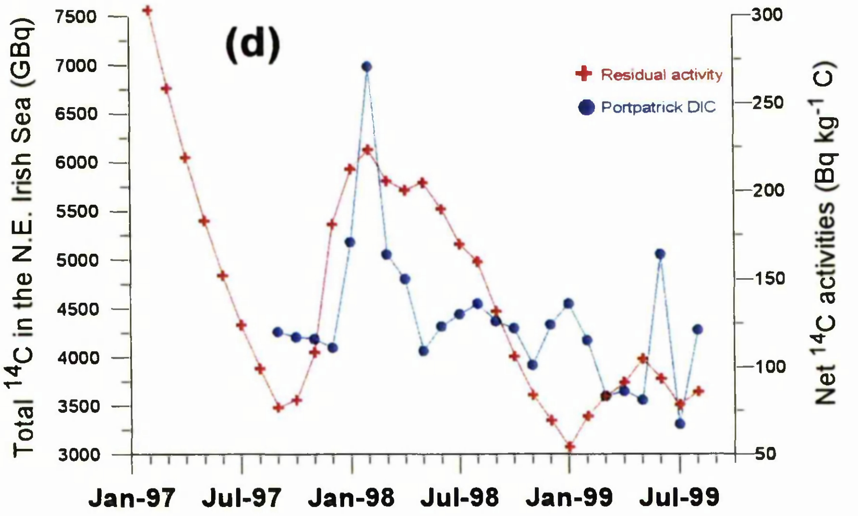
$$I_{(T)} = \sum_{(t=0,\,T)} D_{(t)} e^{-L(T-t)}$$

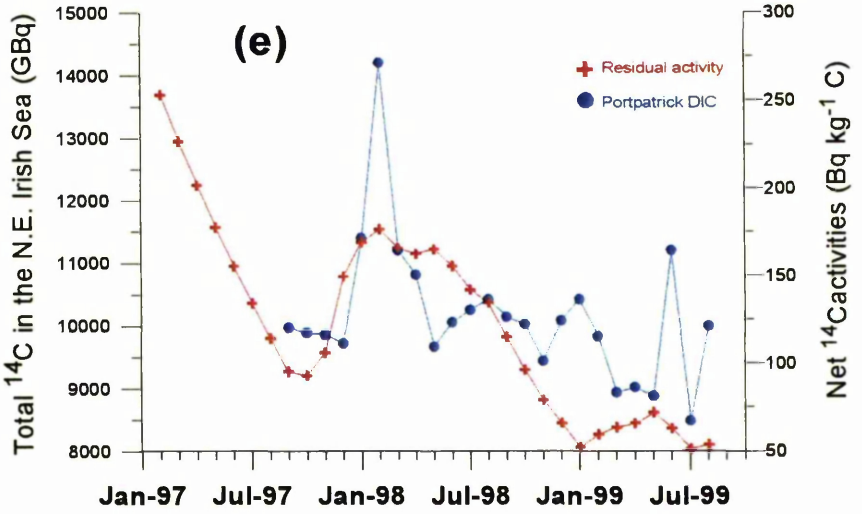
where D = discharge, L = ln $2/D_{½}$ (analogous to the decay constant in radioactive decay) where $D_{½}$ is the halving time, T = time of measurement. In a well mixed system, the ^{14}C activity (concentration) in seawater will be proportional to the inventory. Thus, if the activity in waters leaving the system *via* North Channel is assumed to be equal that of seawater in the Irish Sea, the above equation can be used to estimate temporal variations in activity on the basis of assumed values for $D_{½}$. On this basis, estimated temporal variations in activity were derived using halving times of 30, 60, 90, 180 and 365 days and the resultant estimates of ^{14}C activities were plotted along with the measured ^{14}C activity above ambient background in the DIC fraction of the water column at Portpatrick in Figure 3.9. Using this approach it can be seen from Figure 3.9 that of the values tried, a halving time of one month gave the best fit to the Portpatrick DIC activities from August 1997 until March 1998, consistent with short transit times to Portpatrick and rapid removal of ^{14}C in the DIC from the NE Irish Sea. However, it can be seen that while a one month halving time fits the first nine months data from Portpatrick it does not give a good fit for the rest of the data.

It is clear from Figure 3.9 that longer halving times do not fit the data and "flatten and broaden" the trends of peaks in the discharge. As a constant halving time of one month does not fit the whole data set it was decided to vary the halving time to fit the data at Portpatrick and, as shown in Fig. 3.10, this procedure gives halving times ranging from 10 to 60 days. The halving times calculated from January to August 1997, inclusive, are estimates as there is little variation in the discharges during this time or in the activities in the DIC between August and November 1997, inclusive. These halving times are shorter than those calculated by Jefferies

Figure 3.9 Net ^{14}C activities at Portpatrick and ^{14}C activity of the DIC in the NE Irish sea assuming (a) a one month halving time (b) a two month halving time (c) a three month halving time (d) a six month halving time and (e) a twelve month halving time







et al. (1973) but agree with work of Leonard *et al.* (1997) where the halving times observed were shorter than those expected from the work of Jefferies *et al.* (1982). In conclusion, it appears that with known discharge activities and measured activity data, the system can be modelled retrospectively using a simple box model approach. However, this method does not provide information on the underlying hydrological mechanisms that control the halving times in the Irish Sea and so on its own would be incapable of predictive modelling.

Calculation of the total ^{14}C activity removed from the Irish Sea in the form of DIC through the North Channel is considered along with the removal of ^{14}C in the form of PIC, POC and DOC and dissolved ^{137}Cs in section 3.2.4.

Figure 3.10 (a) calculated and observed DIC ^{14}C activities using variable halving time to match calculated activities with the net activities in the DIC at Portpatrick and (b) halving times (days) calculated from Figure 3.10(a).

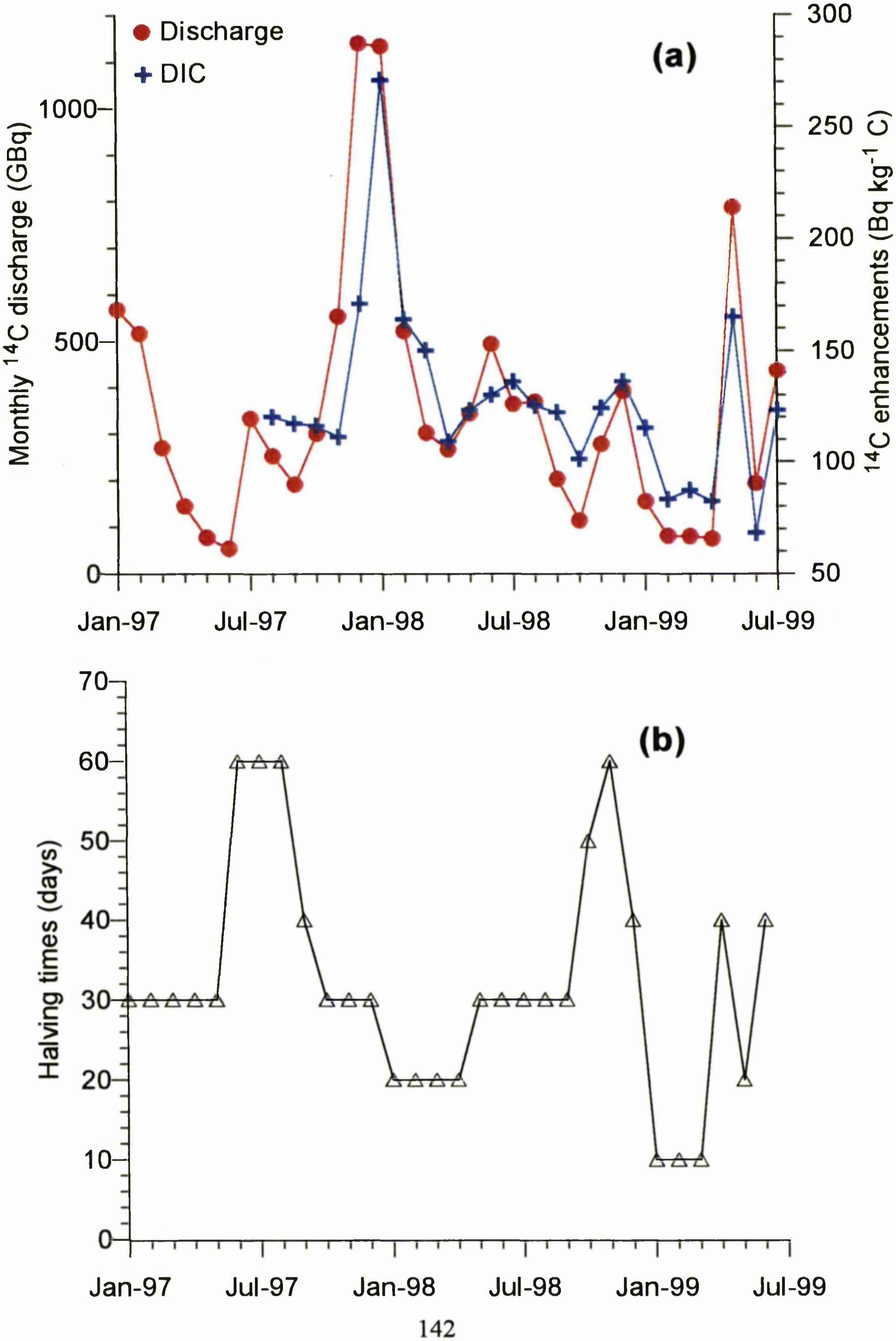


Figure 3.11 Comparison of variable transit times and halving times.

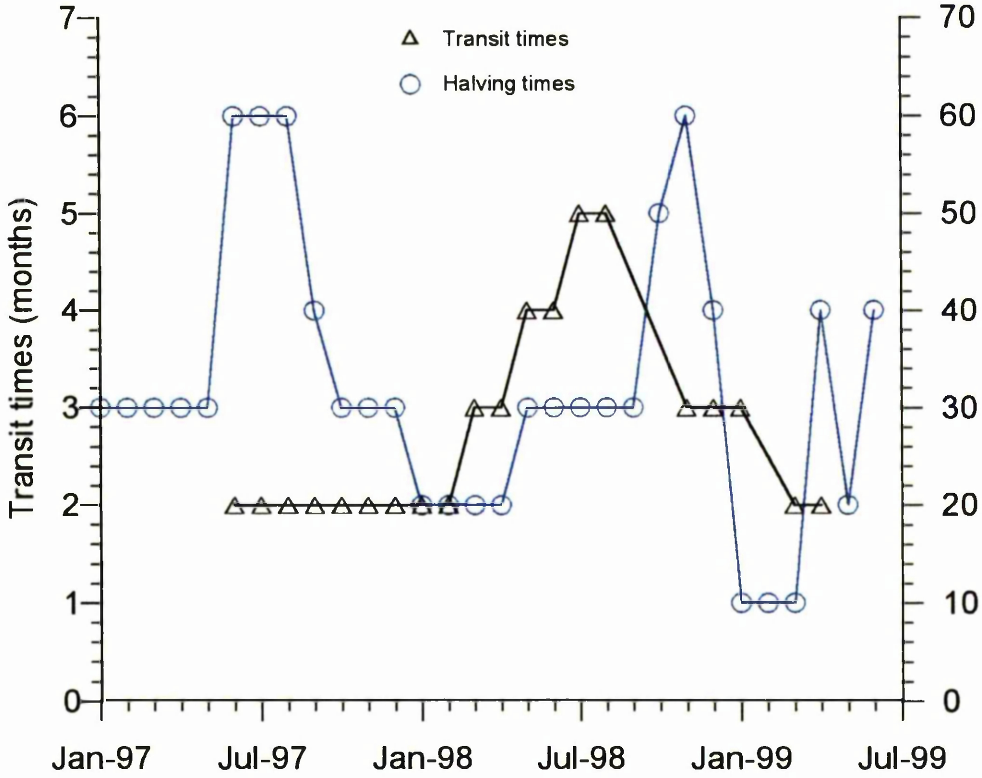


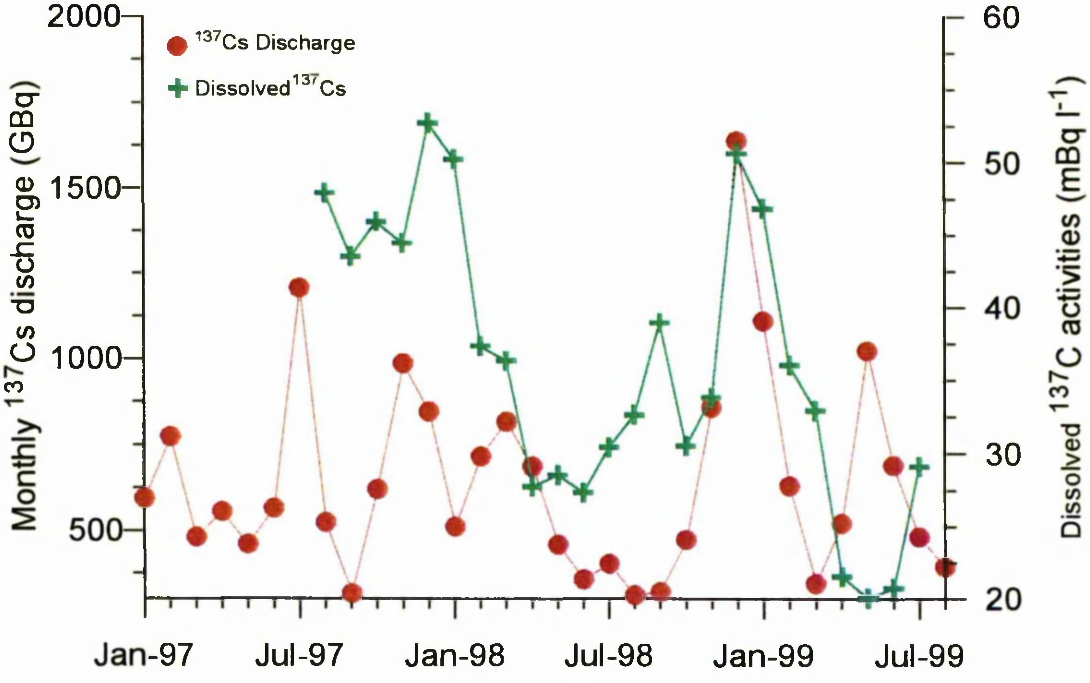
Figure 3.11 shows that there is come discrepancy between the estimated variable transit times and halving times for activity in the NE Irish Sea as described above. This is most probably due to the "simple" modelling approaches taken in this work, where no account is taken of the influence of wind forcing on the area under investigation. Moreover, while there is evidence from this study that the assumption that the transfer of ^{14}C from the DIC is negligible is valid, the data set is small and there is a (small) possibility that the transfer of ^{14}C from the DIC is seasonally affected.

$\delta^{13}C$ ‰ values (relative to PDB) for the DIC are presented in Table 3.6 and range from - 0.1 to + 2.0 ‰. The DIC $\delta^{13}C$ ‰ values in the present work are typically within this range for marine DIC, with higher values occurring in March, June and July of each year and in August of 1998.

^{137}Cs

Dissolved ^{137}Cs was analysed in seawater samples collected on a monthly basis from August 1997 to July 1999 and activities ranged between 20 ± 2 and 53 ± 2 mBq l^{-1} (Table 3.6), comparable to those reported for the North Channel by Cook *et al.* (1997), but lower than reported by McKay and Baxter (1986) and Begg *et al.* (1991) of 1.2 x 10^3 and 1.3 x 10^2 mBq l^{-1}, respectively. This is consistent with the trend of decreasing ^{137}Cs activities in the Irish Sea since the 1980s. Like the gross DIC activities in seawater, the dissolved ^{137}Cs activities at Portpatrick are lower that those measured at Nethertown. From Figure 3.12 it can be seen that there is no apparent resemblance between variations in the measured ^{137}Cs activities in seawater at Portpatrick and variations in the monthly ^{137}Cs discharges from Sellafield. Activities greater than 50 mBq l^{-1} were observed in December and January 1997 and December 1998 while the lowest activities of less than 30 mBq l^{-1} were observed between February and June 1997. This is possibly evidence of an annual variation in ^{137}Cs activity at the Portpatrick site, with higher activities in the winter months.

Figure 3.12 Monthly ^{137}C discharges from Sellafield and dissolved ^{137}C activities in seawater at Portpatrick



The variable halving times estimated for ^{14}C were used to model the ^{137}Cs discharge data (assuming that there was only one discharge a month by adding the fortnightly discharges). From this predicted ^{14}C and ^{137}Cs activities removed from the Irish Sea were calculated. Assuming that both ^{14}C and ^{137}Cs behave conservatively, then the activity ratio of predicted ^{14}C:^{137}Cs should be the same as the measured ^{14}C:^{137}Cs activity ratio at Portpatrick, where ^{14}C activity is net activity (mBq l^{-1}). Using the net ^{14}C activities (Table 3.6) and the discharge data (T. Parker, BNFL, Pers. Comm), dissolved ^{137}Cs activities (mBq l^{-1}) at Portpatrick due to the Sellafield discharges were estimated. Subtracting these estimated "discharge only" activities from the measured dissolved ^{137}Cs activities gives dissolved ^{137}Cs activities at Portpatrick due to re-dissolution (Table 3.7).

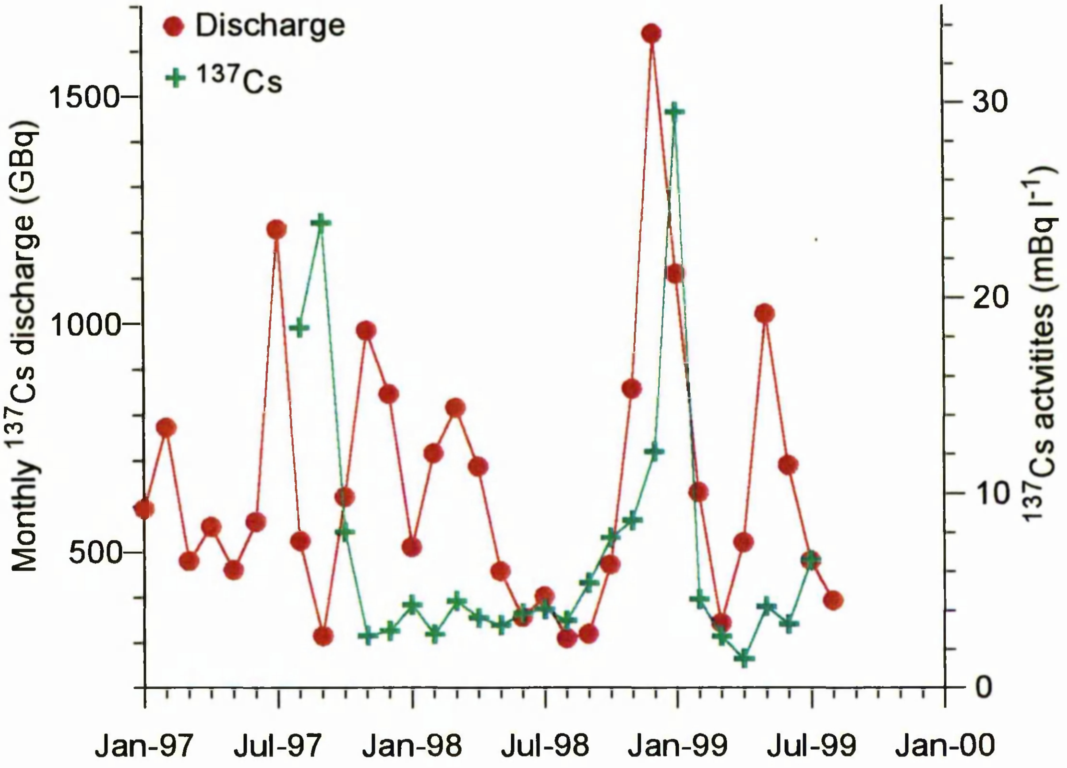
Plotting the estimated activity for ^{137}Cs (mBq l^{-1}) due solely to the discharges along with the monthly ^{137}Cs discharges shows that there is some similarity between the trends in the discharges and trends in the estimated activity (Figure 3.13). The similarities are not as pronounced as those between the DIC and ^{14}C discharge, but this is probable due to the fact that the data is based on a simple model that could be improved on in the future.

An estimate of the total activity of ^{137}Cs removed from the NE Irish Sea *via* the North Channel can be estimated and this is addressed along with removal of ^{14}C in Section 3.2.4.

Table 3.7 Calculated dissolved ^{137}Cs activities (mBq l^{-1}) at Portpatrick due to recent ^{137}Cs discharges and to re-dissolution from the sediments

Collection Date	Estimated activities due to discharges (mBq l^{-1})	Estimated activities due to re-dissolution (mBq $^{-1}$)
Aug. '97	18	30
Sept. '97	24	20
Oct. '97	8	38
Nov. '97	3	41
Dec. '97	3	50
Jan. '98	4	46
Feb. '98	3	34
Mar. '98	4	32
Apr. '98	4	24
May '98	3	26
June '98	4	23
July '98	4	26
Aug. '98	3	29
Sept. '98	5	34
Oct. '98	8	23
Nov. '98	9	25
Dec. '98	12	39
Jan. '99	30	17
Feb. '99	5	31
Mar. '99	3	30
Apr. '99	1	21
May '99	4	16
June '99	43	18
July '99	7	22
Average activity	8.8	29.0

Figure 3.13 Monthly discharges (GBq) of ^{137}Cs and estimated activity (mBq l^{-1}) of ^{137}Cs at Portpatrick (assuming no input from re-dissolution)



Biogeochemical fractions

Samples were collected on a quarterly basis from November 1997 until February 1999 inclusive, for the analysis of the four biogeochemical fractions of seawater (DIC, DOC, PIC and POC) and the results are presented in Table 3.8. Figure 3.14 illustrates little resemblance between the activities in the DIC, DOC, PIC and POC fractions and the monthly ^{14}C discharge from Sellafield. In the case of the DOC, the results are preliminary (Section 2.4.3) and it is difficult to form conclusions about long term trends in the DOC fraction as there are only three DOC results to compare to 18 months of discharges. The results presented here for the DIC are averages of the duplicate samples analysed each month.

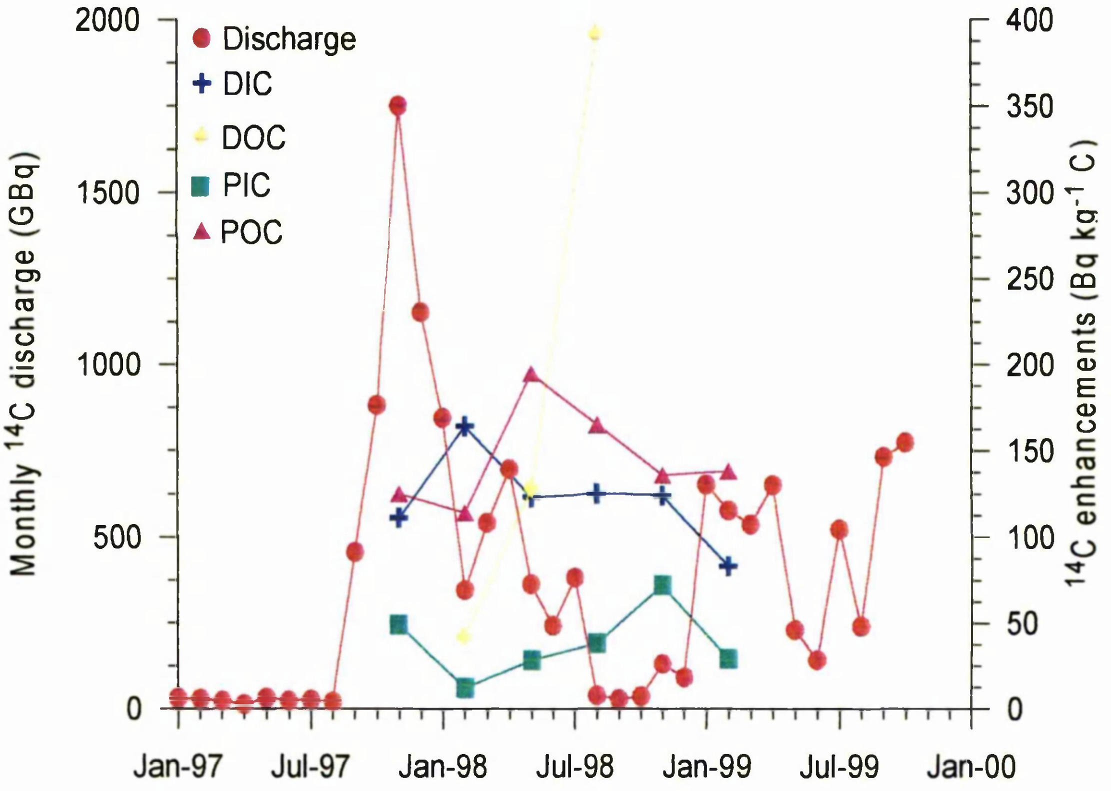
The gross ^{14}C activities ranged from 335 ± 3 to 416 ± 2 Bq kg^{-1} C for the DIC, 218 ± 1 to 568 ± 2 Bq kg^{-1} C for the DOC, 156 ± 1 to 193 ± 1 Bq kg^{-1} C for the PIC and 320 ± 1 to 239 ± 1 Bq kg^{-1} C from the POC. Apart from the DOC in August 1998, the DIC has the highest gross ^{14}C activity of the biogeochemical fractions.

Table 3.8 Gross ^{14}C activities (Bq kg^{-1} C ± 1σ) and net ^{14}C activities (Bq kg^{-1} C ± 1σ)(*ie.* above ambient background) in the DIC, DOC, PIC and POC fractions of seawater, collected on a quarterly basis at Portpatrick (Latitude 54^0 51' N, Longitude 05^0 07' W). Background activities are 252 ± 3, 176 ± 4, 144 ± 10 and 125 ± 6Bq kg^{-1} C ± 1σ, respectively.

Date	Gross DIC	Net DIC	Gross DOC	Net DOC	Gross PIC	Net PIC	Gross POC	Net POC
Nov. 97	363 ± 1	111 ± 3	F	-	193 ± 1	49 ± 10	250 ± 1	125 ± 6
Feb. 98	416 ± 2	164 ± 4	218 ± 1	42 ± 4	156 ± 1	12 ± 10	239 ± 1	114 ± 6
May 98	375 ± 1	123 ± 3	304 ± 2	128 ± 5	172 ± 1	28 ± 10	320 ± 1	195 ± 6
Aug.98	377 ± 2	125 ± 4	568 ± 2	392 ± 5	182 ± 1	38 ± 10	290 ± 1	165 ± 6
Nov. 98	376 ± 2	124 ± 4	F	-	216 ± 1	72 ± 10	261 ± 4	136 ± 7
Feb 99	335 ± 3	83 ± 4	F	-	173 ± 1	29 ± 10	263 ± 1	138 ± 6

F Analysis Failed

Figure 3.14 Monthly ^{14}C discharges from Sellafield and quarterly net DIC, DOC, PIC and POC at Portpatrick.



Interestingly, however, the POC has higher net ^{14}C activities (apart from February 1998) than the DIC fraction. This could possibly indicate that the assumed ambient background for the POC is too high. The net ^{14}C activity of the DOC in May 1998 was 1.5 times that of the net DIC activity in May 1998 and the net ^{14}C activity of DOC in August 1998 was slightly greater than 3 times that of the net DIC activity during the same month. The activity of the DOC relative to the DIC is higher than that reported by Cook *et al.* (1995), unfortunately this data set is too small to make any conclusions about possible long term changes in the activity of the DOC fraction of seawater at the North Channel.

Normalising the gross ^{14}C specific activity (Bq kg^{-1} C) of the biogeochemical fractions to the specific activity (Bq kg^{-1} C) of the DIC (Table 3.9) shows differences in the transfer of ^{14}C between the carbon fractions. In comparison with the normalised results from Cook *et al.* (1995), the normalised results for the DIC and PIC are similar, while the normalised results for the POC are much higher. However, it is difficult to compare between the studies as

Cook *et al.* (1995) only collected samples from Portpatrick on one occasion. The normalised results for the DOC display an increasing trend until the activity of the DOC exceeds that of the DIC in August 1998. It is unfortunate that there are no more results for the DOC as it would be interesting to see if this was an anomaly or a long term trend.

The normalised distributions for the PIC show little change over the course of the study, but in contrast, the normalised distributions for the POC exhibited significant variations. It is difficult to see any stable relationship in the DOC and POC fractions normalised to the DIC from this limited data set. A more detailed study, including an index for primary production (*eg* chlorophyll measurements) would be needed to investigate the stability of the relationship, between the biogeochemical fractions of seawater of the North Channel.

Table 3.9 Normalised results for the biogeochemical fractions of the water column at Portpatrick from this study and from Cook *et al.* (1995).

Date of Collection	DIC	DOC	PIC	POC
December 1989	1	0.54	0.46	0.42
November 1997	1		0.53	0.69
February 1998	1	0.52	0.38	0.57
May 1998	1	0.81	0.46	0.85
August 1998	1	1.51	0.48	0.77
November 1998	1		0.57	0.69
February 1999	1		0.52	0.79

$\delta^{13}C$ values (‰ relative to PDB) are presented in Table 3.10. The results for the DIC fraction of the water column are the same as those in Table 3.6. With the exception of the November 1998 sample, the $\delta^{13}C$ values for the PIC (- 2.4 to + 0.4) are within the range - 1.0 to + 1.0 ‰ (relative to PDB), indicating a mainly marine origin for PIC during this study. For the organic fractions, the $\delta^{13}C$ values range between - 19.3 and - 28.0 ‰ for the DOC and - 21.1

and - 22.4 ‰ for the POC. Organic mater produced in the marine environment has a $\delta^{13}C$ value between - 18.0 and - 22.0 ‰, while that of terrestrially produced organic matter varies between - 24.0 and - 32.0 ‰. For the POC, there is little apparent influence of terrestrial carbon, while the DOC fraction exhibits probable terrestrial influences in August and November 1998. It is possible that the sampling site was influenced by a terrestrial source which was low in PIC and POC but rich in dissolved organic material at this time.

Table 3.10 $\delta^{13}C$ ‰ values (relative to PDB) for the biogeochemical fractions of the water column at Portpatrick.

Date of Collection	DIC	DOC	PIC	POC
November 1997	+ 0.7	- 19.3	- 0.3	- 22.1
February 1998	+ 0.6	- 23.5	+ 0.3	- 21.7
May 1998	- 0.1	- 22.7	+ 0.4	- 20.3
August 1998	+ 1.1	- 26.1	+ 0.2	-20.6
November 1998	+ 0.4	- 28.0	- 2.4	-22.4
February 1999	+ 0.4	F	- 0.0	-21.9

F analysis failed

Calculation of the total ^{14}C activity in the form of PIC, POC and DOC removed from the NE Irish Sea through the North Channel is considered, along with that of ^{14}C in the DIC and dissolved ^{137}C in Section 3.2.4.

3.2.4. Total ^{14}C activity in the DIC, DOC, PIC and POC fractions of seawater, and dissolved ^{137}Cs activity removed from the NE Irish Sea *via* the North Channel.

Removal of contaminant radionuclides from the Irish Sea is predominantly *via* the North Channel. Therefore, estimates of the removal of ^{14}C and ^{137}Cs can be determined from the average activities above ambient background in the DIC, DOC, PIC and POC fractions of the water column and the measured dissolved ^{137}Cs activities at Portpatrick, together with an average water flux through the North Channel.

While there is a wide range of published values (from - 14.7 to 12.1 km^3 d^{-1}) for the flux of water through the North Channel (Section 1.7), a value of 5 km^3 day^{-1} has been used successfully in previous studies of radionuclide transport from the Irish Sea through the North Channel (Pentreath *et al.* 1984; Cook *et al* 1997) and this value was used for calculations within this study. Using the net ^{14}C specific activities for DIC in seawater at Portpatrick, monthly ^{14}C discharge data and values of flushing time for the Irish Sea from the literature of 304 days (no wind) and 187 days (average wind speeds), (Prandle 1984), the flow through the North Channel during the period of this study was calculated to be 2.8 and 4.6 km^3 day^{-1}, respectively (Prandle Pers. Comm.) The value of 4.6 km^3 day^{-1} is in good agreement with the range of values calculated in previous studies for flow through the North Channel (Table 1.5) despite being based on a data set of only 23 observations at monthly intervals in a less than optimum position for modelling flows through the North Channel.

Calculation of ^{14}C activity removed from the NE Irish Sea

To calculate the removal of ^{14}C from the NE Irish Sea through the North Channel, the activities of the four carbon fractions above ambient background must first be converted from Bq kg^{-1} C to mBq l^{-1} (Appendix 1). The values are presented in Table 3.11. Using the average ^{14}C excesses converted to mBq l^{-1} (DIC: 3.1 mBq l^{-1}, DOC: 2.7 x 10^{-1} mBq l^{-1}, PIC: 3.2 x 10^{-3} mBq l^{-1}, and POC: 1.8 x 10^{-2} mBq l^{-1}) and the above water flux gives an estimated removal during the 2 year study period of 11.4 ± 0.7 TBq in the DIC fraction, 0.9 TBq in the DOC fraction, <0.01 TBq in the PIC fraction and 0.07 TBq in the POC fraction. It must be stressed that the DOC calculation is based on only 3 provisional values. This gives a total of 12.4 TBq of ^{14}C removed from the Irish Sea through the North Channel between August 1997 and July 1999. Total discharges from Sellafield over the study period were 11.3 TBq indicating that approximately 100% of the ^{14}C discharged from Sellafield is rapidly removed from the NE Irish Sea *via* the North Channel with > 90% of the ^{14}C removed incorporated into the DIC fraction.

This approach, however, does not take into account the standing crop of ^{14}C present at the start of this study. To encompass this, the simple modelling approach used to estimate the halving times for activity in the NE Irish Sea was used to calculate the standing crop of ^{14}C in the NE Irish Sea due to discharges prior to August 1997. Using a halving time of one month the estimated removal of ^{14}C from the NE Irish Sea was 10.5 TBq from August 1997 to July

Table 3.11 ^{14}C activities (mBq l^{-1}), above ambient background in the DIC, DOC, PIC and POC fractions of the water column at Portpatrick.

Date	^{14}C DIC mBq l^{-1}	^{14}C DOC mBq l^{-1}	^{14}C PIC mBq l^{-1}	^{14}C POC mBq l^{-1}
August '97	2.6 ± 0.2			
Sept. '97	2.8 ± 0.2			
Oct '97	3.1 ± 0.2			
Nov. '97	2.7 ± 0.2	F	$4.4E^{-3} \pm 2^{-4}$	$1.5E^{-2} \pm 1^{-3}$
Dec. '97	4.4 ± 0.3			
Jan. '98	6.2 ± 0.3			
Feb. '98	4.3 ± 0.3	0.05 ± 0.005	$6.0E^{-3} \pm 3^{-4}$	$1.3E^{-2} \pm 1E^{-3}$
March '98	3.6 ± 0.2			
April '98	2.7 ± 0.2			
May '98	2.9 ± 0.2	0.21 ± 0.008	$8.4E^{-4} \pm 5^{-4}$	$2.3E^{-2} \pm 1E^{-3}$
June '98	3.3 ± 0.2			
July '98	3.1 ± 0.2			
August '98	3.2 ± 0.2	0.54 ± 0.007	$1.9E^{-3} \pm 9^{-5}$	$1.8E^{-2} \pm 1E^{-3}$
Sept. '98	2.9 ± 0.2			
Oct. '98	2.6 ± 0.2			
Nov. '98	3.2 ± 0.2	F	$2.2E^{-3} \pm 1^{-4}$	$8.2E^{-3} \pm 4E^{-3}$
Dec. '98	3.5 ± 0.2			
Jan. '99	3.0 ± 0.2			
Feb. '99	2.2 ± 0.2	F	$3.7E^{-3} \pm 2^{-4}$	$2.9E^{-2} \pm 2E^{-3}$
March '99	2.2 ± 0.2			
April '99	2.1 ± 0.2			
May '99	3.8 ± 0.2			
June '99	1.4 ± 0.1			
July '99	2.7 ± 0.2			
Mean ± SE	3.1 ± 0.19	0.27 ± 0.007	$3.2E^{-3} \pm 5.5E^{-4}$	$1.8E^{-2} \pm 3E^{-3}$

F Analysis failed

1998 inclusive. Using the variable halving times from Figure 3.10 this modelling approach gave an estimated removal of 10.8 TBq over the study period. These estimates for the removal of ^{14}C in the DIC are in good agreement with the total discharges during the sampling period of 11.3 TBq and with the estimated removal of 12.4 TBq of ^{14}C using a flux of 5 km^3 day^{-1}.

Calculation of ^{137}Cs activity removed from the NE Irish Sea

During the 2 year period of this study, the total discharges of ^{137}Cs were 15.6 TBq. Using the value of 5 km^3 day^{-1} for the flow through the North Channel and an average ^{137}Cs activity in the water column at Portpatrick (from Table 3.6) of 36.3 ± 2.0 mBq l^{-1}, the total activity lost through the North Channel in the dissolved phase during the study period was 133 ± 7 TBq. This value is considerably larger than the total discharge, and is consistent with continuing re-dissolution from the underlying sediment, in agreement with previous observations (Hunt and Kershaw 1990; McCartney *et al. 1994*; Cook *et al.* 1997).

In order to calculate the individual contributions, due to (a) the discharge during the study period and (b) re-dissolution from the sediments, to the total dissolved ^{137}C activity removed, the values from Table 3.7 were used. Average activities of (a) 8.8 mBq l^{-1} and (b) 29.0 mBq l^{-1} (Table 3.7) were used along with the flow of 5 km^3 day^{-1} through the North Channel to give removal of (a) 32 TBq due to the discharges and (b) 110 TBq due to re-dissolution. The value of 32 TBq due to the discharges is not in good agreement with the published discharges of 15.6 TBq from Sellafield. This is probably due to inaccuracies in one or more of the assumptions made in calculating the dissolved ^{137}Cs activities (mBq l^{-1}) at Portpatrick.

A further estimate of the removal of ^{137}Cs from the NE Irish Sea can be calculated from the simple model (Appendix 2). The activity of ^{137}Cs removed using a halving time of one month is calculated to be 15.5 TBq which is very close to the discharged activity for the study period of 15.6 TBq. The activity of ^{137}Cs removed using the variable halving times calculated in Figure 3.10 is 17.0 TBq, which is also very close in activity to the total discharges during the study period. Subtracting these values from the total removed activity of 133 ± 7 TBq gives estimates of activity due to re-dissolution of between 117.5 and 166.0 TBq that were removed from the

Irish Sea during the period August 1997 to July 1999, over 7 times greater than the activity removed during the same time due to current discharges.

3.3 ^{14}C Activities in intertidal biota of the Irish Sea and North Channel.

3.3.1 Activities in mussel flesh, shells and in Fucus sp. from Nethertown

Mussels *(Mytilus edulis)*

Mussel samples were collected from August 1997 to February 1999, inclusive, and gross ^{14}C activities, net ^{14}C activities above ambient background (Section 3.1) and δ^{13}C ‰ values for mussel flesh and shells are presented in Table 3.12 and Figure 3.15. The net mussel flesh activity above ambient background ranged between 813 ± 4 and 1,983 ± 8 Bq kg^{-1} C during the course of the study. Figure 3.15 illustrates the comparison between the monthly enhancements in mussel flesh and valves and (a) ^{14}C discharges from Sellafield, (b) the net ^{14}C activity in the DIC at Nethertown and (c) the quarterly net ^{14}C activity in the POC at St Bees Head.

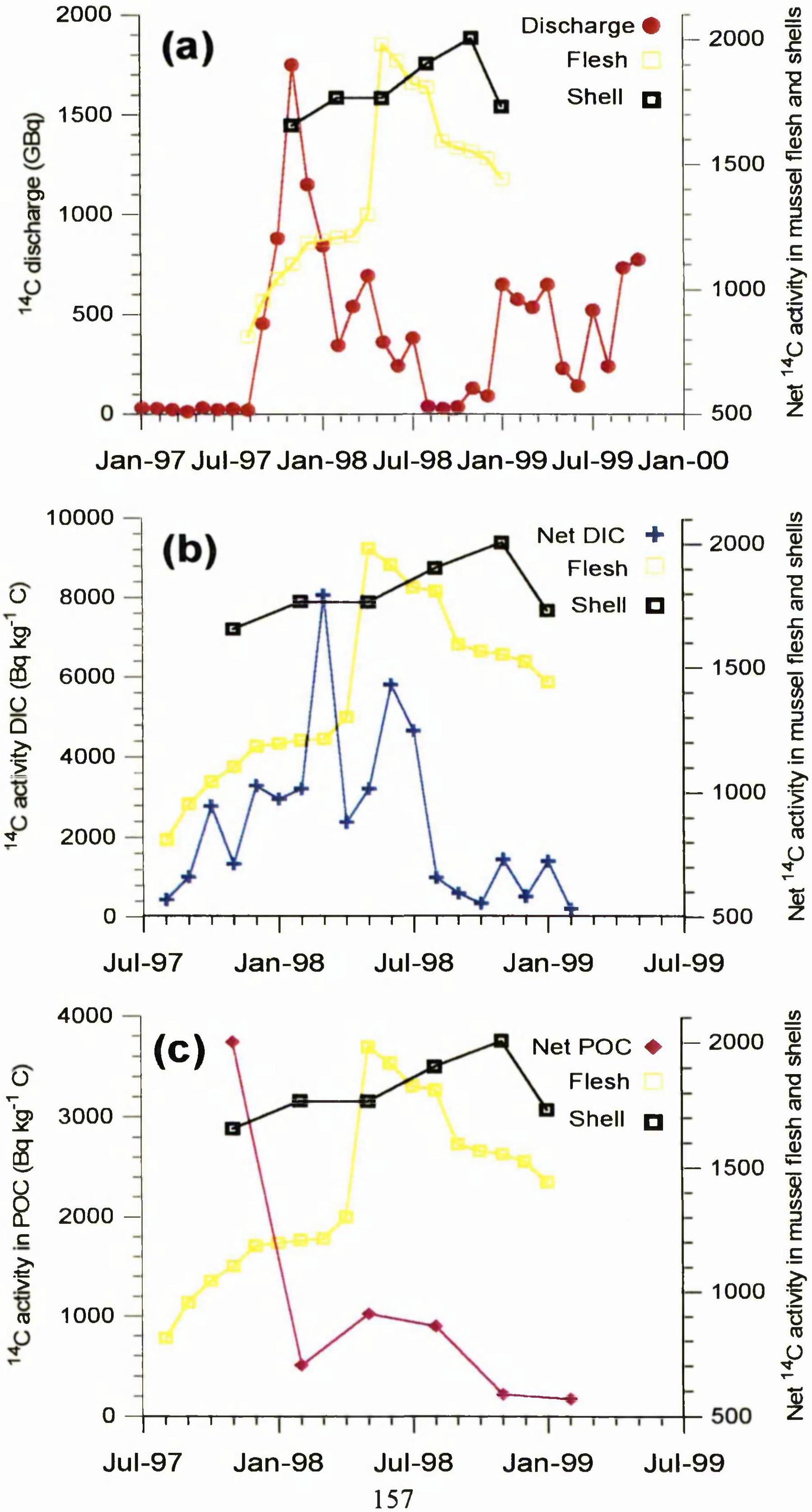
Mussels are particle size selective filter feeders, feeding on the POC fraction of the water column. Carbon isotopic compositions of animals reflect those of the diet to within about 1‰ (Michener and Schell 1994), and from the δ^{13}C values for mussel flesh in Table 3.12 it can be seen that the main food source for mussels is marine in origin (- 18 to -22 ‰, Stuiver and Polach 1977). As mussels are longer lived than their prey, the phytoplankton, their flesh will exhibit an integrated activity with respect to previous POC intake, which in turn will reflect the activity of the DIC fraction of the water column. It was expected, therefore, that the activity of the mussel flesh would respond to trends in the activity of the POC at St Bees Head (assuming that the activity of the POC at St Bees head is similar to that of the POC at Nethertown). From Figure 3.15 however, it is not apparent that there is any connection between the activity of the POC and that of the mussel flesh, indicating that either there are (spatial) differences in the activity of the POC in the NE Irish Sea, as there are in DIC activities, or that the true effect of the POC on the activity of the mussel flesh is hidden by the differences in the sampling intervals (monthly *vs* quarterly). Examination of the data shows a more than

Table 3.12 Gross ^{14}C activities (Bq kg^{-1} C ± 1σ) and net ^{14}C activities (*ie.* above ambient background) and δ^{13}C values (‰ relative to PDB) in mussel flesh and shells (*Mytilus edulis)* from samples collected at Nethertown (Latitude 54^0 27' N, Longitude 03^0 33'W). Ambient backgrounds are 246 ± 9 and 256 ± 1 Bq kg^{-1} C ± 1σ respectively.

Collection Date	Gross flesh activity (Bq kg^{-1} C ± 1σ)	Net flesh activity (Bq kg^{-1} C ± 1σ)	δ^{13}C ‰ (relative to PDB)	Gross shell activity (Bq kg^{-1} C ± 1σ)	Net shell activity (Bq kg^{-1} C ± 1σ)	δ^{13}C ‰ (relative to PDB)
Aug. '97	1059 ± 4	813 ± 4	- 19.3			
Sept. '97	1202 ±7	956 ± 7	- 19.7			
Oct. '97	1291 ± 4	1045 ± 4	- 18.8			
Nov. '97	1350 ± 4	1104 ± 4	- 19.3	1914 ± 6	1658 ± 5	- 0.3
Dec. '97	1434 ± 5	1188 ± 5	- 18.9			
Jan. '98	1443 ± 6	1197 ± 6	- 19.1			
Feb. '98	1456 ± 6	1210 ± 6	- 18.8	2025 ± 5	1769 ± 5	+ 0.4
Mar. '98	1462 ± 6	1216 ± 5	- 19.0			
Apr. '98	1546 ± 6	1300 ± 5	-19.2			
May '98	2229 ± 8	1983 ± 8	- 18.4	2023 ± 8	1767 ± 8	- 0.1
June '98	2164 ± 8	1918 ± 8	- 18.8			
July '98	2073 ± 9	1827 ± 8	- 18.8			
Aug. '98	2058 ± 7	1812 ± 7	- 17.9	2161 ± 6	1905 ± 6	+ 0.4
Sept. '98	1842 ± 7	1596 ± 6	N/A			
Oct. '98	1815 ± 9	1569 ± 9	- 18.7			
Nov. '98	1801 ± 8	1555 ± 7	N/A	2263 ± 5	1733 ± 5	+ 0.3
Dec. '98	1772 ± 10	1526 ± 10	- 18.4			
Jan. '99	1690 ± 7	1444 ± 7	- 18.4	1989±5	1733 ± 5	- 0.1

twofold increase in the activity of mussel flesh (September 1997 to May 1998) indicating a reasonably rapid response in the activity of the mussel flesh at Nethertown to either changes in the discharge activities (peak in discharges was in November 1997) or to the peak activity of the DIC at Nethertown in March 1998.

Figure 3.15 Net mussel flesh and shell activities and (a) ^{14}C discharges from Sellafield, (b) the net ^{14}C activity in the DIC at Nethertown and (c) the quarterly net ^{14}C activity in the POC at St Bees Head.



It can be seen that increases in the flesh and shell material occur at different times with the highest activity in the shell occurring in November 1998, six months after the peak in flesh activity. The mussel shell material is composed of both organic and inorganic material with the organic component being derived from metabolic carbon while the inorganic component is taken directly from the DIC fraction of seawater (Tanaka 1986; Putten 2000). For this study the mussel shells were pre-combusted before analysis to remove the organic component and the $\delta^{13}C$ values for the shells (- 0.3 to + 0.4 ‰) in Table 3.12 show that this method was fairly successful (Putten *et al.* 2000 reported $\delta^{13}C$ values of between 0 and - 6 ‰ for total shell calcium carbonate). Like the mussel flesh the shell material gives an integrated activity reflecting the differing activities in the water column over the lifetime of the mussel. It was therefore expected that trends the activity of the shell material would reflect trends in either the discharge activities or in the DIC. From Figure 3.15 it can be seen that there is no obvious correlation between trends in the shell activities and trends in the discharge or the DIC activities. Putten *et al.* (2000) observed that shell growth in *Mytilus edulis* was greatest in autumn/early winter, so it is interesting to note the increase in activity occurs in November 1998. Perhaps this increase was due to the higher activities in 1998 than in 1997 and the additional shell material due to growth was of sufficient mass to increase the overall activity. It has been shown in previous studies that the inorganic carbon fraction of the sediment is mainly marine in origin. From Section 3.1 it can be seen that there is a suggestion that the activity of the inorganic sediment has been increasing since the beginning of radioactive discharges from Sellafield. However, the PIC fraction of seawater has not shown activities above the modern value of 226 Bq kg^{-1} C. Once a mollusc dies, broken shell material is also a source of inorganic carbon to the sediments. While these mussel shells are not representative of the activity of mussel and other mollusc shells prior to the increase in discharges in 1994/95, it does show a possible mechanism for addition of inorganic carbonate with a ^{14}C activity above modern to the sediments. In order to calculate the total activity contributed to the sediments from mollusc shell a much larger date set would be needed that spans species, temporal and spatial variations in the incorporation of ^{14}C into shell material and the degradation of this material once the animal dies.

Fucus

Seaweed samples were collected on a quarterly basis from February 1998 to November 1999 inclusive. Results for the measured ^{14}C activities, the net ^{14}C activities above ambient background (Section 3.1) and $\delta^{13}C$ values (‰ relative to PDB) are presented in Table 3.13.

Table 3.13 Gross ^{14}C and net ^{14}C activities (*ie.* above ambient background of 253 ± 1 Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ values (‰ relative to PDB) in seaweed (*Fucus* sp.) from samples collected at Nethertown (Lat. 54^0 51' N; Long. 05^0 07' W)

Collection date	gross ^{14}C activity (Bq kg^{-1} C)	Net ^{14}C activity (Bq kg^{-1} C)	$\delta^{13}C$ value (‰ relative to PDB)
February 1998	566 ±2	313 ± 3	- 17.9
May 1998	844 ± 3	591 ± 4	- 18.4
August 1998	810 ±3	557 ± 4	- 17.5
November 1998	296 ± 2	43 ± 3	- 17.3

The net ^{14}C activities in seaweed ranged between 43 ± 3 and 591 ± 4 Bq kg^{-1}C. In agreement with the work of Begg (1991) the activity of the seaweed is lower than that of the mussels for the same month. This is due to the ability of seaweed (including *Fucus* species) to utilise atmospheric CO_2 (which may have a lower ^{14}C activity than the DIC) for photosynthesis when they are exposed at low tide. Indeed it has been estimated that in some months > 50% of the carbon balance of *Fucus spiralis* is atmospheric carbon (Maberly and Madsen 1990). From this limited data set and with the added complication of an additional (but unquantifiable) source of carbon to *Fucus* it is difficult to say if there is any correlation between trends in the discharge and trends in the activity of *Fucus*.

3.3.2 Activities in the mussel flesh and Fucus sp. from Killantringan Bay (near Portpatrick).

Mussels *(Mytilus edulis)*

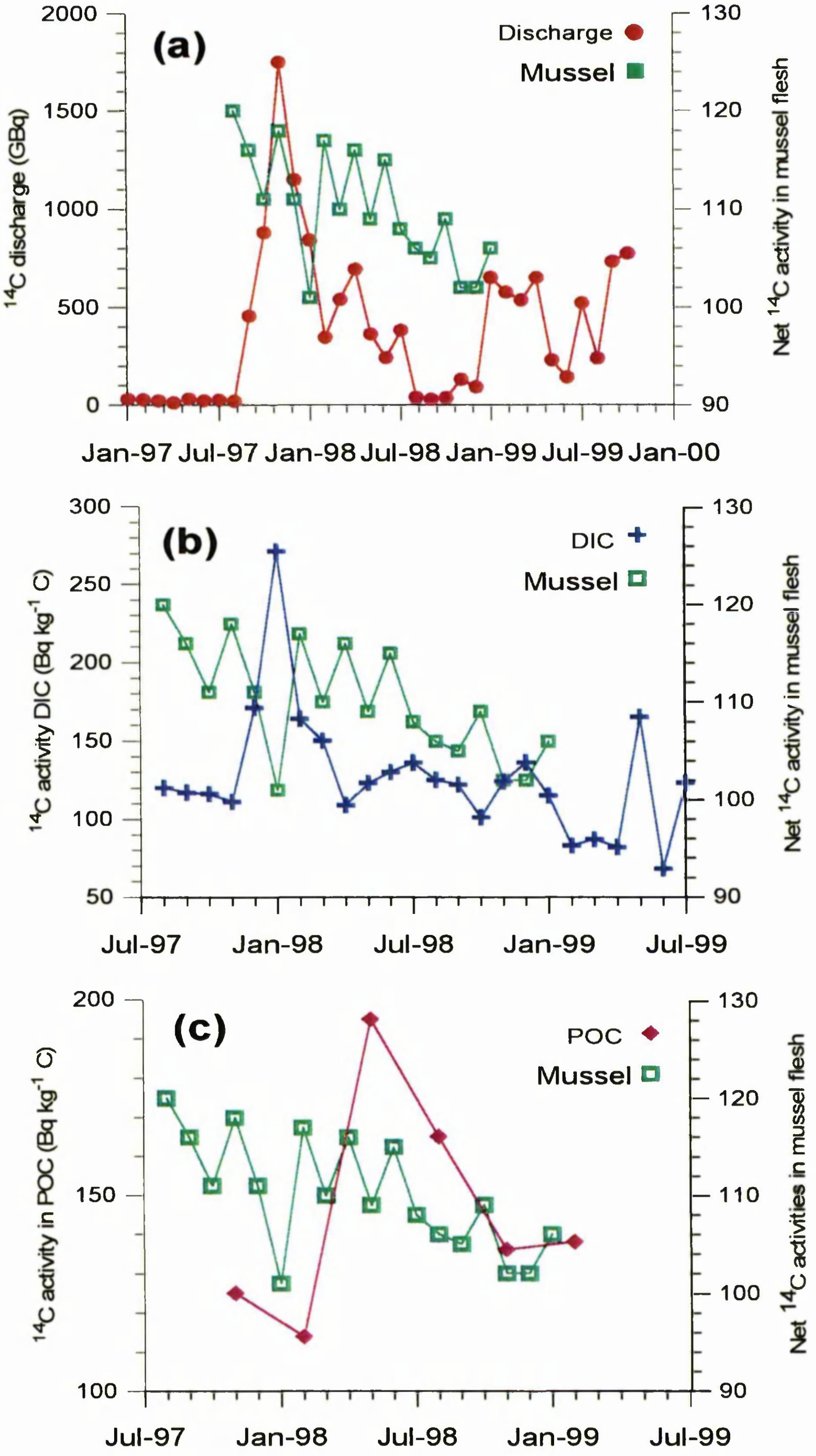
Mussel samples were collected from August 1997 to February 1999, inclusive, and gross ^{14}C activities, net ^{14}C activities above ambient background (Section 3.1) and $\delta^{13}C$ ‰ values (relative to PDB) for mussel flesh are presented in Table 3.14. The net flesh activities were significantly lower than those at Nethertown and ranged between 101 ± 4 and 120 ± 4 Bq kg^{-1} C during the course of the study. From Figure 3.16 it can be seen that there was little variation in the activity of mussel flesh during the study in comparison to the variations in the monthly discharge activities and the activities in the DIC above ambient background. It is readily apparent that the mussels do not respond significantly to transient peaks in either the discharges or in the activity of the DIC (Figure 3.16).

$\delta^{13}C$ values (‰ relative to PDB) for mussel flesh range between - 18.4 and -19.6 ‰ relative to PDB (Table 3.14), similar to those for mussel flesh at Nethertown, indicating that the main food source for these mussels is of marine in origin. As with the Nethertown mussels it was expected that the activity of the mussel flesh would respond to trends in the activity of the POC. From Figure 3.16 however, it is not apparent that there is any connection between the activity of the POC and that of the mussel flesh. As mussels are longer lived than their prey the phytoplankton, their flesh will exhibit an integrated activity with respect to previous POC meals. It is possible that the effect of the POC on mussel flesh activity could be hidden by the fact that the POC activity was analysed on a quarterly basis while the activity of the mussel flesh was analysed on a monthly basis.

Table 3.14. Gross ^{14}C activities (Bq kg^{-1} C ± 1σ) and net ^{14}C activities (*ie.* above ambient background of 246 ± 1 Bq kg^{-1} ± 1σ) in mussel (*Mytilus edulis)* flesh from samples collected at Killantringan Bay (Lat. 54^0 51' N; Long. 05^0 07' W)

Collection Date	Gross ^{14}C activity (Bq kg^{-1} C ± 1σ)	Net ^{14}C activity (Bq kg^{-1} C ± 1σ)	δ^{13} C ‰ (relative to PDB)
Aug. '97	366 ± 2	120 ± 4	- 19.3
Sept. '97	362 ± 2	116 ± 4	- 19.4
Oct. '97	357 ± 2	111 ± 4	- 19.2
Nov. '97	364 ± 2	118 ± 4	- 19.3
Dec. '97	357 ± 2	111 ± 4	- 18.9
Jan. '98	347 ± 2	101 ± 4	- 19.4
Feb. '98	363 ± 2	117 ± 4	-18.8
Mar. '98	356 ± 5	110 ± 5	-18.4
Apr. '98	362 ± 2	116 ± 4	-19.6
May '98	354 ± 2	108 ± 3	- 19.3
June '98	361 ± 2	115 ± 4	-19.6
July '98	354 ± 2	108 ± 4	-19.6
Aug. '98	352 ± 3	106 ± 4	-19.6
Sept. '98	351 ± 2	105 ± 4	- 19.3
Oct. '98	355 ± 2	109 ± 4	-19.5
Nov. '98	348 ± 2	102 ± 4	- 19.2
Dec. '98	348 ± 2	102 ± 4	- 19.4
Jan. '99	352 ± 2	106 ± 4	-19.2

Figure 3.16 Net mussel flesh activities at Killantringan Bay and (a) ^{14}C discharges from Sellafield, (b) the net ^{14}C activity in the DIC at Portpatrick and (c) the quarterly net ^{14}C activity in the POC at Portpatrick.



Seaweed (*Fucus* species)

Seaweed samples were collected on a quarterly basis from February 1998 to November 1999 inclusive. Results for the measured ^{14}C activity, the net ^{14}C activity above ambient background (Section 3.1) and $\delta^{13}C$ values (‰ relative to PDB) are presented in Table 3.15.

Table 3.15 Gross and net ^{14}C activities (*ie.* above ambient background of 253 ± 1 Bq kg^{-1} C ± 1σ and $\delta^{13}C$ values (‰ relative to PDB) in seaweed (*Fucus* sp.) from samples collected at Killantringan Bay (Lat. 54^0 51' N; Long. 05^0 07' W)

Collection date	gross ^{14}C activity (Bq kg^{-1} C)	Net ^{14}C activity (Bq kg^{-1} C)	$\delta^{13}C$ value (‰ relative to PDB)
February 1998	313 ±2	60 ± 3	- 17.5
May 1998	311 ± 2	58 ± 3	-18.0
August 1998	312 ± 2	59 ± 3	-17.9
November 1998	297 ± 2	44 ± 3	-17.4

The net ^{14}C activities in seaweed ranged between 44 ± 3 and 60 ± 3 Bq $kg^{-1}C$. In agreement with the work of Begg (1991) and the activities in the mussel flesh and seaweed at the Nethertown site, the activity of the seaweed is lower than that of the mussels for the same month. This is due to the ability of seaweed (including *Fucus* species) to utilise atmospheric CO_2 for photosynthesis when they are exposed at low tide. As with the seaweed at the Nethertown site it is difficult to make any conclusions based on the small data set and the fact that the seaweed will have incorporated an unknown amount of atmospheric CO_2 *via* photosynthesis.

2.3.3 Mollusc shell activities at Sandyhills Bay

A sample of mixed mollusc shells was collected from a shell bank at Sandyhills Bay (on the south west coast of Scotland) in January 1999. The sample was chosen as an indicator of the activities in the shell material of molluscs at distance from Sellafield. The mixed shell sample had a $\delta^{13}C$ value of - 1.4 ‰ (relative to PDB), a gross ^{14}C activity of 588 ± 2 (Bq kg^{-1} C) and a net ^{14}C activity of 332 ± 2 (Bq kg^{-1} C). These activities are clearly higher than the modern marine ^{14}C background activity, with the excess ^{14}C being Sellafield derived. This excess inorganic carbon will eventually be incorporated into the sediments. This is approximately 4.5 times lower than the activity of mussel shells at Nethertown. Unlike the mussel samples which were collected live form Nethertown, the shells collected at Sandyhill Bay were from a shell bank and there is no way of knowing how long the animals had been dead or indeed if all the shells were contemporary (*ie* growing at the same time), so it is difficult to say whether or not the difference in activity between the shells at Nethertown and Sandyhills Bay is due to the distance from the pipeline, differences in uptake of ^{14}C by different species or related to the time in which each shell formed, potentially reflecting different years of discharge from Sellafield.

Despite the distance from Sellafield it is clear that mollusc shells contain Sellafield derived ^{14}C, as these shells will eventually be broken down and incorporated into the inorganic carbon fraction of the sediment these results show a viable pathway for incorporation of Sellafield derived ^{14}C into the inorganic carbon fraction of the sediments of the NE Irish Sea.

3.3.4 Dose calculation from consumption of mussel flesh from Nethertown.

As the bulk of the sampling during this study was carried out in 1998, consumption rates for 1998 (SEPA, RIFE 1999) were used and calculated doses from activities measured during this study were compared with those published for 1998. The dose to the Sellafield seafood-consuming critical group was calculated as follows: (i) by taking an average value for the net ^{14}C activities of mussel flesh from Nethertown of 1,403 ± 10 Bq kg^{-1} C, (ii) using the average wet:dry weight ratio of 5.05 and percent carbon content of 35 % to convert ^{14}C activities from units of Bq kg^{-1} C to Bq kg^{-1} fresh weight, (iii) using the consumption rates for the Sellafield fishing group (formerly the Sellafield critical group), given in SEPA (RIFE 1999) of 45 kg y^{-1} (cod and plaice), 28 kg y^{-1} (crab, nephrops and lobster) and 15 kg y^{-1} (winkles and other molluscs) and (iv) dose per unit intake by ingestion values (5.80×10^{-10} Sv Bq^{-1} for ^{14}C) from ICRP-60 (ICRP, 1991). The obvious deviation from the method is that this study only considers the mussel flesh. Assuming that the activities of the fish, crustacea and molluscs are similar to that of the mussel flesh this gives a dose of 0.005 mSv due to ^{14}C. This value is very close to that of 0.006 mSv for the individual radiation exposure of the Sellafield fishing community due to ^{14}C present in consumed fish and thus for dose implications it would appear that increasing the weight of mussels from Nethertown eaten by the Sellafield critical group would not significantly increase the individual radiation exposure due to ^{14}C present in consumed fish and shellfish from the Irish Sea.

Alternatively, calculating the dose to the Sellafield fishing group from the above data due only to consumption of mussels (15 kg) gives a dose of 4.08 x 10^{-4} mSv Bq^{-1}, showing that the dose from consumption of mussels alone is low and indeed is one order of magnitude lower than the overall dose of 0.006 mSv Bq^{-1} published by SEPA (RIFE) 1998 for the Sellafield fishing group.

3.4 Distributions and inventories of Sellafield derived ^{14}C, ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239,240}Pu$ in the sediments of the NE Irish Sea

The sediments of the NE Irish Sea have been extensively studied both as repositories of Sellafield derived radionuclides and to investigate the continuing re-distribution of these radionuclides. Seven Pederson (Kemp 1976) cores and five Van Veem grabs (Section 2.1.5) were collected during the course of this study and analysed for ^{14}C (in the inorganic and organic carbon fractions), ^{137}Cs and ^{241}Am activities. In addition, three of the cores (1, 4 and 7)were also analysed for ^{238}Pu and $^{239,240}Pu$ activities. The sediment regime in the NE Irish Sea is one of low accumulation rates, rapid and intense mixing and re-distribution. The intensity of sediment mixing has been inferred from the distribution of Sellafield-derived radionuclides and more specifically, their activity ratios in previous studies Kershaw *et al.* 1983; 1984; Mackenzie *et al.* 1998). In accordance with this procedure, which is discussed in detail in MacKenzie *et al.* (1998), each of cores 1-7 was subdivided into zones of differing mixing intensities, based on the ^{137}Cs and ^{241}Am activities and the activity ratios as follows: ^{137}Cs:^{241}Am ratios (a) of <1 - indicative of very high intensity mixing, (b) ratios of <2 indicative of high intensity mixing (c) 2 to 6 - indicative of medium intensity mixing, (d) ratios of >6 - indicative of low intensity mixing. This was done in order to relate the depth of penetration of Sellafield derived ^{14}C (in both the inorganic and organic carbon fraction) to the physical mixing characteristics of the sediment column.

Discussion of the cores is presented according to latitude, starting with the southernmost. Results for individual cores are discussed in Sections 3.4.1 to 3.4.7, followed by a discussion of trends between cores in Section 3.4.8. The grabs samples are discussed in section 3.4.9 and calculations of the total inventories of ^{137}Cs, ^{241}Am, ^{238}Pu, $^{239/240}Pu$ and Sellafield derived ^{14}C

activities in the inorganic and organic carbon fractions of the sediment for the NE Irish Sea are presented in Section 3.4.10.

3.4.1 Core 1 (PC 186)

Core 1 (PC186) was 90 cm in length and was the southernmost core collected at Latitude 54^0 05'N, Longitude 03^0 30' W. This core was analysed for ^{137}Cs, and ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) in the bulk sediments and ^{14}C activities (Bq kg^{-1} C) in the bulk inorganic and organic carbon fraction of the sediments.

3.4.1.1 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry sediment) and ^{137}Cs:^{241}Am activity ratios

The ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight) and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.16 and Figure 3.17. The ^{137}Cs specific activities range from 40 ± 0.1 to 523 ± 0.6 Bq kg^{-1}, with a broad subsurface peak between 20 and 40 cm depth. The ^{241}Am specific activities ranged from 0.6 ± 0.03 to 558 ± 1.1 Bq kg^{-1}. In contrast to the ^{137}Cs profile, there are two distinct ^{241}Am subsurface peaks between 4-6 and 20 - 25 cm. It was observed during the processing of this core that the sediment in the 4-6 cm section appeared to contain more fine grained material than other sections. Previous studies have shown that ^{241}Am is associated with fine grained sedimentary particles (McDonald *et al.* 1990; McCartney *et al.* 1994) so it is possible that the peak at 4 - 6 cm is due to elevated clay particle concentration in this section. Unfortunately this project did not have the scope for sediment grain size analysis, but it would be recommended that particle size analysis is carried out in future studies. It is clear from Figure 3.17 that the peak in activities at 20-25 cm corresponds to the ^{137}Cs peak in activities.

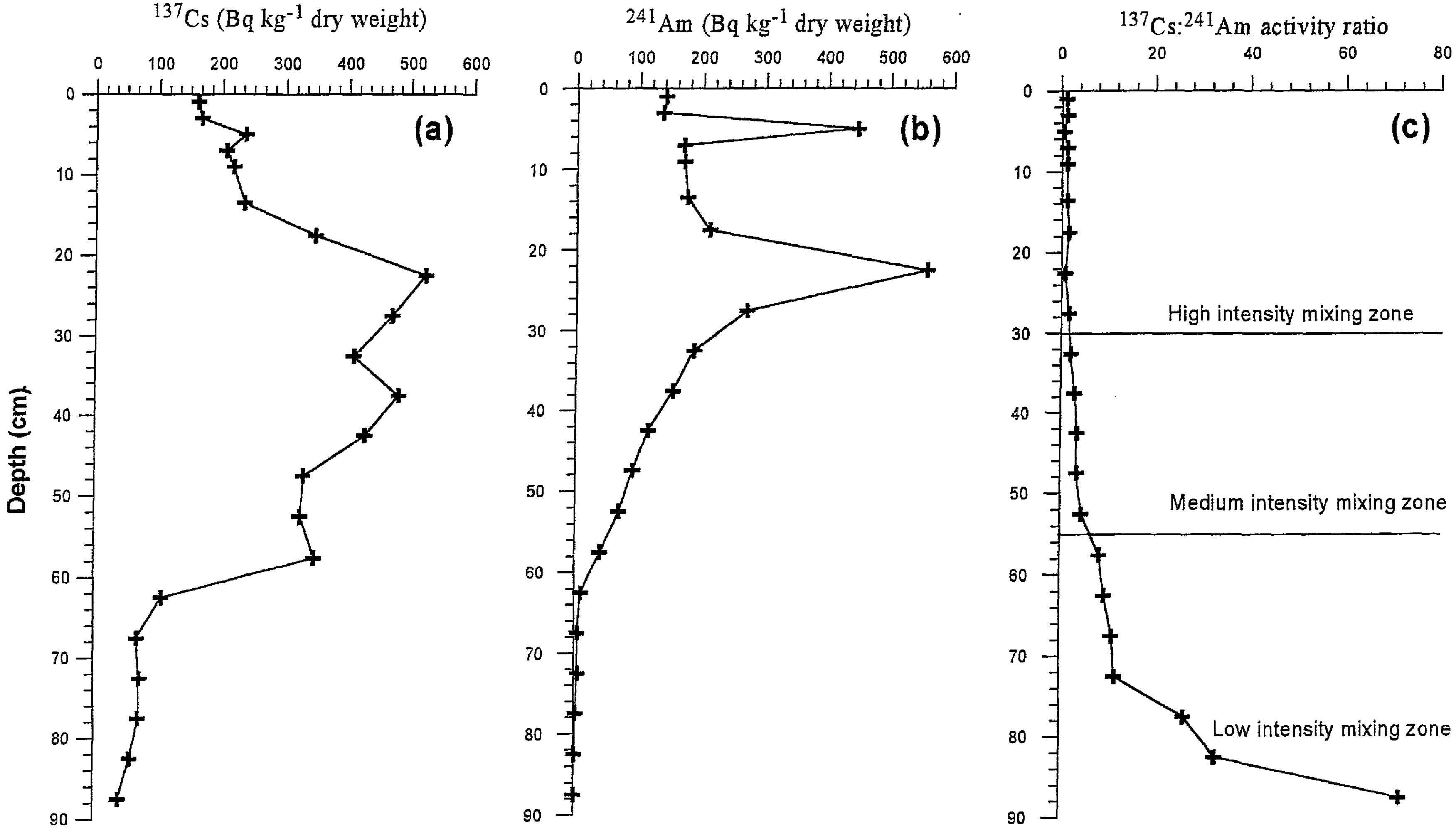
^{137}Cs:^{241}Am activity ratios in Core 1 were used to define zones with differing mixing intensities with the high, medium and low intensity mixing zones penetrating from 0 - 30 cm, 30 - 55cm and 55 cm to the base of the core, respectively. The lowest ^{137}Cs:^{241}Am ratios were found between 0 and 8 cm (with the exception of 20 to 25 cm segment) indicative of loss of ^{137}C from the surface sediment to the overlying water column. The activity ratios between 75 cm and the base of the core are much higher than expected on the basis of previously reported values for surface sediments (Hetherington *et al.* 1975, MAFF 1978-1995; Environment agency/SEPA 1995-1998) and records of activity ratios preserved in accumulating sediments

(Kershaw *et al.* 1990; 1992; MacKenzie *et al.* 1994; MacKenzie and Scott 1993; Pulford *et al.* 1998). These high activity ratios are possibly due to dissolution of ^{137}Cs to the sediment pore waters followed by diffusive transport of ^{137}Cs from areas of high concentration to areas of low concentration deeper in the sediments.

Table 3.16 ^{137}Cs, ^{241}Am activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 1 (PC186). Latitude 54^{0} 05'N, Longitude 03^{0} 30' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratio
0-2	161 ± 0.1	141 ± 0.2	1.1 ± 0.001
2-4	167 ± 0.2	136 ± 0.3	1.2 ± 0.003
4-6	236 ± 0.4	446 ± 1.3	0.5 ± 0.002
6-8	206 ± 0.2	170 ± 0.3	1.2 ± 0.003
8-10	218 ± 0.2	171 ± 0.3	1.3 ± 0.003
10-15	235 ± 0.3	176 ± 0.4	1.3 ± 0.003
15-20	347 ± 0.4	211 ± 0.4	1.6 ± 0.004
20-25	523 ± 0.6	558 ± 1.1	0.9 ± 0.002
25-30	470 ± 0.6	271 ± 0.6	1.7 ± 0.004
30-35	409 ± 0.5	187 ± 0.4	2.2 ± 0.006
35-40	481 ± 0.9	155 ± 0.5	3.1 ± 0.011
40-45	427 ± 0.8	116 ± 0.3	3.7 ± 0.013
45-50	330 ± 0.6	91 ± 0.3	3.6 ± 0.012
50-55	325 ± 0.4	70 ± 0.1	4.6 ± 0.011
55-60	348 ± 0.4	41 ± 0.1	8.6 ± 0.027
60-65	108 ± 0.1	11 ± 0.04	9.8 ± 0.037
65-70	69 ± 0.1	6 ± 0.04	11.5 ± 0.017
70-75	73 ± 0.1	6 ± 0.04	12.2 ± 0.017
75-80	70 ± 0.1	3 ± 0.04	23.3 ± 0.037
80-85	58 ± 0.1	2 ± 0.03	29.0 ± 0.056
85-90	40 ± 0.1	0.6 ± 0.03	66.7 ± 0.334

Figure 3.17 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c) ^{137}Cs:^{241}Am activity ratios for Core 1 (PC186)



3.4.1.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

The ^{14}C activities (Bq kg^{-1} C ± 1σ), ages (y BP) and $\delta^{13}C$ values (‰ relative to PDB) in the inorganic and organic carbon fractions of the sediment are presented in Table 3.17 and Figure 3.18. The ^{14}C specific activity of the inorganic carbon fraction of the sediment ranged from 43 ± 2 to 49 ± 1 Bq kg^{-1} C. There is no variation in the inorganic carbon activities in this core, with the lowest and highest values being within 2σ of each other. In agreement with conclusions from previous studies (Cook *et al.* 1995, Wolstenholme *et al.* 1999), it is clear from the ages that there is pre-Holocene inorganic carbon present in the sediment (>10,000 y BP) of Core 1. The $\delta^{13}C$ values for the inorganic carbon fraction of the sediment range from + 0.6 to + 0.7 indicating a marine origin. The activities and $\delta^{13}C$ values are similar to those reported by previous authors for the inorganic fraction of sediment from the NE Irish Sea (Kershaw 1986; Kershaw *et al.* 1988; Cook 1995; Wolstenholme 1999).

The ^{14}C specific activities of the organic carbon fraction of the sediment ranged from 119 ± 2 to 348 ± 2 Bq kg^{-1} C and exhibited a trend of decreasing activity with depth. The regional marine background ^{14}C specific activity used during this study was approximately 250 Bq kg^{-1} C (Section 3.1) while the surface (0 - 2 cm) activity of this core was 48 Bq kg^{-1} C, significantly higher than the background level and consistent with a significant input of Sellafield derived ^{14}C to the organic carbon fraction the sediment. The elevated ^{14}C specific activities in both the DIC and POC in this area (Section 2.3) suggest that the transfer route is from DIC to POC *via* primary production and subsequent settling of organic material from the water column. Woodhead (1988) and MacKenzie *et al.* (1998) have shown that there is rapid (approximately 1 year) mixing of the upper sections (0 - 10 cm) of the sediment in this area while mixing to about 18 cm takes approximately 5 years. The ^{14}C specific activity of organic carbon in the 15-20 cm section of Core 1 is lower than the 0-2 cm section and the current ambient background, but is significantly higher than that of the lower sections.

The $\delta^{13}C$ values for the organic carbon fraction of the sediment ranged from - 23.5 to - 24.6 ‰ indicating a mixture of marine and terrestrial organic carbon.

Table 3.17 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ), ages (yBP) and δ^{13}C values (‰ relative to PDB) and in sediment from Core 1 (PC186). Latitude 54^0 05'N, Longitude 03^0 30' W

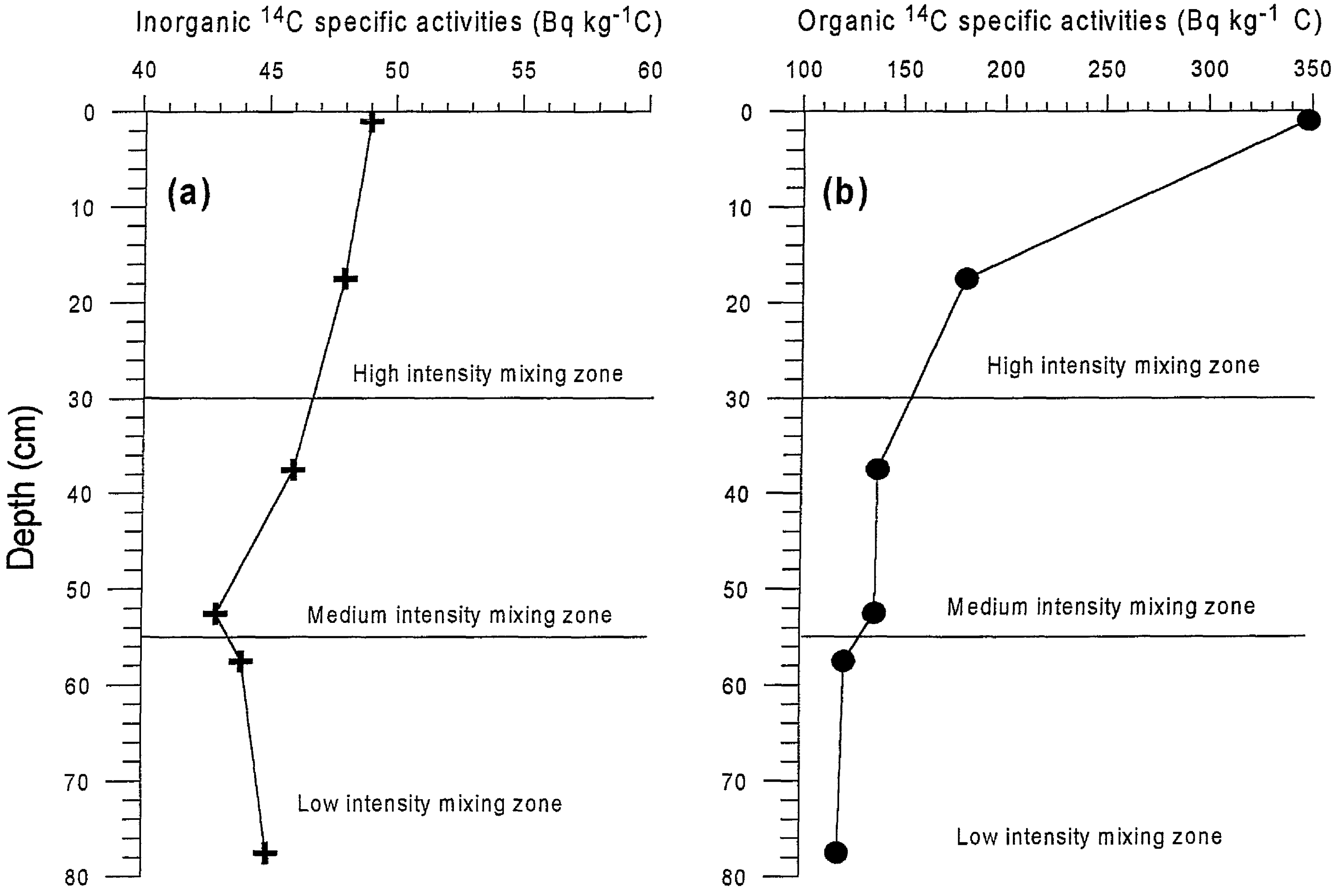
Depth (cm)	^{14}C Inorganic (Bq kg^{-1} C)	Inorganic ^{14}C ages (yBP)	inorganic δ^{13}C values	^{14}C Organic (Bq kg^{-1} C)	Organic ^{14}C ages (yBP)	organic δ^{13}C values
0-2	49 ± 1	12,585 ± 95	N/A	348 ± 2	modern	N/A
15-20	48 ± 1	12,830 ± 180	+ 0.6	181 ± 3	1,760 ± 100	- 23.6
35-40	46 ± 2	13,210 ± 220	+ 0.6	138 ± 2	3,920 ± 100	- 23.5
50-55	43 ± 2	13,680 ± 180	+ 0.6	127 ± 2	4,630 ± 110	- 23.8
55-60	44 ± 3	13,600 ± 390	+ 0.6	122 ± 2	4,890 ± 100	- 24.4
75-80	45 ± 1	13,390 ± 140	+ 0.7	119 ± 2	5,100 ± 130	- 24.6

3.4.1.3.Radionuclide inventories in Core 1 (PC186)

Inventories were calculated for the radionuclides present in Cores 1 to 7, however the inventories have some limitations as the cores are of differing lengths, most notably Cores 2 and 7 which are significantly shorter than the other cores. In the case of ^{137}Cs, ^{241}Am ^{238}Pu and ^{239,240}Pu the inventories should be calculated from cores which penetrate the sediment to below the depth of radionuclide penetration. In none of the cores collected were any of these radionuclides below the limit of detection so the inventories presented here are best estimates based on the data available.

For the inorganic and organic carbon fractions of the sediment, firstly a suitable background activity must be found. The difficulties in choosing suitable ^{14}C background activities for the inorganic and organic carbon fractions of the sediment were discussed in Section 3.1. Backgrounds which represent the lower limit for the origional sediment activity were taken from a saltmarsh core (Wolstenholme 1999) and represent the upper limit for inventory calculations as these activities probably underestimate the pre-Sellafield activity of the

Figure 3.18. Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 1 (PC186).



sediment. The higher values were calculated from the activities measured in the low activity mixing zones and represent the lower limit for inventory calculations as they almost certainly overestimate the pre-Sellafield activity of the sediments as they almost certainly contain some ^{14}C from nuclear weapons testing and historical Sellafield discharges. These background activities are 0 and 45 Bq kg^{-1} C for the inorganic carbon fraction of the sediment and 131 and 98 Bq kg^{-1} C for the organic carbon fraction of the sediment.

Radionuclide inventories for ^{137}Cs and ^{241}Am (Appendix 4) were calculated for each section of core using the sediment dry weight (Appendix 3), the core diameter of 8.25 cm and the measured activities presented in Table 3.16 for ^{137}Cs and ^{241}Am, giving total inventories in Core 1 of 3.1 x 10^5 Bq m^{-2} for ^{137}Cs and 1.5 x 10^5 Bq m^{-2} for ^{241}Am (Table 3.18).

Using the wet:dry weight ratios, the % inorganic and % organic carbon (Appendix 5), the diameter of the core tubing and the ^{14}C activities presented in Table 3.17, ^{14}C inventories were calculated for the mixing zones and for the total core using both sets of backgrounds giving the results shown in Table 3.18. This calculation suggests upper and lower limits for the ^{14}C inventory in the inorganic fraction of 534 and 17 Bq m^{-2} respectively and corresponding values of 624 and 428 Bq m^{-2} for the organic fraction.

Table 3.18 ^{137}Cs, ^{241}Am, and inorganic and organic ^{14}C activity inventories (Bq m^{-2}) in Core 1 PC(186)

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	Upper limit ^{14}C inorganic (Bq m^{-2})	Lower limit ^{14}C inorganic (Bq m^{-2})	Upper limit ^{14}C organic (Bq m^{-2})	Lower limit ^{14}C organic (Bq m^{-2})
3.1 x 10^5	1.5 x 10^5	534	17	624	428

3.4.2 Core 2 (PC85)

Core 2 (PC85) was 60 cm in length and was collected at Latitude 54^0 11' N, Longitude 03^0 31' W (the same location as the Sellafield South core reported by Wolstenholme (1999)). Core 2 was analysed for ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight ± 1σ) in the bulk sediment and ^{14}C specific activities (Bq kg^{-1} C ± 1σ) in the inorganic and organic carbon fractions.

3.4.2.1 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry sediment)

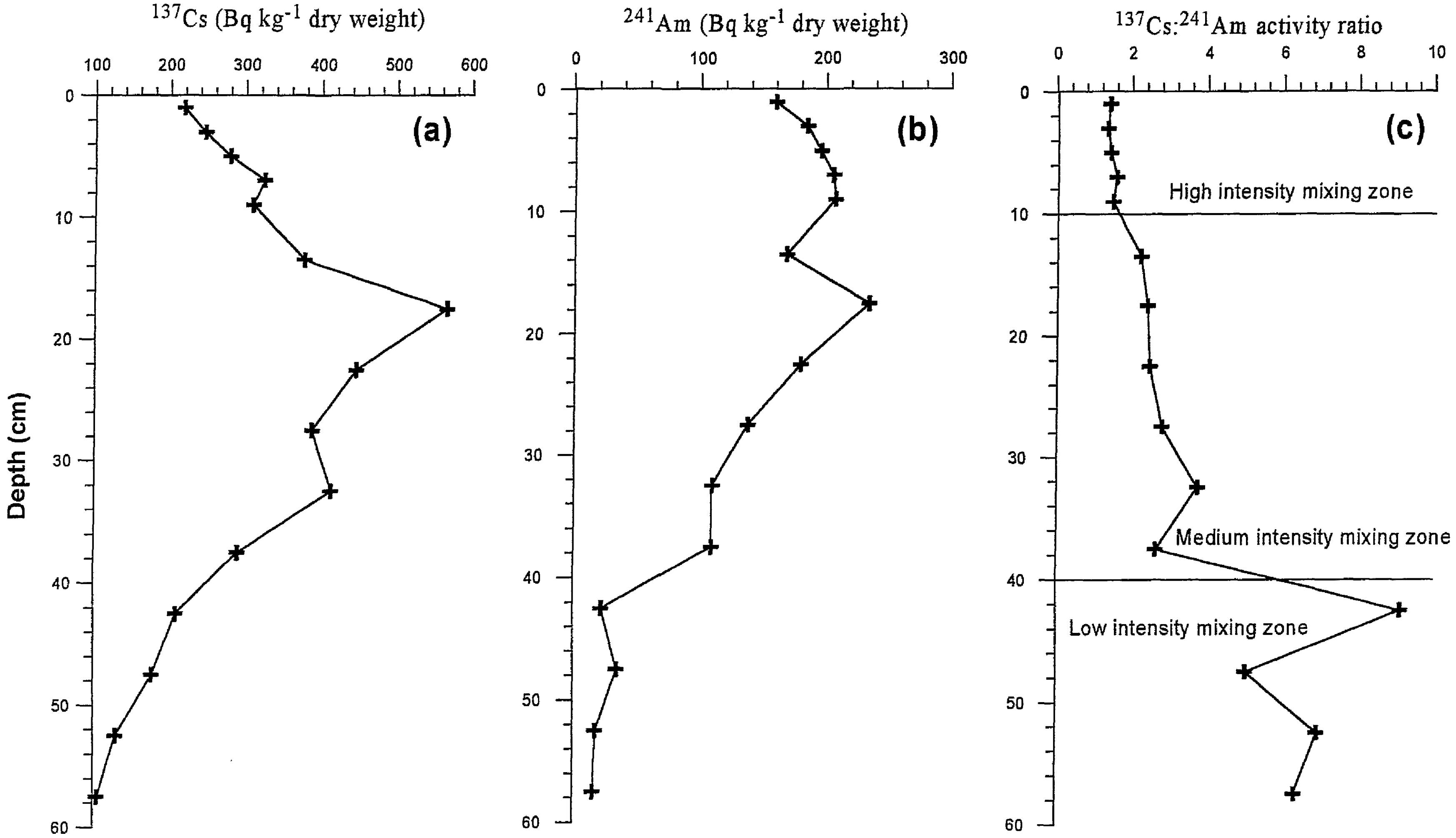
The ^{137}Cs and ^{241}Am specific activities and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.19 and Figure 3.19. The ^{137}Cs specific activities ranged from 106 ± 0.1 to 567 ± 0.6 Bq kg^{-1} and exhibited a subsurface maximum (Figure 3.19a) at 15-20 cm depth. The ^{241}Am specific activities ranged from 17 ± 0.1 to 235 ± 0.5 Bq kg^{-1} and, like the ^{137}Cs, exhibited a subsurface peak at 15-20 cm (Figure 3.19b). These ranges are slightly lower than those of 59 - 757 for ^{137}Cs and 15 ± 1 and 315 ± 6 for ^{241}Am reported by Wolstenholme (1999) for a core ("Sellafield South" core) collected from this location in 1995. Previous studies have shown that the distribution of radionuclides in sediments of the NE Irish Sea is not homogeneous, for example Kershaw *et al.* (1983) reported different activities for different subsamples from the same box core, so caution must be exercised in drawing direct comparisons between activities in Wolstenholmes "Sellafield South" core and Core 2. However, some similarities are apparent, with both having a peak in both ^{137}Cs and ^{241}Am activities at 15-20 cm depth. However, in surface sediments (0-8 cm) ^{137}Cs activities were higher in the Sellafield South core than in Core 2 (with average activities of 278 Bq kg^{-1} dry weight $\pm 1\sigma$ compared to 266 Bq kg^{-1} dry weight $\pm 1\sigma$, respectively) as were the ^{241}Am activities (with average activities of 200 Bq kg^{-1} dry weight $\pm 1\sigma$ compared to 186 Bq kg^{-1} dry weight $\pm 1\sigma$, respectively). These differences could represent temporal variations in the radionuclide activities and inventories at this location, but, as indicated above they may simply reflect heterogeneity in the distribution of radionuclides in the sediment.

^{137}Cs:^{241}Am activity ratios in Core 2 ranged from 1.4 to 9.1 (Table 3.19 and Figure 3.19c). Using the method described by MacKenzie *et al.* (1998), Core 2 was divided into mixing intensity zones of; 0-10 cm; high intensity mixing, 10 - 40 cm; medium intensity mixing and > 40 cm; low intensity mixing. The depths of the mixing zones for Core 2 are shallower than those of Core 1 and it is possible that this is due to a difference in infaunal species composition influenced by sediment texture (Core 1 was collected from an area of sandy mud, while Core 2 was collected from an area of muddy sand, Institute of Geological Studies; Sheet Number 54N 04W), but no information on species composition was gathered during the course of this project. While the ^{137}Cs:^{241}Am activity ratios for Wolstenholmes "Sellafield South" core were similar to those of Core 2, mixing zones for the "Sellafield South" core were slightly different ranging from 0 - 16 cm for the high intensity mixing zone, 16 - 64 cm for the medium intensity mixing zone and 64 cm to the base of the core for the low intensity mixing zone.

Table 3.19 ^{137}Cs and ^{241}Am specific activities (Bq kg-1 dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 2 (PC85) Latitude 54^{0} 11' N, Longitude 03^{0} 31' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratio.
0-2	218 ± 0.1	159 ± 0.2	1.4 ± 0.001
2-4	246 ± 0.3	184 ± 0.4	1.3 ± 0.003
4-6	279 ± 0.3	196 ± 0.4	1.4 ± 0.002
6-8	324 ± 0.4	206 ± 0.4	1.6 ± 0.002
8-10	309 ± 0.4	208 ± 0.4	1.5 ± 0.002
10-15	377 ± 0.4	169 ± 0.4	2.2 ± 0.002
15-20	567 ± 0.6	235 ± 0.5	2.4 ± 0.003
20-25	446 ± 0.5	180 ± 0.5	2.5 ± 0.003
25-30	388 ± 0.4	138 ± 0.3	2.8 ± 0.003
30-35	413 ± 0.5	110 ± 0.2	3.8 ± 0.005
35-40	291 ± 0.3	110 ± 0.2	2.7 ± 0.003
40-45	210 ± 0.2	23 ± 0.1	9.1 ± 0.009
45-50	179 ± 0.2	35 ± 0.1	5.0 ± 0.013
50-55	130 ± 0.2	19 ± 0.1	6.9 ± 0.011
55-60	106 ± 0.1	17 ± 0.1	6.2 ± 0.006

Figure 3.19 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c) ^{137}Cs:^{241}Am activity ratios for Core 2 (PC85)



3.4.2.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

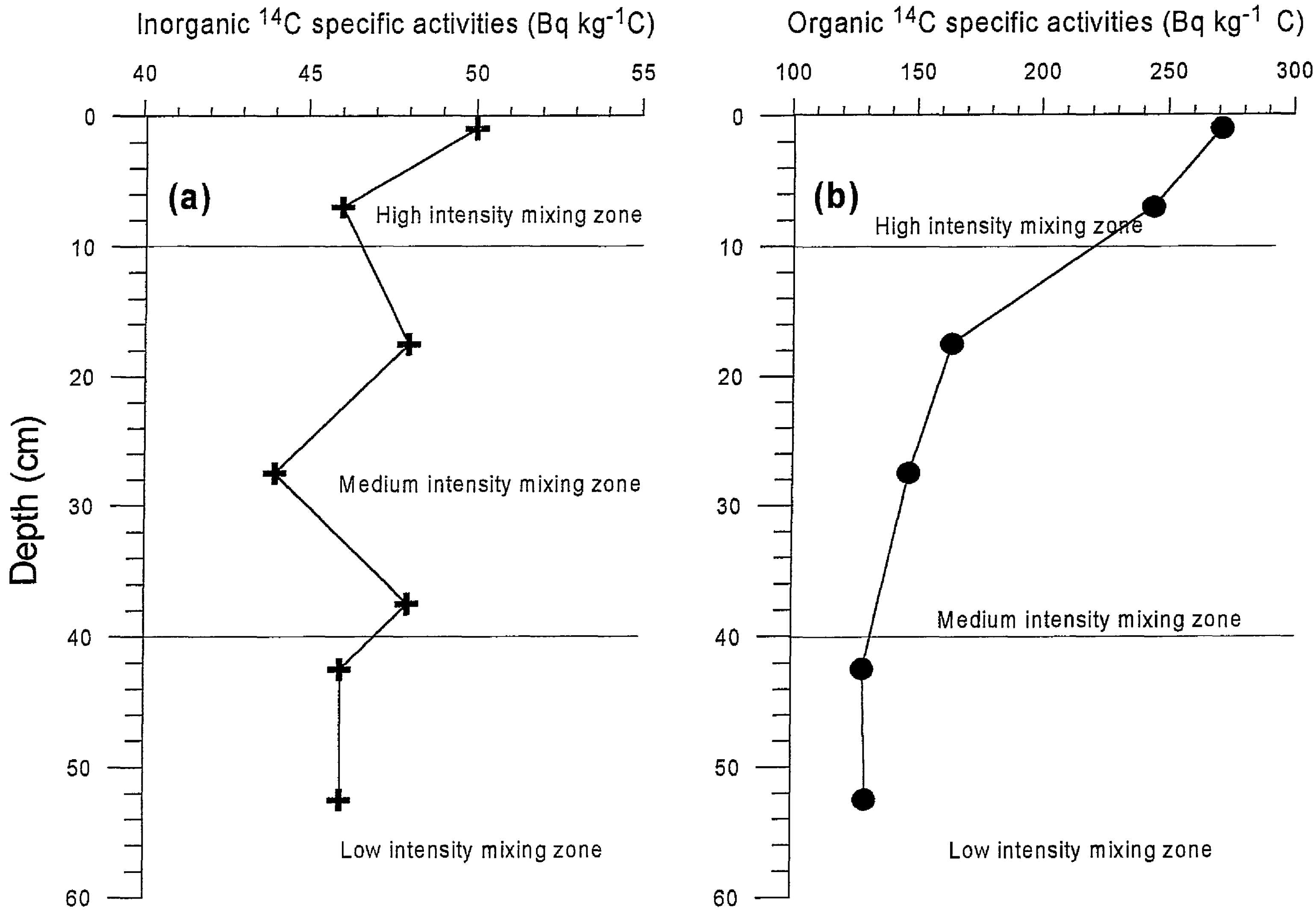
The inorganic and organic ^{14}C specific activities, ages and δ^{13}C values relative to PDB for Core 2 are presented in Table 3.20 and Figure 3.20. The ^{14}C specific activity of the inorganic fraction of the sediment ranged from 44 ± 0.4 to 50 ± 1 Bq kg^{-1} C. It can be seen from Figure 3.20 that there is little variation in the activity with depth. As with Core 1, it is clear from the ages (y BP) of the inorganic sediment that pre-Holocene material is present in the inorganic carbon fraction. The δ^{13}C values ranged from + 0.3 to + 0.6 ‰ (relative to PDB) and as with Core 1, demonstrate a marine origin for inorganic carbon in this core.

Table 3.20 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ) and ages (y BP) and δ^{13}C values (‰ relative to PDB) in sediment from Core 2(PC85) Latitude 54^0 11' N, Longitude 03^0 31' W

Depth	^{14}C Inorganic (Bq kg^{-1} C)	Inorganic ^{14}C ages (y BP)	Inorganic δ^{13}C values	^{14}C Organic (Bq kg^{-1} C)	Organic ^{14}C ages (y BP)	Organic δ^{13}C values
0-2 cm	50 ± 1	12,515 ± 80	+ 0.6	271 ± 2	modern	- 26.1
6-8 cm	46 ± 2	13,140 ± 95	+ 0.6	244 ± 2	modern	N/A
15-20 cm	48 ± 2	12,780 ± 70	+ 0.4	164 ± 2	2,560 ± 70	- 22.9
25-30 cm	44 ± 0.4	13,520 ± 80	+ 0.2	147 ± 1	3,500 ± 80	- 19.3
35-40 cm	48 ± 1	12,760 ± 170	+ 0.3	129 ± 3	4,440 ± 100	- 24.7
40-45 cm	46 ± 1	13,195 ± 90	+ 0.6	129 ± 2	4,570 ± ^{14}0	- 18.6
50-55 cm	46 ± 1	13,080 ± 80	+ 0.3	130 ± 1	4,420 ± 60	- 23.6

The ^{14}C activity of the organic carbon fraction of the sediment ranged from 129 ± 3 to 271 ± 2 Bq kg^{-1} C and it can be seen from Figure 3.20 that there is a trend of decreasing activity with depth in this core. As with Core 1, it is clear that there has been a recent (within the past 5

Figure 3.20 Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 2 (PC85).



years) input of ^{14}C enhanced (Sellafield derived) organic material to the surface sediment. The activities from 35 cm to the base of the core are within 2σ error of each other and are similar to the estimated activity of 131 Bq kg^{-1} C for Holocene production suggesting that little Sellafield ^{14}C in the organic fraction has been mixed to this depth. The δ^{13}C values ranged from - 18.6 to - 26.1 ‰ (relative to PDB) suggesting a mixture of marine and terrestrial origin for organic carbon to the sediment in this core. It is interesting that the marine ^{13}C signal is at depth in the core and it is unfortunate that the δ^{13}C value for 6- 8 cm depth increment is not available, as it would be interesting to see if the terrestrial signal that is found in the surface segment (0 - 2 cm) is also to be found in the 6 - 8 cm section.

3.4.2.3 ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight) and ^{238}Pu:^{239,240}Pu and ^{241}Am:^{239,240}Pu activity ratios

^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight)and ^{238}Pu:^{239,240}Pu and ^{241}Am:^{239,240}Pu activity ratios for Core 2 (PC85) are presented in Table 3.21 and Figure 3.21. The ^{238}Pu specific activities ranged between 0.4 ± 0.08 and 28 ± 2 Bq kg^{-1} while those of ^{239,240}Pu ranged from 3 ± 0.2 to 166 ± 6 Bq kg^{-1}. In comparison with the frequency of sampling for ^{137}Cs and ^{241}Am, sampling for the plutonium radioisotopes is less frequent, however the distribution of specific activities with depth for both ^{238}Pu and ^{239,240}Pu is similar to that of the other radionuclides, exhibiting a subsurface maxima at approximately 15 - 20 cm.

The ^{238}Pu:^{239,240}Pu activity ratios in the 4 - 6 and 15 - 20 cm sections are close to the value for the time integrated Sellafield discharge (to 1997) of 0.182 (Gray *et al.* 1995; BNFL 1998) indicating that the sediment is well mixed and homogenous with respect to the integrated discharges to a depth of 20cm. Below 20 cm the activity ratios are more variable and range from, 0.126 to 0.214, confirming that the sediment is less well mixed at depth. The variability in the activity ratios is not as large as that in the annual Sellafield ^{238}Pu:^{239,240}Pu discharge ratios which range from 0.029 to 0.361 (Gray *et al.* 1995). The ^{241}Am:^{239,240}Pu activity ratios in Core 2 range from 1.34 ± 0.003 to 3.40 ± 0.025 while that for the time integrated Sellafield discharge (accounting for decay of ^{241}Pu to ^{241}Am) to 1997 is 1.67 (Gray *et al.* 1995; BNFL 1998). From Table 3.21 it can be seen that the activity ratio in the surface sediment is higher than the time integrated ratio, while those for sediment between 15 and 45 cm are similar to the time integrated ratio. From the ^{137}Cs:^{241}Am and ^{238}Pu:^{239,240}Pu ratios it has been shown that the surface sediment is well mixed so to a depth of 20 cm, implying that the high ^{241}Am:^{239,240}Pu ratio in the surface sediments is due to an additional process that is either adding ^{241}Am with respect to ^{239,240}Pu or reducing ^{239,240}Pu with respect to ^{241}Am. Pentreath *et al.* (1984) Cook *et al.* (1997) have shown that plutonium is re-dissolving from the sediment, so it is more likely that the high surface ^{241}Am:^{239,240}Pu ratios are due to re-dissolution of ^{239,240}Pu. The highest ^{241}Am:^{239,240}Pu ratio (3.40 ± 0.009) is found in the 55 - 60 cm section, this value is within the range of annual ^{241}Am:^{239,240}Pu Sellafield discharge ratios of 0.69 - 3.92 (allowing for ingrowth of ^{241}Pu). It is very similar to the discharge ratio for 1974 of 3.2, and so implies lower mixing rates at depth in the sediment.

Table 3.21 ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight), ^{238}Pu:^{239,240}Pu and ^{241}Am:^{239,240}Pu activity ratios in Core 2 (PC85). Latitude 54^{0} 11' N, Longitude 03^{0} 42' W

Depth in core	^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu	^{241}Am:^{239,240}Pu
4 - 6 cm	18 ± 1	102 ± 8	0.176 ± 0.011	2.02 ± 0.009
15 - 20	24 ± 1	127 ± 6	0.189 ± 0.012	1.85 ± 0.008
25 - 30	13 ± 1	103 ± 2	0.126 ± 0.001	1.34 ± 0.003
40 - 45	3 ± 0.2	14 ± 3	0.214 ± 0.024	1.64 ± 0.008
55 - 60	0.8 ± 0.08	5 ± 0.2	0.160 ± 0.016	3.40 ± 0.025

3.4.2.4 Radionuclide inventories in Core 2 (PC85)

^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu inventories (Bq m^{-2}) (Appendix 5 for plutonium inventory calculation) were calculated in Core 2 (PC85)to be 2.1 x 10^{5} Bq m^{-2} for ^{137}Cs, 0.8 x 10^{5} Bq m^{-2} for ^{241}Am 6.8 x 10^{3} Bq m^{-2} for ^{238}Pu and 4.6 x 10^{4} Bq m^{-2} for $^{239/240}$Pu (Table 3.22a). The ^{137}Cs and ^{241}Am activity inventories are lower than those found in Core 1, possibly due to the difference in core length (90cm for Core 1 and 60 cm for Core 2).

Upper and lower limits for ^{14}C inventories (Bq m^{-2}) were calculated (Table 3.22b) as described in Section 3.4.1.3 giving inventories of 375 and 18 Bq m^{-2} for the inorganic carbon fraction of the sediment and of 214 and 125 Bq kg^{-1} C for the organic carbon fraction of the sediment. Similar to the ^{137}Cs and ^{241}Am inventories the inorganic and organic ^{14}C activity inventories are lower than those found in Core 1.

Figure 3.21 (a) ^{238}Pu specific activities (Bg kg^{-1} dry weight), (b) $^{239/240}$Pu specific activites (Bq kg^{-1} dry weight), (c) ^{238}Pu:$^{239/240}$Pu and (d) ^{241}Am:^{239,240}Pu activity ratios for Core 2 (PC85)

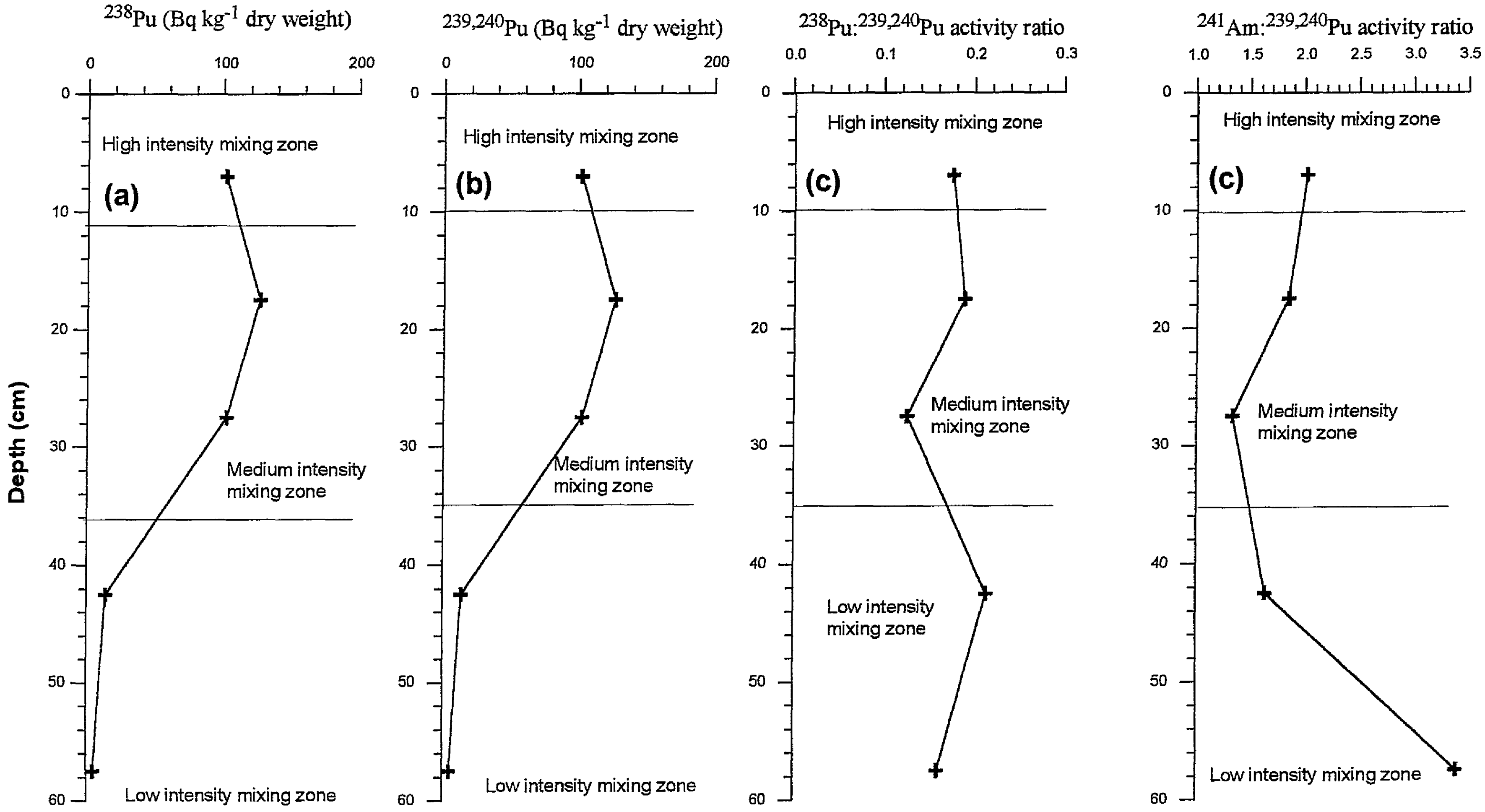


Table 3.22(a) ^{137}Cs, ^{241}Am, ^{238}Pu, $^{239/240}$Pu inventories (Bq m^{-2}) in Core 2 PC(85). Latitude 54^0 11' N, Longitude 03^0 31' W

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	^{238}Pu (Bq m^{-2})	$^{239/240}$Pu (Bq m^{-2})
2.1 x 10^5	7.9 x 10^4	6.8 x 10^3	4.6 x 10^4

Table 3.22(b) Upper and lower limits for inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 2 PC(85). Latitude 54^0 11' N, Longitude 03^0 31' W

Upper limit ^{14}C inorganic (0 Bq kg^{-1} C)	Lower limit ^{14}C inorganic (45 Bq kg^{-1} C)	Upper limit ^{14}C organic (98 Bq kg^{-1} C)	Lower limit ^{14}C organic (131 Bq kg^{-1} C)
375	18	214	125

3.4.3 Core 3 (PC87)

Core 3 (PC87) was 90 cm in length and was collected from Latitude 54^0 17' N, Longitude 03^0 38' W, the same location as the "Sellafield" core presented by Wolstenholme (1999). Core 3 was analysed for ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight) in the bulk sediment and ^{14}C specific activities (Bq kg^{-1} C) in the bulk inorganic and organic carbon fractions of the sediment.

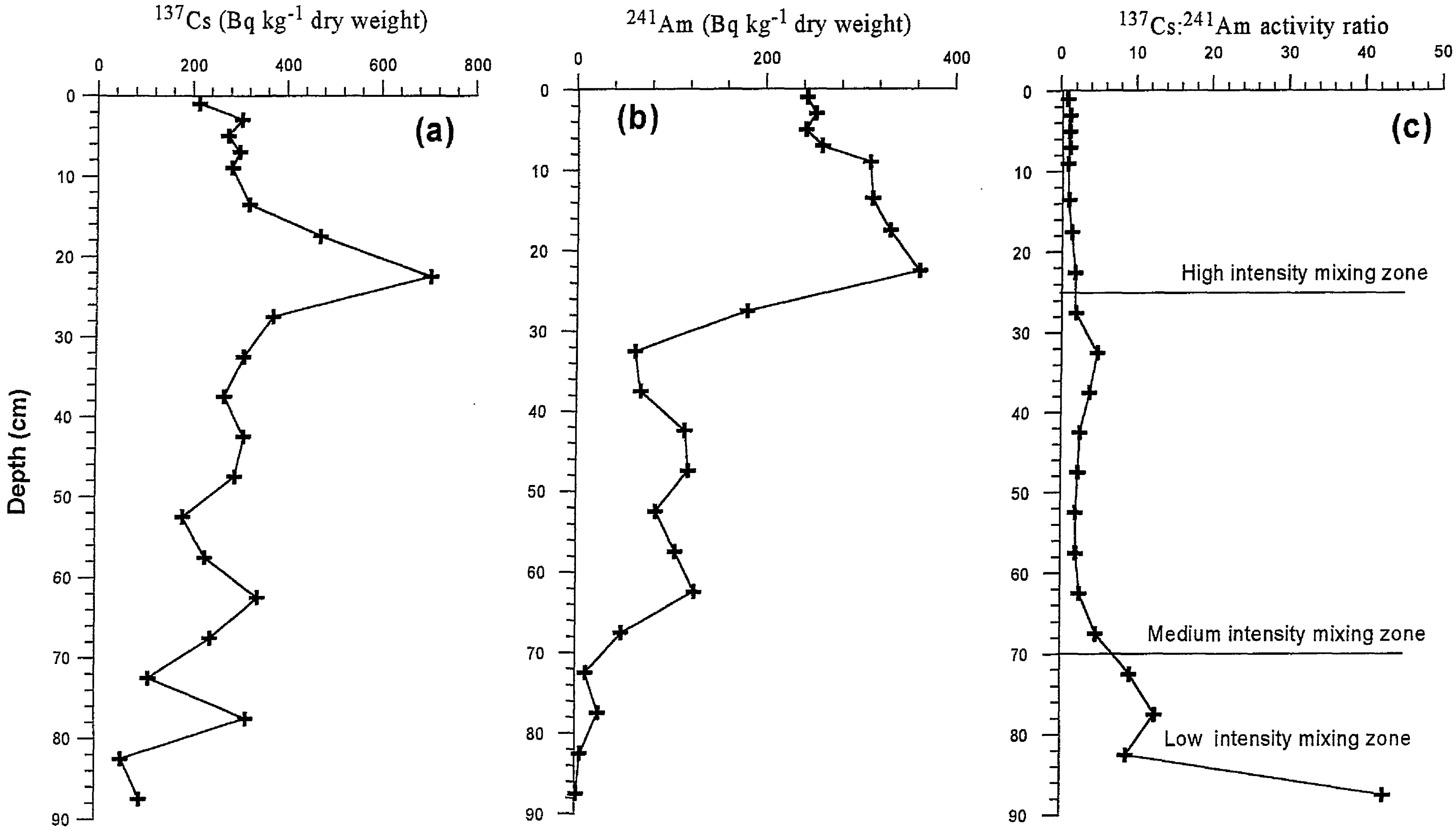
3.4.3.1 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight)

Results for the ^{137}Cs and ^{241}Am specific activities and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.23 and Figure 3.22. ^{137}Cs specific activities ranged from 56 ± 0.1 to 705 ± 0.6 (Bq kg^{-1}). From Figure 3.23 it can be seen that there is a distinct subsurface maximum for ^{137}Cs at a depth of between 20 and 25 cm. The surface activity of ^{137}Cs for Core 3 is similar to that of Core 2 (PC85) but higher than that of Core 1 (PC186). The ^{241}Am activities for Core 3 ranged between 2.2 ± 0.1 and 362 ± 0.7 Bq kg^{-1} with a subsurface maximum at 20 - 25 cm depth. For Core 3, the ^{241}Am activities from the surface to 30 cm are higher than those of either Core 1 or 2. The surface (0-8 cm) ^{137}Cs and ^{241}Am specific activities in Core 3 are lower then those reported for Wolstenholmes "Sellafield" core. The ^{137}Cs:^{241}Am activity ratios in Core 3 range from 0.9 ± 0.004 to 42.7 ± 0.134 (Table 3.23) and as with Cores 1 and 2, Core 3 was divided into zones of different mixing intensities based on the ^{137}Cs:^{241}Am activity ratios: high intensity

Table 3.23 ^{137}C and ^{241}Am specific activities (Bq kg^{-1} dry wt ± 1σ) and ^{137}Cs:^{241}Am activity ratios for sediment from Core 3 (PC87). Latitude 54^{0} 17' N, Longitude 03^{0} 38' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratio
0-2	213 ± 0.1	243 ± 0.3	0.9 ± 0.004
2-4	304 ± 0.3	252 ± 0.3	1.2 ± 0.002
4-6	275 ± 0.3	242 ± 0.5	1.1 ± 0.001
6-8	298 ± 0.3	259 ± 0.5	1.2 ± 0.001
8-10	283 ± 0.3	310 ± 0.6	0.9 ± 0.001
10-15	320 ± 0.4	312 ± 0.6	1.0 ± 0.001
15-20	472 ± 0.5	331 ± 0.7	1.4 ± 0.001
20-25	705 ± 0.6	362 ± 0.7	1.9 ± 0.002
25-30	373 ± 0.4	181 ± 0.4	2.1 ± 0.002
30-35	310 ± 0.3	63 ± 0.1	4.9 ± 0.004
35-40	270 ± 0.3	69 ± 0.1	3.9 ± 0.004
40-45	311 ± 0.3	116 ± 0.2	2.7 ± 0.003
45-50	293 ± 0.3	120 ± 0.2	2.4 ± 0.003
50-55	184 ± 0.2	85 ± 0.2	2.2 ± 0.002
55-60	231 ± 0.3	106 ± 0.2	2.2 ± 0.003
60-65	343 ± 0.4	127 ± 0.3	2.7 ± 0.003
65-70	243 ± 0.3	50 ± 0.1	4.9 ± 0.006
70-75	113 ± 0.1	12 ± 0.1	9.4 ± 0.009
75-80	318 ± 0.4	25 ± 0.1	12.7 ± 0.016
80-85	56± 0.1	6.3 ± 0.1	8.9 ± 0.018
85-90	94 ± 0.1	2.2 ± 0.1	42.7 ± 0.134

Figure 3.22 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c)^{137}Cs:^{241}Am activity ratios for Core 6 (PC87)



mixing (0-25 cm), medium intensity mixing (25-70 cm) and low intensity mixing (70 cm to the base of the core). In the high intensity mixing zone, the 0-2 cm depth increment has a ^{137}Cs:^{241}Am activity ratio of 0.9 indicating that there has been prolonged exposure of this sediment to seawater leading to re-dissolution of ^{137}Cs from the sediment (Mackenzie *et al.* 1998; Wolstenholme 1999). In the low intensity mixing zone, the lowermost section has a ^{137}Cs:^{241}Am activity ratio of 42.8, which indicates, as with Core 1, that there has been dissolution of ^{137}Cs from the sediment into the pore waters followed by diffusive transport to depth in the sediment. The ^{137}Cs:^{241}Am activity ratios at depth in Core 3 are similar to those in Core 1. The ^{137}Cs:^{241}Am activity ratios for the "Sellafield" core studied by Wolstenholme (1999) were similar to those for Core 3 at the same depths. The depths of the different mixing intensity zones were also similar in both cores.

3.4.3.2 ^{14}C activities in the inorganic and organic carbon fractions of the sediment

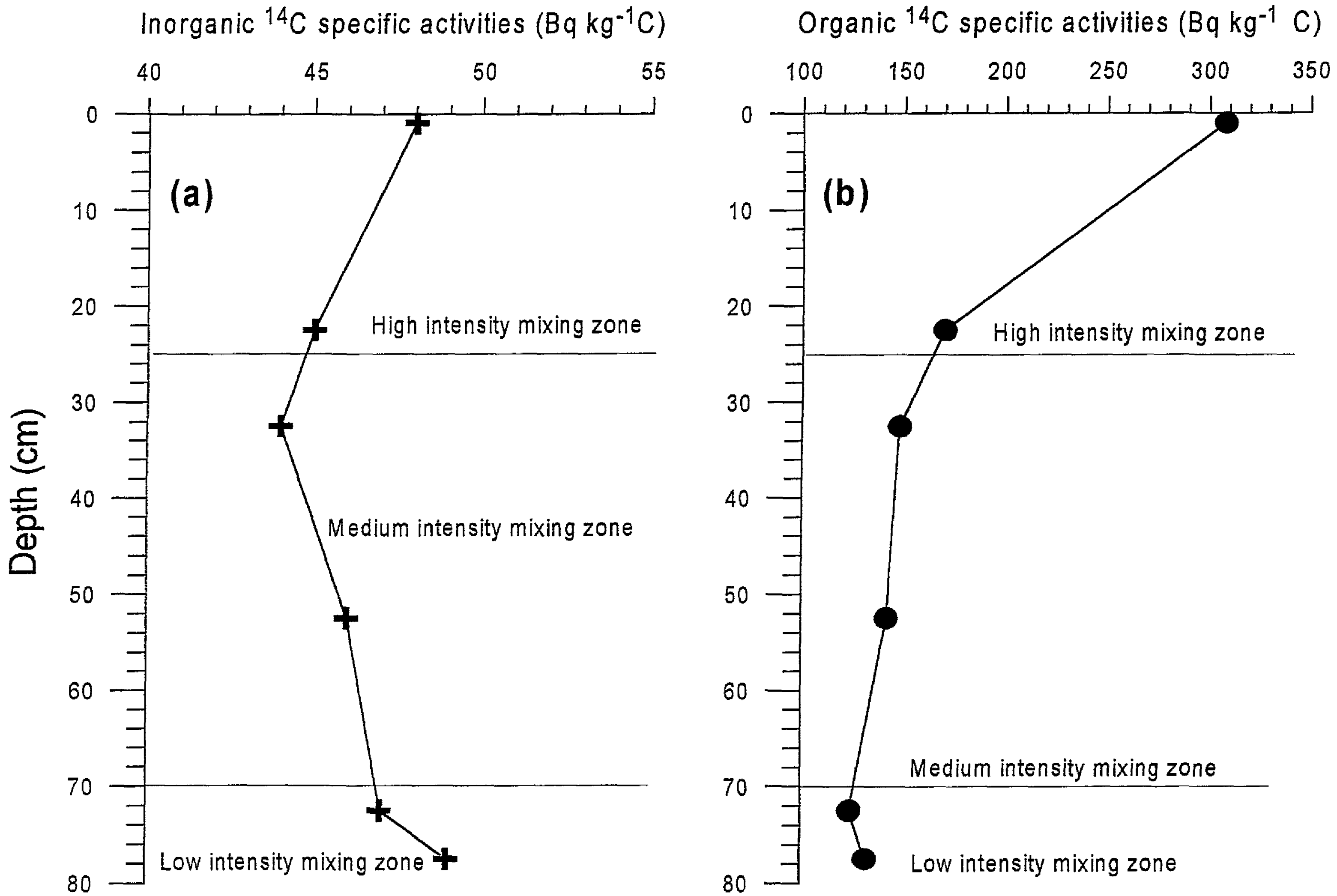
The ^{14}C activities in the inorganic and organic carbon fractions of the sediment are presented in Table 3.24 and Figure 3.23. The inorganic ^{14}C activities ranged from 44 ± 1 to 48 ± 1 Bq kg^{-1} C. It is clear that there is little variation in the inorganic ^{14}C activities as the lowest and highest activities in this core are within 2σ error. As with Cores 1 and 2, the ages of the inorganic carbon fraction of the sediment show that there is pre-Holocene material present in the inorganic carbon fraction of this core. These values are similar to the inorganic ^{14}C values for Cores 1 and 2 and to the activities of the Sellafield Core reported by Wolstenholme (1999) which ranged between 46 ± 1 and 53 ± 2 (Bq kg^{-1} C). The δ^{13}C values for the inorganic carbon fraction of the sediment ranged from + 0.5 to + 0.6 ‰ (relative to PDB) indicating a marine origin for the inorganic carbon for the sediment in this core.

The ^{14}C activities for the organic carbon fraction of the sediment ranged from 124 ± 2 to 308 ± 2 Bq kg^{-1} C and exhibit a trend of decreasing activity with depth in the core. The activity of 308 ± 2 Bq kg^{-1} C in the 0-2 cm section is higher than that found at the same depth in Core 2 but is lower than that found at the same depth in Core 1 As with Core 1 and 2, this activity shows that there has been a recent input of ^{14}C enhanced (Sellafield derived) organic material to the surface sediments. The δ^{13}C value for the 0-2 cm section indicates that this organic matter is of marine origin. The activities in the low intensity mixing zone are close to the estimated activity of 131 Bq kg^{-1} C for average production during the Holocene. The surface sediment organic ^{14}C activities in Core 3 are higher than those reported for the Sellafield core presented by Wolstenholme (1999), but similar in activity to the medium and low intensity mixing zones. The organic carbon $\delta^{13}C$ values ranged between - 19.9 and - 23.6 ‰ (relative to PDB) values that are less negative than those found in Core 1 or 2 and seem to exhibit a trend of increasingly negative $\delta^{13}C$ values with depth in the core. It would seem that this core has had recent inputs of marine organic matter but that in the past there have been inputs of terrestrial organic matter. It is possible the increasingly terrestrial $\delta^{13}C$ value with depth in the core is due to the removal by biota and bacteria of the more labile organic compounds, which are of marine origin, leaving behind the less nutritious organic material such as humic acids, which are of terrestrial origin.

Table 3.24 Inorganic and organic ^{14}C specific activities (Bq kg^{-1} C ± 1σ) ages (y BP) and $\delta^{13}C$ values (‰ relative to PDB) in sediment from Core 3 (PC87). Latitude 54^0 17' N, Longitude 03^0 38' W

Depth	^{14}C Inorganic	Inorganic ^{14}C ages (y BP)	Inorganic $\delta^{13}C$ values	^{14}C Organic	Organic ^{14}C ages (y BP)	Organic $\delta^{13}C$ values
0-2 cm	48 ± 1	12,840 ± 85	+ 0.5	308 ± 2	modern	- 20.5
20-25 cm	45 ± 1	13,360 ± 100	+ 0.5	170 ± 2	2,320 ± 70	- 19.9
30-35 cm	44 ± 1	13,480 ± 100	+ 0.5	148 ± 2	3,390 ± 80	-22.7
50-55 cm	46 ± 1	13,170 ± 80	+ 0.5	142 ± 2	3,740 ± 70	- 22.6
70-75 cm	47 ± 1	13,050 ± 130	+ 0.6	124 ± 2	4,830 ± 90	- 22.3
75-80 cm	49 ± 1	12,670 ± 80	+ 0.6	132 ± 2	4,280 ± 90	- 23.6

Figure 3.23 Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 3 (PC87).



3.4.3.3 Radionuclide inventories in Core 3 (PC87)

Using the same method as with the other cores (Appendix 4) ^{137}Cs and ^{241}Am inventories were calculated, giving values of 2.8 x 10^5 and 1.3 x 10^5 Bq m^{-2} for ^{137}Cs and ^{241}Am respectively (Table 3.25).

Using the method described in section 3.4.1.3 upper and lower limits for inorganic and organic ^{14}C inventories were calculated for Core 3, giving ^{14}C inventories of 457 and 19 Bq m^{-2} for the inorganic carbon fraction and 421 and 247 Bq m^{-2} for the organic carbon fraction (Table 3.25). Wolstenholme (1999) calculated an organic ^{14}C inventory (using a background value of 131 Bq kg^{-1} C) of 180 Bq m^{-2} for the "Sellafield" core. As no errors have been ascribed to these inventories it is difficult to know whether these values are similar or not, but possibly indicate an overall increase in Sellafield derived ^{14}C to the organic carbon fraction of the sediment in this area since 1996.

Table 3.25 ^{137}Cs, ^{241}Am, and inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 3 PC(87). Latitude 54^0 17' N, Longitude 03^0 38' W

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	Upper limit $^{14}C_{inorg}$ (Bq m^{-2})	Lower limit $^{14}C_{inorg}$ (Bq m^{-2})	Upper limit $^{14}C_{org}$ (Bq m^{-2})	Lower limit $^{14}C_{org}$ (Bq m^{-2})
2.8 x 10^5	1.3 x 10^5	457	19	421	247

3.4.4. Core 4 (PC89)

Core 4 (PC89) was 95 cm in length and was collected at Latitude 54^0 19' N, Longitude 03^0 42' W. The bulk sediment was analysed for ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight) and the inorganic and organic carbon fractions were analysed for ^{14}C activities (Bq kg^{-1} C).

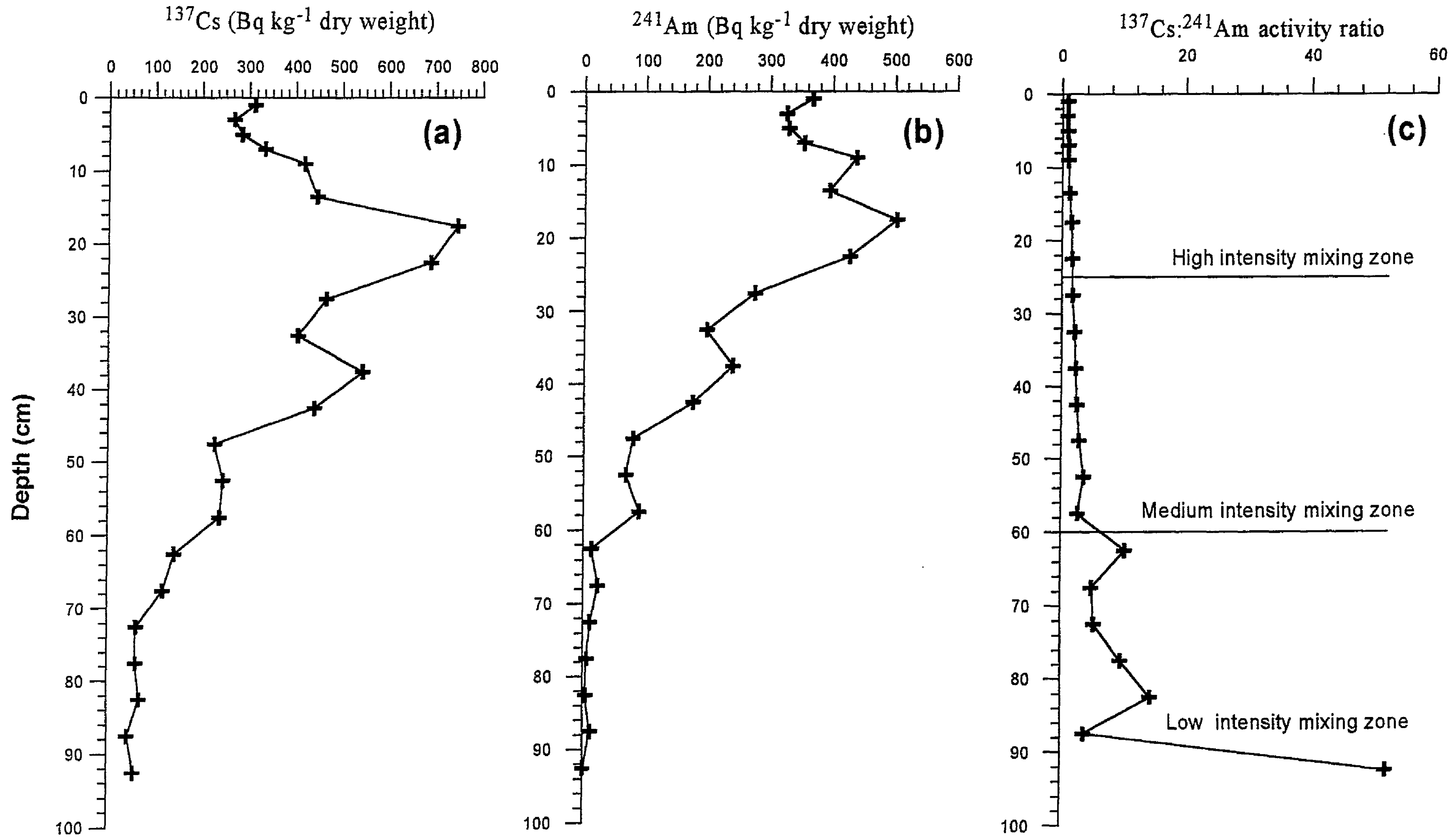
3.4.4.1 ^{137}Cs and ^{241}Am specific activities

The ^{137}Cs and ^{241}Am specific activities and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.26 and Figure 3.24. The ^{137}Cs specific activities ranged between 44 ± 0.1 and 689 ± 0.8 Bq kg^{-1} with two subsurface peaks the larger at 15-20 cm depth, and the smaller at 35-40 cm depth. Surface sediment (0-8 cm) ^{137}Cs specific activities are higher in Core 4 than in Cores 1

Table 3.26 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 4 (PC89). Latitude 54^0 19' N, Longitude 03^0 42' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratio
0-2	312 ± 0.1	368 ± 0.3	0.8 ± 0.001
2-4	268 ± 0.1	326 ± 0.3	0.8 ± 0.001
4-6	284 ± 0.3	329 ± 0.7	0.9 ± 0.001
6-8	334 ± 0.4	354 ± 0.7	0.9 ± 0.001
8-10	418 ± 0.5	438 ± 0.9	1.0 ± 0.001
10-15	426 ± 0.5	394 ± 0.8	1.1 ± 0.001
15-20	747 ± 0.8	502 ± 1.0	1.5 ± 0.002
20-25	689 ± 0.8	427 ± 0.8	1.6 ± 0.002
25-30	466 ± 0.5	276 ± 0.6	1.7 ± 0.002
30-35	406 ± 0.4	199 ± 0.4	2.0 ± 0.002
35-40	545 ± 0.6	241 ± 0.5	2.3 ± 0.003
40-45	442 ± 0.5	177 ± 0.4	2.5 ± 0.003
45-50	229 ± 0.3	80 ± 0.2	2.9 ± 0.004
50-55	247 ± 0.3	69 ± 0.1	3.6 ± 0.004
55-60	240 ± 0.3	91 ± 0.2	2.6 ± 0.003
60-65	143 ± 0.2	14 ± 0.1	10.2 ± 0.015
65-70	119 ± 0.2	24 ± 0.1	5.0 ± 0.008
70-75	62 ± 0.1	12 ± 0.1	5.2 ± 0.008
75-80	61 ± 0.1	6 ± 0.1	10.2 ± 0.026
80-85	69 ± 0.1	5 ± 0.1	13.8 ± 0.020
85-90	44 ± 0.1	12 ± 0.1	3.7 ± 0.009
90-95	57 ± 0.1	1.1 ± 0.1	51.8 ± 0.519

Figure 3.24 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c) ^{137}Cs:^{241}Am activity ratios for Core 4 (PC89)



to 3. The ^{241}Am specific activities in Core 4 ranged between 1.1 ± 0.1 and 502 ± 1.0 Bq kg^{-1} and exhibited subsurface trends in activity similar to those of ^{137}Cs with a peak at 15 - 20 cm depth. As with ^{137}Cs, the surface sediment (0 - 8 cm) ^{241}Am specific activities for Core 4 are higher than those for Cores 1 to 3. ^{137}Cs:^{241}Am activity ratios for Core 4 range from 0.8 ± 0.001 to 51.8 ± 0.519. As with Cores 1 to 3 the activity ratios were used to divide Core 4 into the following mixing zones, 0 - 8 cm very high intensity mixing zone, 8 - 25 cm high intensity mixing zone, 25 - 60 cm the medium intensity mixing zone and 60 cm to the base of the core the low intensity mixing zone. While the surface activities for ^{137}Cs and ^{241}Am are higher than those for Cores 1 to 3, the surface sediment ^{137}Cs:^{241}Am activity ratios for Core 4 are lower than in the previous cores, with values of < 1.0 found to 8 cm depth, indicating exposure of these sediments to seawater resulting in of ^{137}Cs. In the 90 - 95 cm section, the activity ratio of 51.8 ± 0.52 again suggests downward diffusion of ^{137}Cs.

3.4.4.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

The ^{14}C activities in the inorganic and organic carbon fractions of the sediment are presented in Table 3.27 and Figure 3.25. The inorganic ^{14}C specific activities range between 44 ± 1 and 55 ± 1 Bq kg^{-1} C. The activity of the surface sediment (0-2 cm) is slightly higher than that of Cores 1 - 3, while activities in the medium and low intensity mixing zones of Core 4 are similar to those of Cores 1 to 3. As with cores 1 to 3 the δ^{13}C values for Core 4, which range from + 0.3 to + 0.5, show that the inorganic carbon fraction of the sediment is marine in origin.

The organic ^{14}C activities in Core 4 ranged from 133 ± 2 to 352 ± 2 Bq kg^{-1} C and exhibit a trend of decreasing activity with increasing depth in the sediment. The surface (0 - 2 cm)activity of Core 4 is significantly higher than those of Cores 2 and 3, but is similar in activity to that of Core 1, however, the activities for the medium and low intensity mixing zones in Core 4 are similar to those found in Cores 1 to 3. As in Cores 1 to 3 the ^{14}C specific activity and δ^{13}C value, of the 0 -2 cm section shows that there has been a recent input of ^{14}C enhanced (Sellafield derived) marine organic material to the sediment surface. The δ^{13}C values of the organic carbon fraction of Core 4 ranged from - 20.8 to - 23.1 with increasingly negative δ^{13}C values with increasing depth in the sediment. It is clear from this that the main source of organic carbon to the surface sediments is marine in origin, but there is possibly a terrestrial carbon influence at depth in the core, possibly due to consumption of organic material of marine origin by benthic organisms.

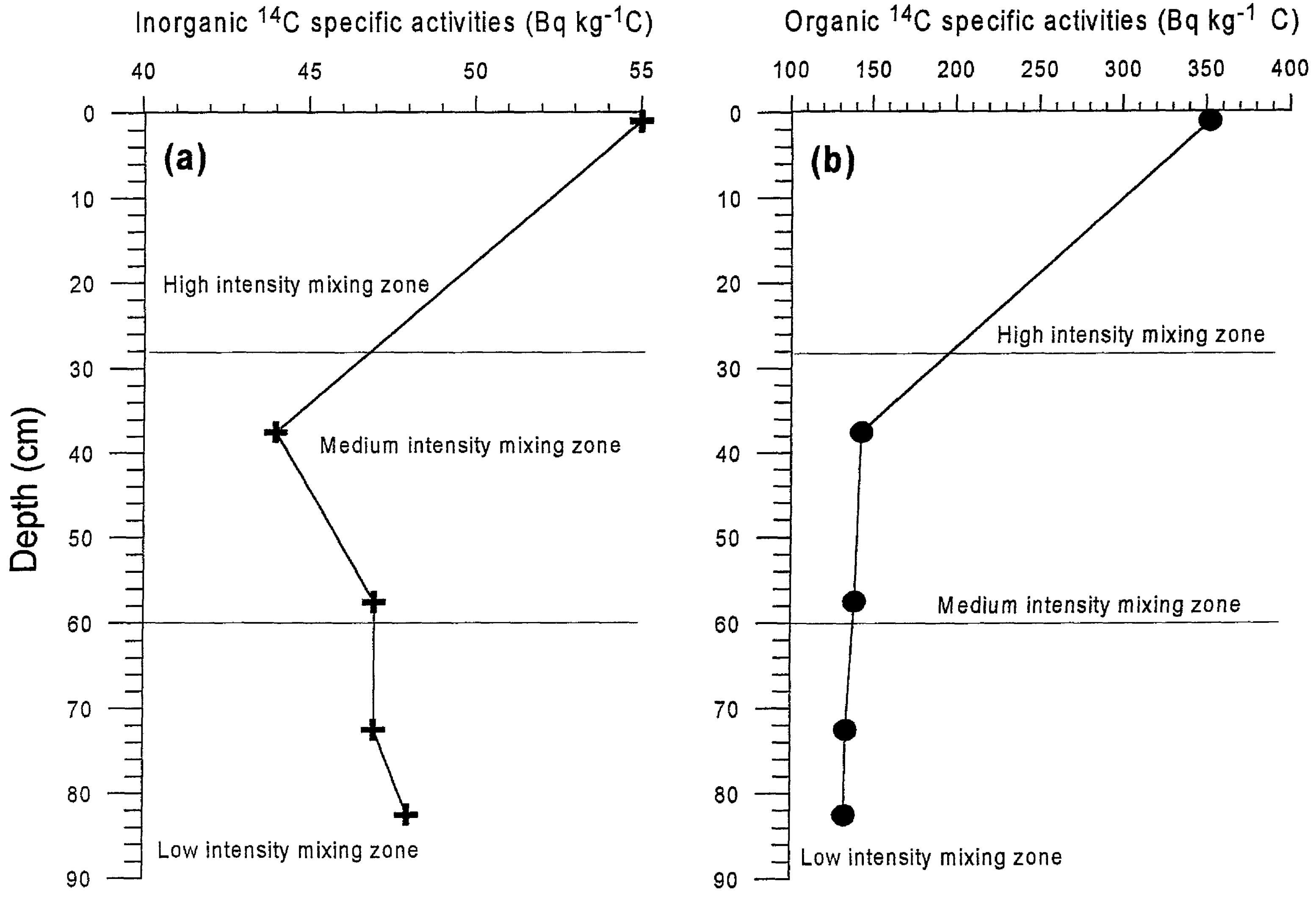
Table 3.27 Inorganic and organic carbon ^{14}C activities (Bq kg^{-1} C ± 1σ), ages (yBP) and $\delta^{13}C$ values (‰ relative to PDB) in sediment from Core 4 (PC89). Latitude 54^0 19' N, Longitude 03^0 42' W

Depth	^{14}C Inorganic (Bq kg^{-1} C)	Inorganic ^{14}C ages (yBP)	inorganic $\delta^{13}C$ values	^{14}C Organic (Bq kg^{-1} C)	Organic ^{14}C ages (yBP)	organic $\delta^{13}C$ values
0-2 cm	55 ± 1	11,655 ± 75	+ 0.4	352 ± 2	modern	- 20.8
35-40 cm	44 ± 1	13,560 ± 100	+ 0.4	143 ± 2	3,720 ± 70	- 21.1
55-60 cm	47 ± 1	12,950 ± 90	+ 0.5	139 ± 2	3,910 ± 70	- 22.5
70-75 cm	47 ± 1	12,970 ± 90	+ 0.5	134 ± 2	4,210 ± 70	- 22.8
80-85 cm	48 ± 1	12,740 ± 70	+ 0.3	133 ± 2	4,260 ± 70	- 23.1

3.4.4.3 ^{238}Pu and $^{239,240}Pu$ specific activities

^{238}Pu and $^{239,240}Pu$ specific activities and activity ratios for Core 4 (PC89) are presented in Table 3.28 and Figure 3.26. The ^{238}Pu specific activities ranged between 0.4 ± 0.08 and 28 ± 2 Bq kg^{-1} while the $^{239,240}Pu$ specific activity ranged between 3 ± 0.2 and 166 ± 6 Bq kg^{-1}. The ^{238}Pu:$^{239,240}Pu$ activity ratios range from 0.133 ± 0.027 to 0.177 ± 0.001. The 4 - 6 cm activity ratio is similar to that of the time integrated discharge, indicating that the sediment column is well mixed with respect to the time integrated discharge ratios to this depth. However, below this, the activity ratios show more variation, indicating that the sediment from 15 cm depth is less well mixed with respect to the time integrated discharge ratios. The activity ratios at depth are not as variable as the annual Sellafield discharge ratios (Gray *et al.* 1995; MacKenzie *et al.* 1998). These ratios agree with ^{238}Pu:$^{239,240}Pu$ activity ratios for three cores collected in the NE Irish Sea presented by MacKenzie *et al.* (1998).

Figure 3.25 Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 4 (PC89).



The ^{241}Am:^{239,240}Pu activity ratios for Core 4 range from 0.63 ± 0.021 to 2.08 ± 0.001. Activity ratios for sediments between 25 and 50 cm depth are similar to those of the time integrated ^{241}Am:^{239,240}Pu ratios to 1997 (allowing for ingrowth of ^{241}Pu) (Gray *et al.* 1995; BNFL 1998) showing that these sediments are well mixed with respect to the time integrated ratio. As with Core 2 the surface ^{241}Am:^{239,240}Pu activity ratio is higher than the ratios found in sediment from 25 - 50 cm implying re-dissolution of plutonium from the surface sediments. The ^{241}Am:^{239,240}Pu ratios at depths greater than 70 cm are variable and fall within the range of annual discharge ratios (Gray *et al.* 1995).

Table 3.28 ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight), ^{238}Pu:^{239,240}Pu and ^{241}Am:^{239,240}Pu activity ratios in Core 5 (PC89). Latitude 54^{0} 19' N, Longitude 03^{0} 42' W

Depth in core	^{238}Pu (Bq kg^{-1})	^{239,240}Pu (Bq kg^{-1})	^{238}Pu:$^{239/240}$Pu	^{241}Am:^{239,240}Pu
4 - 6 cm	28 ± 2	158 ± 8	0.177 ± 0.001	2.082 ± 0.001
25 - 30	24 ± 1	166 ± 6	0.145 ± 0.006	1.662 ± 0.006
45 - 50	6 ± 0.6	44 ± 2	0.136 ± 0.014	1.818 ± 0.083
70 - 75	3 ± 0.2	19 ± 3	0.158 ± 0.014	0.632 ± 0.021
80 - 85	0.4 ± 0.08	3 ± 0.2	0.133 ± 0.027	1.667 ± 0.041

3.4.4.4 Radionuclide inventories in Core 4 (PC89)

For the purposes of inventory calculation the very high and high intensity mixing zones are considered together.

Using the same method as with the Core 2 (Appendices 3, 4 and 5) ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu inventories were calculated for the high, medium and low intensity mixing zones (Table 3.29a and b), giving total inventories in Core 4 (PC89) of 2.9 x 10^{5} Bq m^{-2} for ^{137}Cs, 1.6 x 10^{5} Bq m^{-2} for ^{241}Am, 1.4 x 10^{4} Bq m^{-2} for ^{238}Pu and 8.3 x 10^{4} Bq m^{-2} for ^{239,240}Pu.

Using the same method as with other cores (Appendix 5) upper and lower limits for inorganic and organic ^{14}C inventories for Core 4 were calculated, giving inventories of 531 and 50 Bq m^{-2} for the inorganic carbon fraction and 751 and 548 Bq m^{-2} for the organic carbon fraction.

Figure 3.26 (a) ^{238}Pu specific activities (Bg kg^{-1} dry weight), (b) $^{239/240}$Pu specific activites (Bq kg^{-1} dry weight), (c) ^{238}Pu:$^{239/240}$Pu and (d) ^{241}Am:^{239,240}Pu activity ratios for Core 4 (PC89)

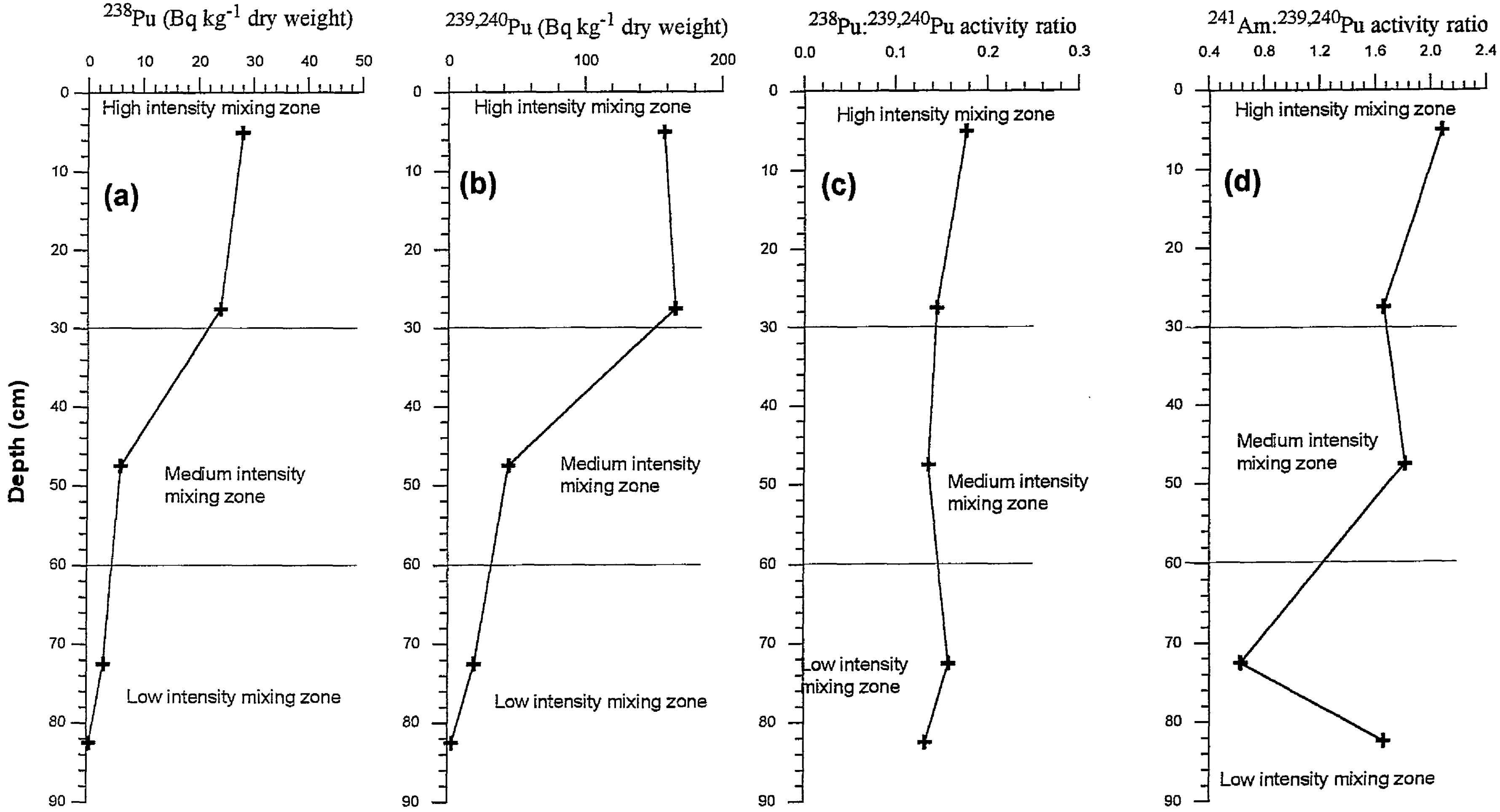


Table 3.29(a) ^{137}Cs, ^{241}Am, ^{238}Pu, $^{239/240}$Pu inventories (Bq m^{-2}) in Core 4 PC(89). Latitude 54^0 19' N, Longitude 03^0 42' W

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	^{238}Pu (Bq m^{-2})	$^{239/240}$Pu (Bq m^{-2})
2.9 x 10^5	1.6 x 10^5	1.4 x 10^4	8.3 x 10^3

Table 3.29(b) Upper and lower limits for inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 4 PC(89). Latitude 54^0 19' N, Longitude 03^0 42' W

Upper limit ^{14}C inorganic (0 Bq kg^{-1} C)	Lower limit ^{14}C inorganic (45 Bq kg^{-1} C)	Upper limit ^{14}C organic (98 Bq kg^{-1} C)	Lower limit ^{14}C organic (131 Bq kg^{-1} C)
531	50	751	548

3.4.5 Core 5 (PC185)

Core 1 (PC185) was 90 cm in length and was collected from Latitude 54^0 05' N, Longitude 03^0 30' W, in an area of muddy sand (Institute of Geological studies; Sheet 54N 03W). The bulk sediment core segments were analysed for ^{137}Cs and ^{241}Am (Bq kg^{-1} dry weight ± 1σ), while ^{14}C activities (Bq kg^{-1} C ± 1σ) were analysed in the inorganic and organic carbon fractions of the sediment.

3.4.5.1 ^{137}Cs and ^{241}Am specific activities

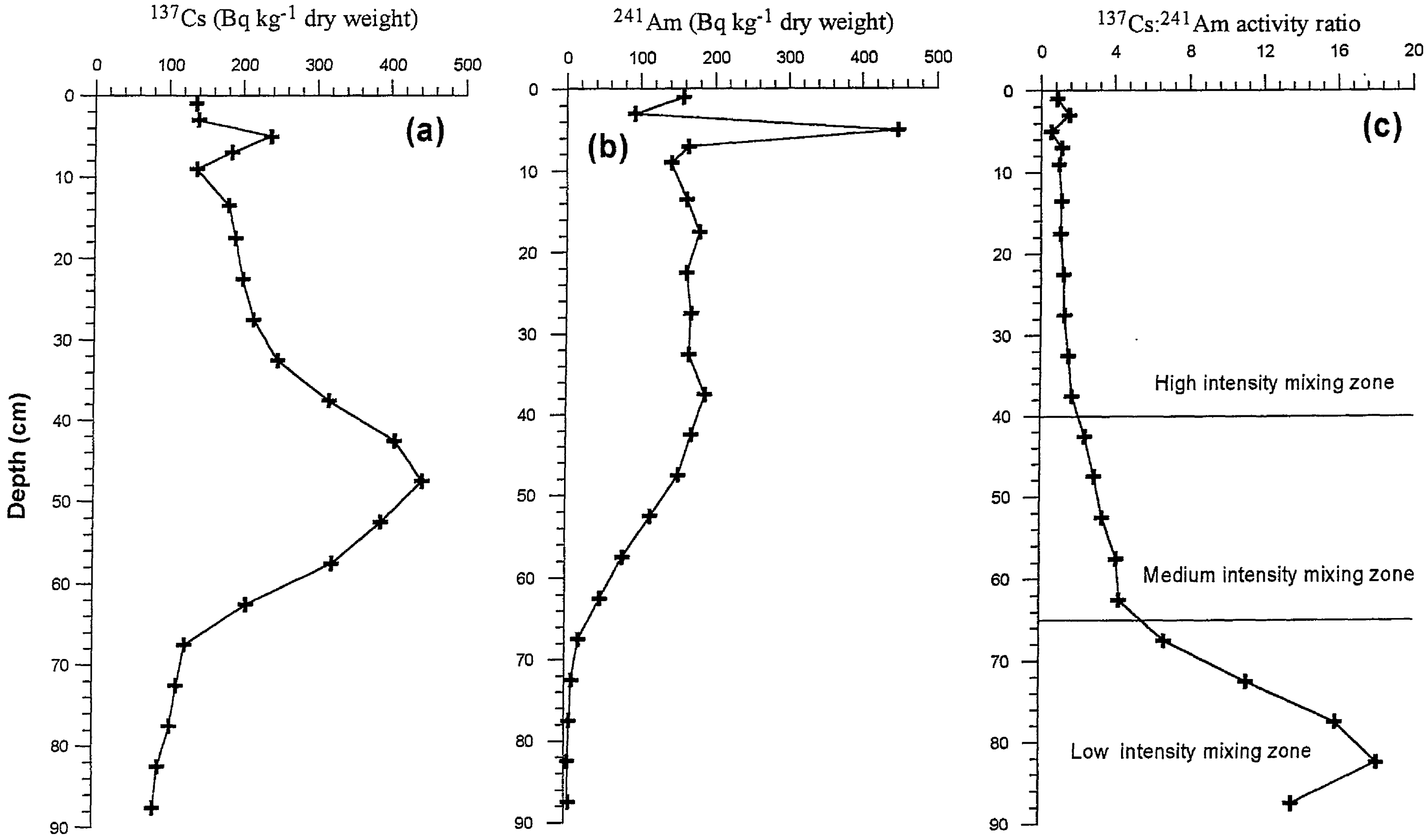
^{137}C and ^{241}Am specific activities are presented in Tables 3.30 and Figure 3.27. The ^{137}C specific activities ranged from 82 ± 0.1 to 443 ± 0.6 Bq kg^{-1}. From Figure 3.27(a) it can bee seen that there are two distinct subsurface peaks for ^{137}Cs, the larger at 45-50 cm and the smaller at 4-6 cm. The ^{241}Am specific activities ranged from 5 ± 0.1 to 447 ± 1.3 Bq kg^{-1}. In contrast to the ^{137}Cs, the ^{241}Am specific activities exhibit only one subsurface peak at a depth of 4-6 cm, coinciding with the smaller ^{137}Cs peak. It was noted during the processing of Core 5 (PC185) that the sediment at 2-4 cm was of finer texture than other samples. Unfortunately grain size analysis of the sediment was outwith the scope of this project but it would be recommended in future to include grain size analysis.

^{137}Cs:^{241}Am activity ratios ranged from 0.5 ± 0.001 to 17.6 ± 0.027. Based on these activity ratios, zones of different mixing intensity were estimated as shown in Figure 3.27(c). The high, medium and low intensity mixing zones ranged from 0 to 40 cm, 40 to 65 cm and 65 cm to base of the core, respectively. The ^{137}Cs:^{241}Am activity ratios for surface sediments in Core 5 are similar to those found in Core 3. The depth of the high intensity mixing zone is greater than that of Cores 1 to 4.

Table 3.30 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 5 (PC185). Latitude 54^0 20'N, Longitude 03^0 55' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratio
0-2	136 ± 0.1	157 ± 0.2	0.9 ± 0.001
2-4	139 ± 0.2	92 ± 0.2	1.5 ± 0.023
4-6	237 ± 0.4	447 ± 1.3	0.5 ± 0.001
6-8	184 ± 0.3	164 ± 0.4	1.1 ± 0.002
8-10	137 ± 0.2	141 ± 0.3	1.0 ± 0.001
10-15	181 ± 0.3	162 ± 0.4	1.1 ± 0.002
15-20	189 ± 0.3	179 ± 0.5	1.1 ± 0.002
20-25	199 ± 0.3	162 ± 0.4	1.2 ± 0.002
25-30	214 ± 0.3	168 ± 0.4	1.3 ± 0.002
30-35	247 ± 0.3	165 ± 0.4	1.5 ± 0.002
35-40	317 ± 0.4	187 ± 0.5	1.7 ± 0.002
40-45	406 ± 0.6	169 ± 0.4	2.4 ± 0.004
45-50	443 ± 0.6	152 ± 0.4	2.9 ± 0.004
50-55	388 ± 0.5	115 ± 0.3	2.5 ± 0.003
55-60	322 ± 0.5	78 ± 0.2	4.1 ± 0.006
60-65	206 ± 0.3	48 ± 0.1	4.3 ± 0.003
65-70	124 ± 0.2	19 ± 0.1	6.5 ± 0.011
70-75	113 ± 0.2	10 ± 0.1	11.3 ± 0.021
75-80	104 ± 0.2	7 ± 0.1	14.9 ± 0.032
80-85	88 ± 0.1	5 ± 0.1	17.6 ± 0.027
85-90	82 ± 0.1	6 ± 0.1	13.7 ± 0.021

Figure 3.27 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c)^{137}Cs:^{241}Am activity ratios for Core 5 (PC185)



3.4.5.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

The ^{14}C specific activity in the inorganic and organic carbon fractions are presented in Table 3.31 and Figure 3.28. The ^{14}C activities for the inorganic fraction of the sediment ranged from 46 ± 1 to 53 ± 1 (Bq kg^{-1} C). It is clear from the ages (y BP) of the inorganic carbon fraction that, as with other cores presented in this study there is pre-Holocene inorganic material present in the sediment. The ^{14}C activity of the surface (0 -2 cm) sediment of this core is similar to that of Cores 2 and 4 but is slightly higher than that of Core 1 and 3. The $\delta^{13}C$ values for the inorganic fraction of the sediment range from + 0.6 to + 0.8 ‰ (relative to PDB) and, as in Cores 1 to 4, indicate that the main source of inorganic material to the sediments is marine in origin.

Table 3.31 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ) and ages (y BP) and $\delta^{13}C$ values (‰ relative to PDB) in sediment from Core 5 (PC185).

Depth	Inorganic ^{14}C activity	Inorganic $\delta^{13}C$ values	Inorganic Age (y BP)	Organic ^{14}C activity	Organic Age (y BP)	Organic $\delta^{13}C$ values
0-2 cm	53 ± 1	N/A	11,980 ± 75	339 ± 2	modern	- 20.1
30-35 cm	51 ± 1	+ 0.6	12,300 ± 160	184 ± 3	1,620 ±100	- 23.9
50-55 cm	46 ± 1	+ 0.8	13,140 ± 140	152 ± 3	3,170 ±110	- 23.2
70-75 cm	47 ± 1	+ 0.7	12,930 ± 190	133 ± 3	4,200 ±140	- 24.2
75-80 cm	50 ± 1	+ 0.7	12,550 ± 150	134 ± 2	4,160 ± 120	- 24.2

N/A Not available

The organic ^{14}C activities in Core 5 range from 133 ± 3 to 339 ± 2 Bq kg^{-1} C and show a decrease in activity with depth. As with Cores 1 to 4, the activity of the 0-2 cm section shows that there has been a recent input of ^{14}C enhanced (Sellafield derived) organic material to the surface sediments. $\delta^{13}C$ values for the organic carbon fraction of the sediment ranged from - 20.1 to - 24.2 ‰ (relative to PDB). The only $\delta^{13}C$ value indicating a marine origin for organic carbon is found in the surface sediment, below this, the $\delta^{13}C$ values indicate a largely terrestrial source for the organic carbon.

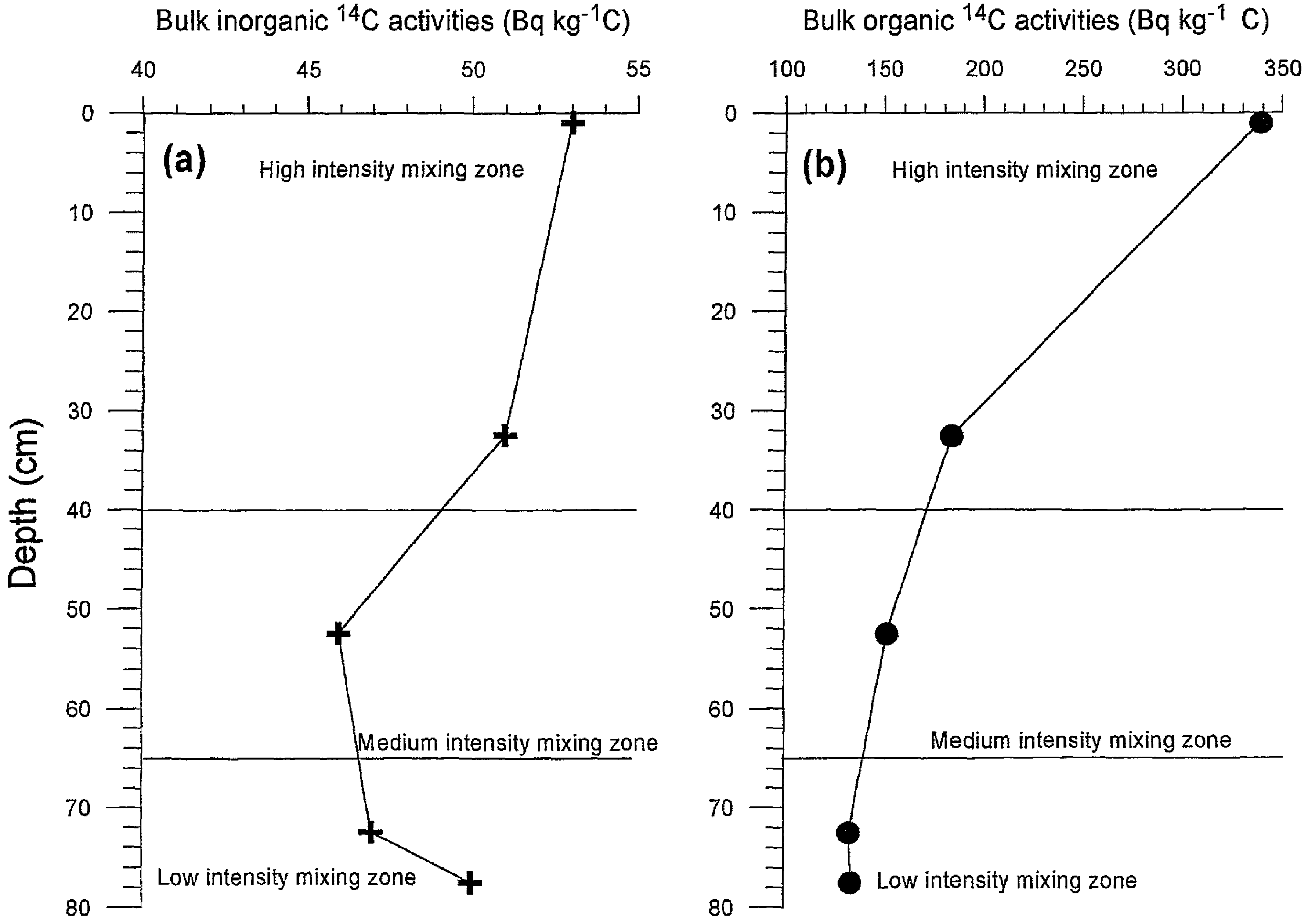


Figure 3.28 Bulk (a) inorganic and (b) organic ^{14}C activities (Bq kg^{-1} C) in Core 5 (PC185).

3.4.5.3 Radionuclide inventories in Core 5 (PC185)

^{137}Cs and ^{241}Am inventories were again calculated giving total inventories in Core 5 (PC185) of 2.8 x 10^5 Bq m^{-2} for ^{137}Cs and 1.5 x 10^5 Bq m^{-2} for ^{241}Am (Table 3.32). The ^{137}Cs and ^{241}Am inventories are similar to those found in Cores 1, 3 and 4 but higher than those found in Core 2. Upper and lower limits for inventories of inorganic and organic ^{14}C were calculated, giving total ^{14}C inventories of 603 and 53 Bq m^{-2} for the inorganic carbon fraction of the sediment and values of 829 and 580 Bq m^{-2} for the organic carbon fraction of the sediment. These inventories are all significantly higher than those calculated for Cores 1 to 3.

Table 3.32 ^{137}Cs and ^{241}Am inventories and upper and lower limits for inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 5 (PC185). Latitude 54^0 20' N, Longitude 03^0 55' W.

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	Upper limit $^{14}C_{inorg}$ (Bq m^{-2})	Lower limit $^{14}C_{inorg}$ (Bq m^{-2})	Upper limit $^{14}C_{org}$ (Bq m^{-2})	Lower limit $^{14}C_{org}$ (Bq m^{-2})
2.8 x. 10^5	1.5 x 10^5	603	53	829	580

3.4.6 Core 6 (PC 92)

Core 6 was 90 cm in length and was collected from Latitude 54^0 25' N, Longitude 03^0 42' W. Bulk sediments core segments were analysed for ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) while ^{14}C specific activities (Bq kg^{-1} C ± 1σ) were analysed in the inorganic and organic carbon fractions of the sediment.

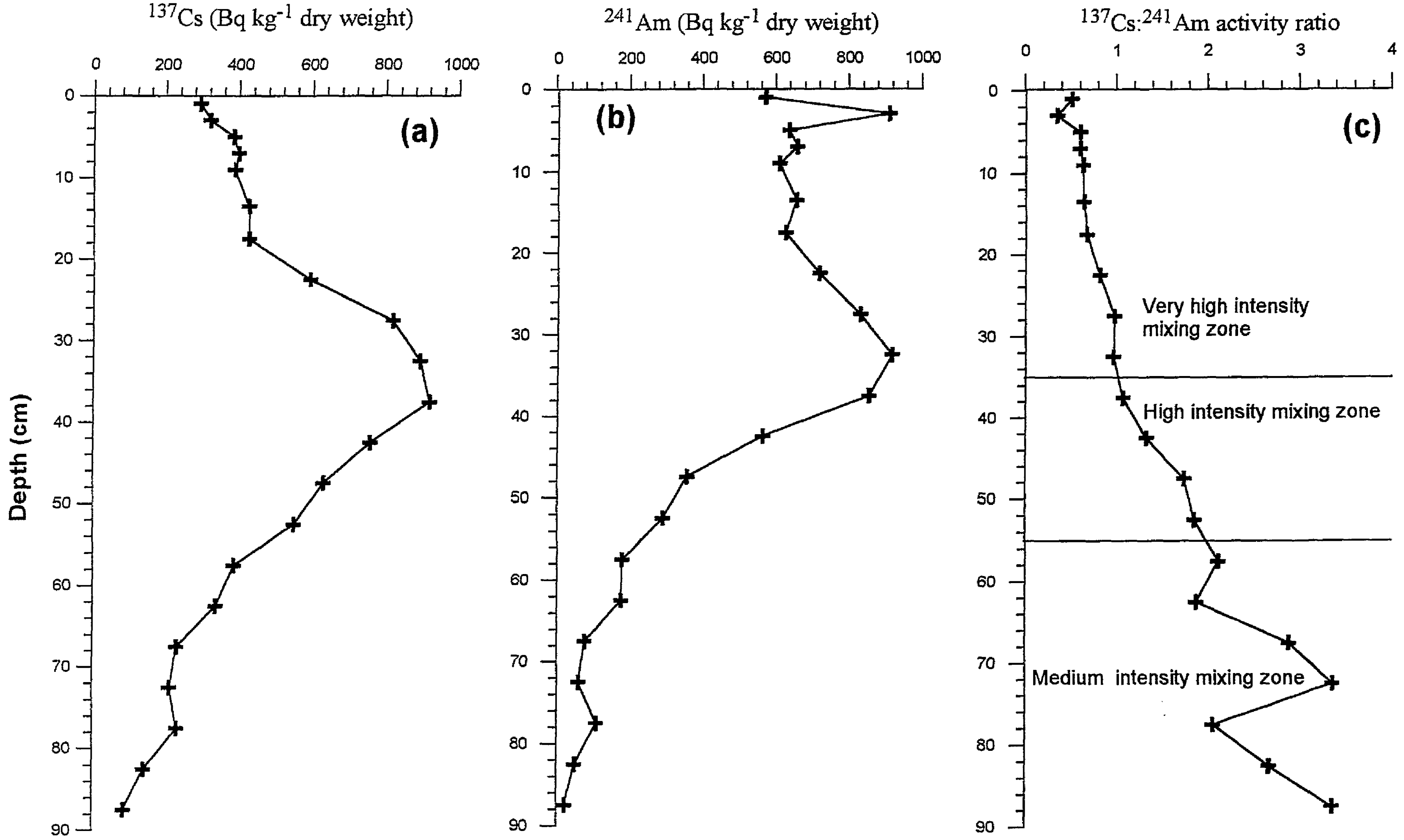
3.4.6.1 ^{137}Cs and ^{241}Am activities (Bq kg^{-1} dry sediment)

^{137}Cs and ^{241}Am specific activities and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.33 and Figure 3.29. ^{137}Cs specific activities in Core 6 (PC92) ranged from 86 ± 1 to 920 ± 1 Bq kg^{-1} and exhibited a distinct subsurface maximum between 30 and 40 cm depth in the sediment. The surface (0 - 8 cm) activities were significantly higher than those of Cores 1 to 5. The ^{241}Am activities ranged from 26 ± 1 to 920 ± 2 Bq kg^{-1} and exhibited a distinct subsurface maximum between 30 and 35 cm depth in the sediment. The ^{137}Cs:^{241}Am activity ratios for Core 6 range between 0.4 ± 0.001 and 3.3 ± 0.043. As with the previous cores, the activity ratios were used to define zones of differing mixing intensity; very high intensity mixing from 0 - 25 cm, high intensity mixing zone from 35 - 55 cm and medium intensity mixing zone from 55 cm to the base of the core. It can be seen from Figure 3.29 that the pattern of mixing zones in Core 6 is different from those of cores 1 to 5. From the activity ratios, it would appear that the sediment from 0 - 25 cm has been in prolonged contact with the overlying water column (MacKenzie *et*

Table 3.33 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 6 (PC92). Latitude 54^0 25' N, Longitude 03^0 42' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratios
0-2	393 ± 1	515 ± 1	0.8 ± 0.002
2-4	321 ± 1	911 ± 2	0.4 ± 0.001
4-6	385 ± 1	638 ± 1	0.6 ± 0.002
6-8	398 ± 1	659 ± 1	0.6 ± 0.002
8-10	388 ± 1	610 ± 1	0.6 ± 0.002
10-15	427 ± 1	658 ± 1	0.6 ± 0.001
15-20	426 ± 1	627 ± 1	0.7 ± 0.002
20-25	593 ± 1	721 ± 1	0.8 ± 0.001
25-30	818 ± 1	832 ± 2	1.0 ± 0.001
30-35	894 ± 1	920 ± 2	1.0 ± 0.001
35-40	920 ± 1	856 ± 2	1.1 ± 0.001
40-45	757 ± 1	567 ± 1	1.3 ± 0.002
45-50	631 ± 1	360 ± 1	1.8 ± 0.003
50-55	550 ± 1	295 ± 1	1.9 ± 0.003
55-60	387 ± 1	182 ± 1	2.1 ± 0.005
60-65	338 ± 1	179 ± 1	1.9 ± 0.006
65-70	232 ± 1	80 ± 1	2.9 ± 0.013
70-75	213 ± 1	63 ± 1	3.4 ± 0.017
75-80	233 ± 1	113 ± 1	2.1 ± 0.009
80-85	143 ± 1	53 ± 1	2.7 ± 0.020
85-90	86 ± 1	26 ± 1	3.3 ± 0.043

Figure 3.29 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c)^{137}Cs:^{241}Am activity ratios for Core 6 (PC92)



al. 1998). These activity ratios are lower than those found in Cores 1 to 5. Reasons for these low ratios are not immediately apparent when the core is considered in isolation, but will be discussed in Section 3.4.8. In addition to the low ratios at the top of the core, there are no values indicative of low intensity mixing in Core 6, unlike Cores 1 to 5 where a low intensity mixing zone has been identified for each core.

3.4.6.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

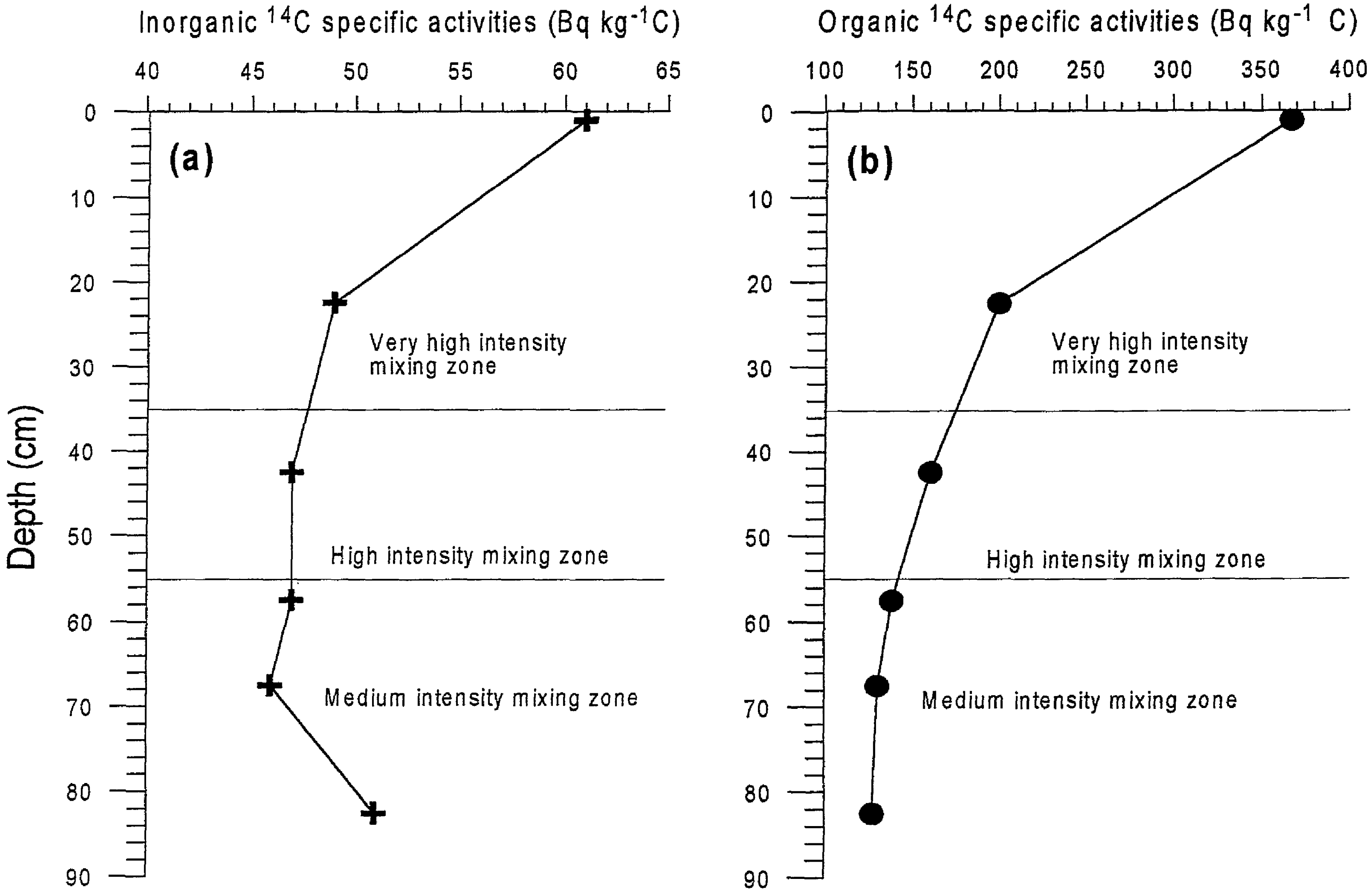
The ^{14}C specific activities (Bq kg^{-1} C) and δ^{13}C values (‰ relative to PDB) in the inorganic and organic carbon fractions of the sediment are presented in Table 3.34 and Figure 3.30. The inorganic ^{14}C activities range from 46 ± 1 to 61 ± 1 Bq kg^{-1} C. From the ages (y BP) it can be

Table 3.34 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ), ages (y BP) and δ^{13}C values (‰ relative to PDB) in sediment from Core 6 (PC92). Latitude 54^0 25' N, Longitude 03^0 42' W

Depth	Inorganic ^{14}C activity	Inorganic δ^{13}C values	Inorganic Age (y BP)	Organic ^{14}C activity	Organic Age (y BP)	Organic δ^{13}C values
0-2 cm	61 ± 1	+ 0.5	10,950 ± 70	368 ± 2	modern	N/A
20-25 cm	49 ± 1	+ 0.5	12,580 ± 110	200 ± 2	960 ± 60	- 22.7
40-45 cm	47 ± 1	+ 0.7	13,030 ± 130	161 ± 2	2,700 ± 60	- 22.4
55-60 cm	47 ± 1	+ 0.6	12,980 ± 100	139 ± 2	3,870 ± 70	- 22.5
65-70 cm	46 ± 1	+ 0.5	13,090 ± 90	131 ± 2	4,350 ± 70	- 23.1
80-85 cm	51 ± 1	+ 0.3	12,360 ± 80	128 ± 2	4,520 ± 80	- 23.7

N/A not available

Figure 3.30 Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 6 (PC92).



seen that there is pre-Holocene material present in the lower section of the core. The ^{14}C specific activity of the surface (0 - 2 cm) sediment is higher in activity than that found in Cores 1 - 5. The $\delta^{13}C$ values for the inorganic carbon fraction of the sediment range from + 0.3 to + 0.7 ‰ (relative to PDB) and indicate a marine origin for inorganic carbon in the sediment of Core 6.

The organic ^{14}C activities for Core 6 (PC92) ranged from 128 ± 2 to 368 ± 2 Bq kg^{-1} C and exhibited a trend of decreasing activity with depth in the sediment column. The surface sediment ^{14}C specific activity (0 - 2 cm) was higher than the surface activities of Cores 1-5, although the specific activities of the lower sections (55 - 60 cm, 65 - 70 and 80- 85 cm) were similar to those of Cores 3-5 but higher than that of Core 1 for corresponding depths. As with Cores 1 - 5 the activity of the 0 - 2 cm section shows that there has ben a recent input of ^{14}C enhanced (Sellafield derived) organic material to the sediment surface, which will be mixed to depth over time. It is unfortunate that the CO_2 for $\delta^{13}C$ value analysis was lost for the 0 - 2 cm as it would have helped indicate the source of the organic matter to the sediment. The specific activities of sediment of > 65 cm depth are similar to the value of 131 Bq kg^{-1} C, calculated for average production during the Holocene. The $\delta^{13}C$ values for the organic carbon fraction of the sediment ranged from - 22.4 to - 23.1 ‰ relative to PDB. The $\delta^{13}C$ values indicate that the source of organic carbon to this core is a mixture of marine and terrestrially produced organic carbon.

3.4.6.3 Radionuclide inventories in Core 6 (PC92)

^{137}Cs and ^{241}Am inventories were calculated for the very high, high and medium intensity mixing zones, giving total inventories in Core 6 (PC92) of 4.9 x 10^5 Bq m^{-2} for ^{137}Cs and 4.5 x 10^5 Bq m^{-2} for ^{241}Am. These inventories are higher than those calculated for Cores 1 to 5. Upper and lower limits for inorganic and organic ^{14}C inventories were calculated, giving total inventories of 467 and 54 Bq m^{-2} for the inorganic carbon fraction of the sediment and values of 707 and 521 Bq m^{-2} for the organic carbon fraction of the sediments.

Table 3.35 ^{137}Cs, ^{241}Am and in inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 6 (PC92). Latitude 54^0 25' N, Longitude 03^0 42' W.

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	Upper limit $^{14}C_{inorg}$ (Bq m^{-2})	Lower limit $^{14}C_{inorg}$ (Bq m^{-2})	Upper limit $^{14}C_{org}$ (Bq m^{-2})	Lower limit $^{14}C_{org}$ (Bq m^{-2})
4.9 x 10^5	4.5 x 10^5	467	54	707	521

3.4.7.Core 7 (PC86)

Core 7 was 60 cm in length and was the northernmost core collected, Latitude 54^0 27' N Longitude 03^0 41' W (the same location as the "Sellafield North" core presented by Wolstenholme (1999)). The core was analysed for ^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight) and ^{14}C specific activities (Bq kg^{-1} C) in the inorganic and organic carbon fractions of the sediment.

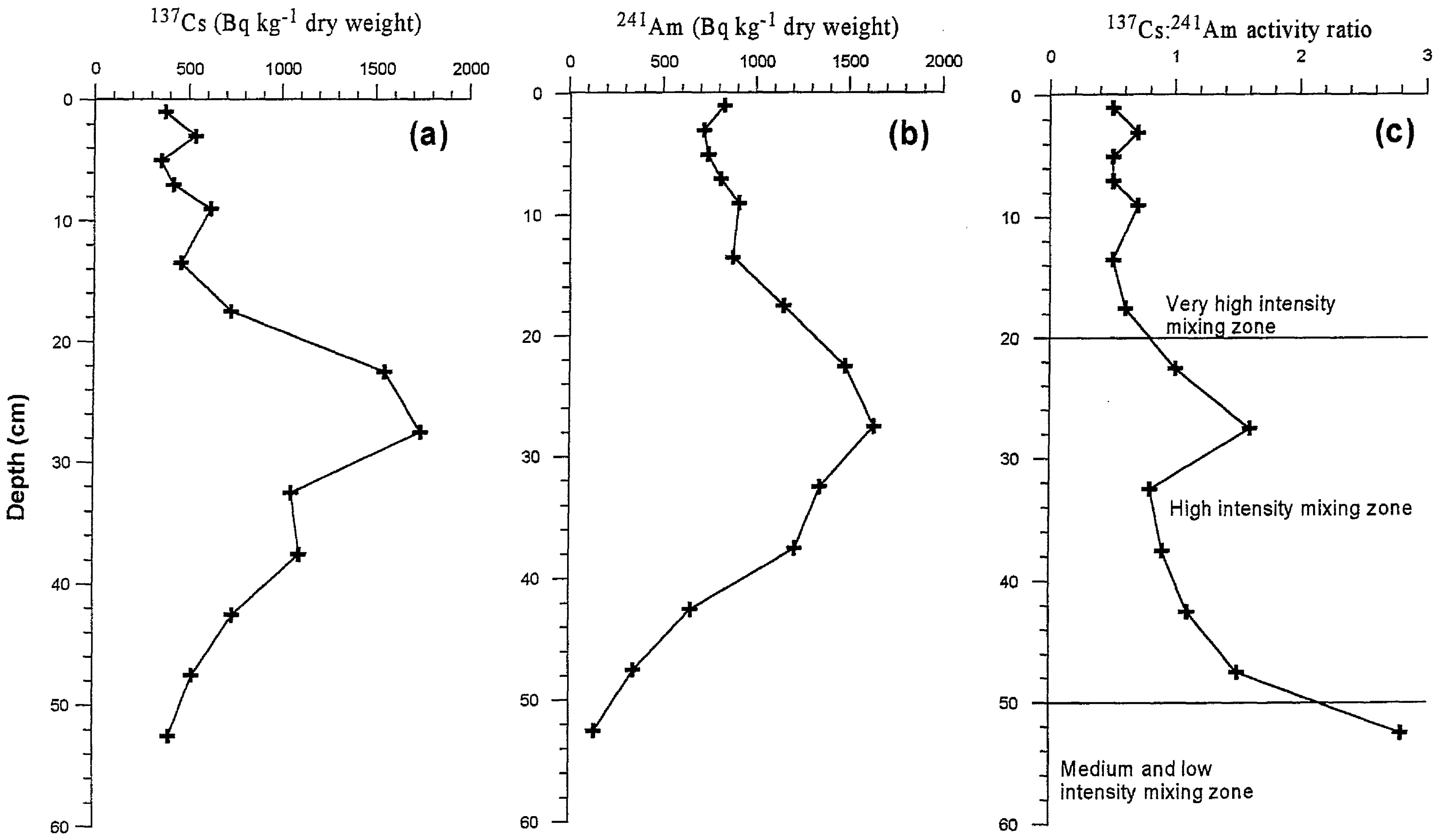
3.4.7.1 ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry sediment)

The ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight) and ^{137}Cs:^{241}Am activity ratios are presented in Table 3.36 and Figure 3.31. The ^{137}Cs specific activities ranged between 106 ± 0.1 and 1740 ± 2 Bq kg^{-1} and exhibited a distinct subsurface maximum at 25-30 cm depth. The specific activities of ^{137}Cs in the surface sediment (0-8 cm) are higher than those of Cores 1- to 6. ^{137}Cs specific activities in the "Sellafield North" core (Wolstenholme 1999) ranged from 346 ± 5 to 1,366 ± 21 and also exhibited a distinct sub surface maximum, at 32 to 34 cm depth. The surface sediment (0-8 cm) specific activities of ^{137}Cs in the "Sellafield North" core were higher than those of Core 7, consistent with loss of ^{137}Cs to the water column since 1996 when the "Sellafield north" core was collected. The ^{241}Am specific activities ranged between 17 ± 0.1 and 1,636 ± 3 Bq kg^{-1} and a sub-surface peak was observed at 25-30 cm depth, consistent with the ^{137}Cs maximum. In the "Sellafield North" core (Wolstenholme 1999), the ^{241}Am specific activities ranged from 106 ± 3 to 1,581 ± 23 with a subsurface maximum at 34-36 cm. ^{137}Cs:^{241}Am activity ratios for Core 7 ranged from 0.5 ± 0.001 to 6.2 ± 0.006 and on the basis of these values mixing zones were estimated as previously described (Figure 3.31). The ratio indicating low intensity mixing is only 6.2, -not much above the chosen cut off activity ratio of 6. The pattern of mixing depths is similar to that of Core 6 and the "Sellafield North" core.

Table 3.36 ^{137}Cs, ^{241}Am specific activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratios in sediment from Core 7 (PC86). Latitude 54^0 27' N Longitude 03^0 41' W

Depth (cm)	^{137}Cs (Bq kg^{-1})	^{241}Am (Bq kg^{-1})	^{137}Cs:^{241}Am activity ratios
0-2	373 ± 0.2	827 ± 1	0.5 ± 0.001
2-4	536 ± 1	717 ± 2	0.7 ± 0.001
4-6	353 ± 1	738 ± 2	0.5 ± 0.001
6-8	416 ± 1	807 ± 2	0.5 ± 0.001
8-10	617 ± 1	906 ± 2	0.7 ± 0.001
10-15	459 ± 1	875 ± 2	0.5 ± 0.001
15-20	727 ± 1	1149 ± 2	0.6 ± 0.001
20-25	1548 ± 1	1481 ± 3	1.0 ± 0.001
25-30	1740 ± 2	1636 ± 3	1.1 ± 0.001
30-35	1054 ± 1	1349 ± 3	0.8 ± 0.001
35-40	1099 ± 1	1216 ± 3	0.9 ± 0.001
40-45	742 ± 1	654 ± 1	1.1 ± 0.001
45-50	525 ± 1	351 ± 1	1.5 ± 0.003
50-55	402 ± 1	143 ± 0.3	2.8 ± 0.007
55-60	106 ± 0.1	17 ± 0.1	6.2 ± 0.006

Figure 3.31 (a) ^{137}Cs specific activities (Bg kg^{-1} dry weight), (b) ^{241}Am specific activites (Bq kg^{-1} dry weight) and (c) ^{137}Cs:^{241}Am activity ratios for Core 7 (PC86)



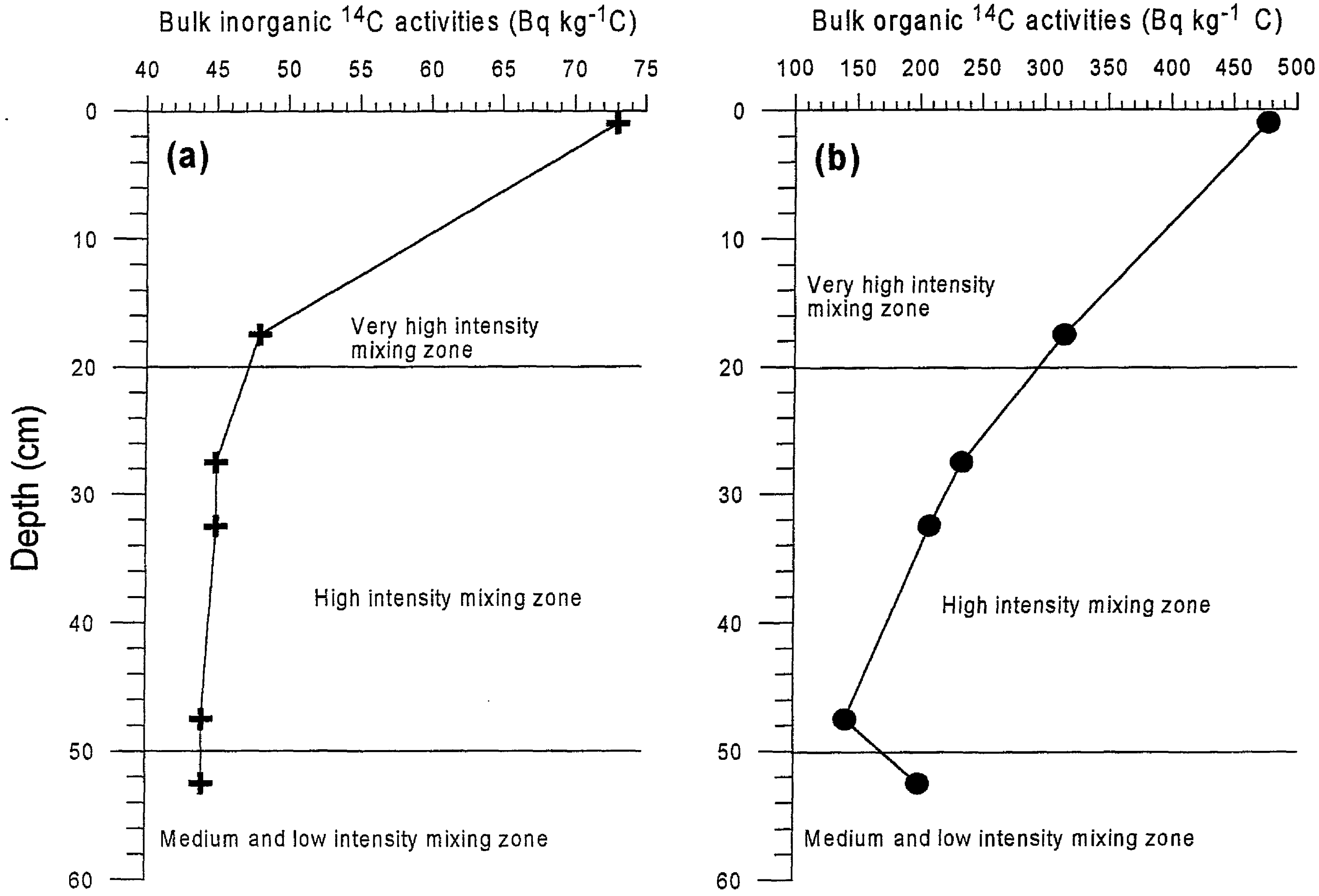
3.4.7.2 ^{14}C specific activities in the inorganic and organic carbon fractions of the sediment

The ^{14}C specific activity of the inorganic and organic carbon fractions of the sediment and δ^{13}C values (‰ relative to PDB) for Core 7 are presented in Table 3.31 and Figure 3.32. The inorganic ^{14}C specific activities ranged from 44 ± 1 to 73 ± 1 Bq kg^{-1} C and exhibited decreasing activity with increasing depth in the sediment column. From the ages, it is apparent that there is pre-Holocene material from 15 cm to the base of the core. The specific activity in the surface sediment (0 - 2 cm) is higher than that of any of the previous cores and is also higher than that reported by Wolstenholme (1999) for surface sediment (0-4 cm) of the "Sellafield North" core (67 ± 1 Bq kg^{-1} C), indicating that the ^{14}C activity of recently deposited inorganic material at this site has increased since 1996. The inorganic δ^{13}C values range between + 0.1 and + 0.6 ‰ relative to PDB indicating a marine source for inorganic sedimentary material.

Table 3.31 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ), ages (yBP) and δ^{13}C values (‰ relative to PDB) in sediment from Core 7 (PC86). Latitude 54^0 27' N Longitude 03^0 41' W

Depth	Inorganic ^{14}C activity	Inorganic δ^{13}C values	Inorganic Age (yBP)	Organic ^{14}C activity	Organic Age (yBP)	Organic δ^{13}C values
0-2 cm	73 ± 1	9,480 ± 65	+ 0.6	477 ± 3	modern	- 20.8
15-20 cm	48 ± 1	12,870 ± 100	+ 0.6	315 ± 2	modern	- 21.0
25-30 cm	45 ± 1	13,280 ± 100	+ 0.2	234 ± 2	modern	- 21.7
30-35 cm	45 ± 1	13,340 ± 100	+ 0.1	208 ± 1	640 ± 60	- 23.0
45-50 cm	44 ± 1	13,490 ± 90	+ 0.3	141 ± 1	3,790 ± 60	- 23.4
50-55 cm	44 ± 1	13,520 ± 95	+ 0.5	199 ± 2	1,005 ± 45	N/A

Figure 3.32 Bulk (a) inorganic and (b) organic ^{14}C specific activities (Bq kg^{-1} C) in Core 7 (PC86).



The organic ^{14}C activities ranged between 141 ± 1 and 477 ± 3 Bq kg^{-1} C and exhibited a trend of decreasing activity with depth in the sediment column apart from the 50 - 55 cm section which had a higher specific activity (199 Bq kg^{-1} C) than the 45-50 cm section (141 Bq kg^{-1} C). The surface (0-2 cm) value is higher than those found in Cores 1 - 6 is almost double that of the "Sellafield North" core (Wolstenholme 1999). As with Cores 1 to 5, it is clear from the activity of the 0-2 cm section that there has been a recent input of ^{14}C enhanced (Sellafield derived) organic material to the sediment surface. Unlike Cores 1 to 6, however, this higher activity material has been mixed to at least 20 cm depth and the activity of the 25 - 30 cm section is also close to the current marine background of 250 Bq kg^{-1} C. From the δ^{13}C values of the 0-2 and 20-25 cm sections it can be seen that the organic matter from these sections is of marine origin. The δ^{13}C values in Core 7 range from - 20.8 to - 23.4 ‰ relative to PDB and exhibit a trend of increasingly negative δ^{13}C values with depth in the core. The δ^{13}C values indicate that there is a mainly marine source of organic material to the sediments of this core, but that at depth in the core there is a more terrestrial value indicating consumption of the more labile, marine derived organic compounds by the benthic biota.

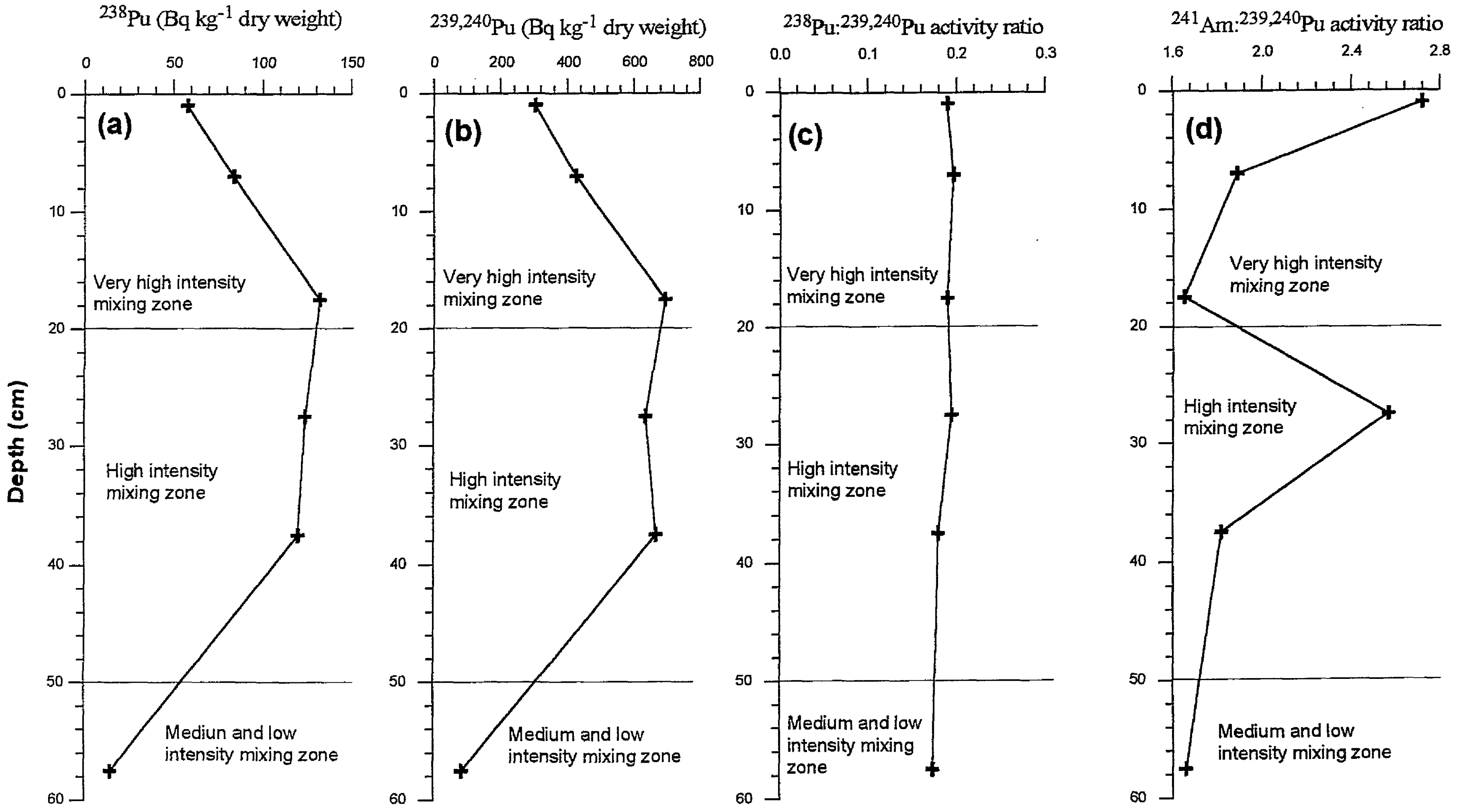
3.4.7.3. ^{238}Pu and ^{239,240}Pu specific activities

^{238}Pu and ^{239,240}Pu specific activities and activity ratios for Core 7 are presented in Table 3.38 and Figure 3.33. The ^{238}Pu specific activities ranged from 15 ± 0.8 to 132 ± 6 Bq kg^{-1}, while the ^{239,240}Pu specific activities ranged from 86 ± 4 to 695 ± 29 Bq kg^{-1} with the highest values between 15 and 40 cm depth and a sharp decrease in activity in the 50 - 55 cm section. All the ^{238}Pu:^{239,240}Pu ratios agree well to within the 2σ level of confidence.

Table 3.38 ^{238}Pu and ^{239,240}Pu specific activities (Bq kg^{-1} dry weight), ^{238}Pu:^{239,240}Pu and ^{241}Am:^{239,240}Pu activity ratios in Core 7 (PC86). Latitude 54^0 27' N, Longitude 03^0 41' W

Depth (cm)	^{238}Pu	^{239,240}Pu	^{238}Pu:^{239,240}Pu	^{241}Am:^{239,240}Pu
0 - 2	58 ± 3	304 ± 16	0.190 ± 0.010	2.720 ± 0.011
6 - 8	84 ± 3	427 ± 14	0.197 ± 0.007	1.890 ± 0.062
15 - 20	132 ± 6	695 ± 29	0.190 ± 0.009	1.653 ± 0.069
25 - 30	124 ± 4	637 ± 18	0.195 ± 0.006	2.568 ± 0.007
35 - 40	120 ± 3	668 ± 14	0.180 ± 0.004	1.820 ± 0.005
50 - 55	15 ± 0.8	86 ± 4	0.174 ± 0.010	1.663 ± 0.077

Figure 3.33 (a) ^{238}Pu specific activities (Bg kg^{-1} dry weight), (b) $^{239/240}$Pu specific activites (Bq kg^{-1} dry weight), (c) ^{238}Pu:$^{239/240}$Pu and (d) ^{241}Am:^{239,240}Pu activity ratios for Core 7 (PC86)



They are also consistent with the time integrated discharge if a 2σ error is applied. The sharp decrease in specific activity of 40-50 cm clearly shows a decrease in mixing intensity. The ^{238}Pu:^{239,240}Pu values suggest highly efficient mixing to a depth of 40 cm, consistent with the ^{137}Cs:^{241}Am activity ratio data.

The ^{241}Am:^{239,240}Pu activity ratios from Core 7 range from 2.72 ± 0.011 to 1.66 ± 0.077. From the ^{137}Cs:^{241}Am and ^{238}Pu:^{239,240}Pu activity ratios it can be seen that the sediment in Core 7 is well mixed to a depth of 50 cm. As with Cores 2 and 4, the ^{241}Am:^{239,240}Pu ratios in the surface sediment are consistent with re-dissolution of plutonium from the sediment. In addition, the ^{241}Am:^{239,240}Pu ratio at 25-30 cm depth also suggests that this sediment has experienced plutonium re-dissolution. This agrees with the lower (<1.0) ^{137}Cs:^{241}Am ratio found between 30 and 40 cm depth, suggesting that these high ratio sediments have been advectively mixed to depth in the sediment. The remaining ^{241}Am:^{239,240}Pu ratios in Core 7 suggest that it is well mixed with respect to the ^{241}Am:^{239,240}Pu cumulative discharge (including ingrowth of ^{241}Pu) of 1.67.

3.4.4.4 Radionuclide inventories in Core 7 (PC86)

^{137}Cs, ^{241}Am, ^{238}Pu and ^{239,240}Pu inventories were calculated to be 6.0 x 10^5 Bq m^{-2} for ^{137}Cs, 6.8 x 10^5 Bq m^{-2} for ^{241}Am, 7.0 x 10^4 Bq m^{-2} for ^{238}Pu and 3.7 10^5 Bq m^{-2} for ^{239,240}Pu (Table 3.39a). The ^{137}Cs and ^{241}Am inventories are significantly higher than those of Cores 1 to 6, despite the short length of Core 7.

The ^{238}Pu inventory in Core 7 is significantly higher than those of Cores 1 and 4, and the ^{239,240}Pu activity inventory is one order of magnitude higher than those of Cores 1 and 4.

Upper and lower limits were calculated for inorganic and organic ^{14}C inventories (Table 3.38b). Total ^{14}C activity inventories of 313 and 37 Bq m^{-2} were calculated for the inorganic carbon fraction of the sediment and 776 and 643 Bq m^{-2} for the organic carbon fraction. Wolstenholme (1999) calculated inorganic and organic inventories for the Sellafield North core of 27 and 292 Bq m^{-2}, respectively (using backgrounds of 45 and 131 Bq kg^{-1} C, respectively), which are lower than those calculated for Core 7, suggesting that there has been an increase in both the inorganic and organic ^{14}C inventories in this area since 1996.

Table 3.39(a) ^{137}Cs, ^{241}Am, ^{238}Pu and $^{239/240}$Pu inventories (Bq m^{-2}) in Core 7 PC(86). Latitude 54^0 27' N, Longitude 03^0 41' W

^{137}Cs (Bq m^{-2})	^{241}Am (Bq m^{-2})	^{238}Pu (Bq m^{-2})	$^{239/240}$Pu (Bq m^{-2})
6.0 x 10^5	6.8 x 10^5	7.0 x 10^4	3.7 x 10^5

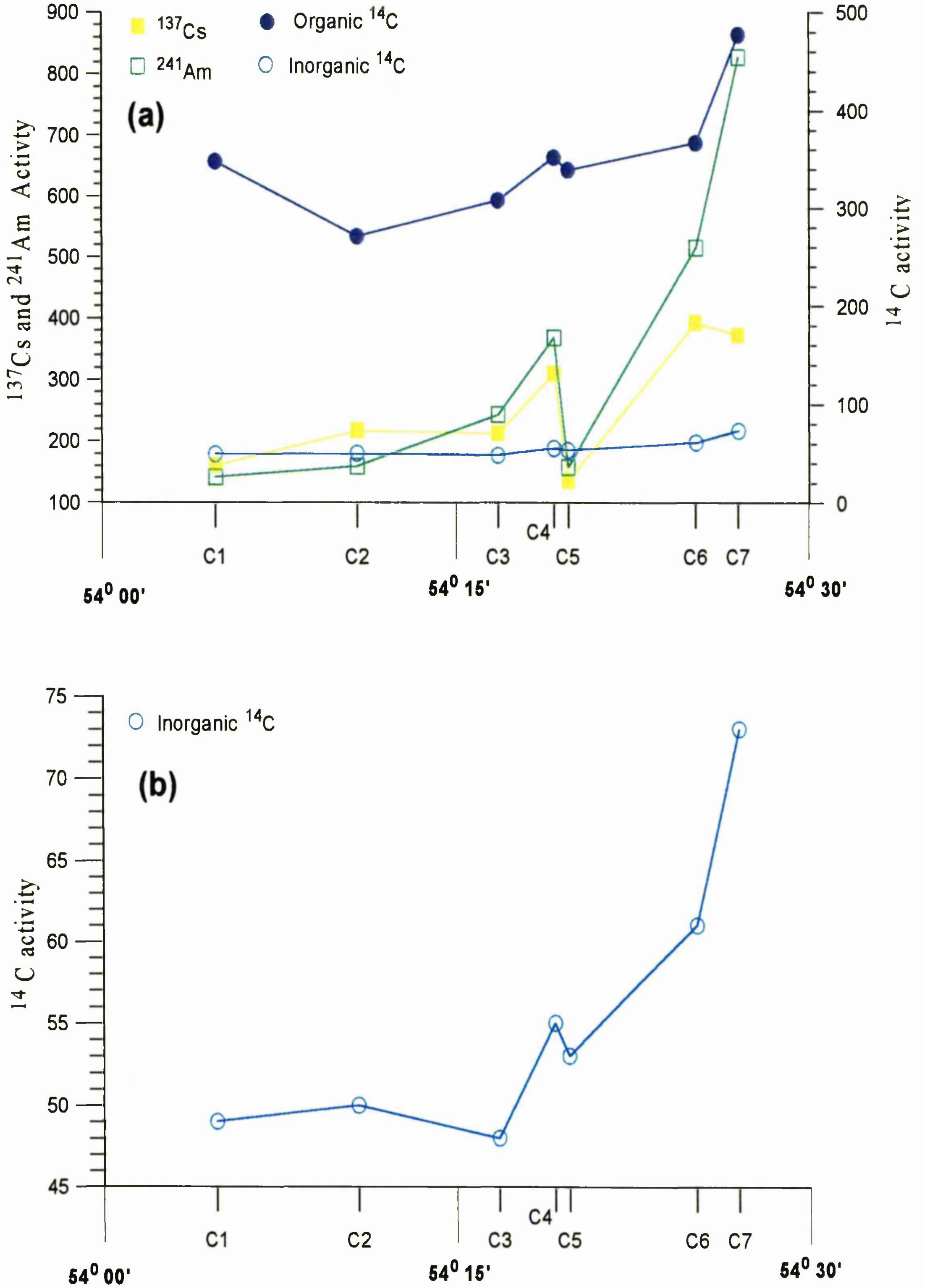
Table 3.39(b) Uupper and lower limits for inorganic and organic ^{14}C inventories (Bq m^{-2}) in Core 7 PC(86). Latitude 54^0 27' N, Longitude 03^0 41' W

Upper limit ^{14}C inorganic (0 Bq kg^{-1} C)	Lower limit ^{14}C inorganic (45 Bq kg^{-1} C)	Upper limit ^{14}C organic (98 Bq kg^{-1} C)	Lower limit ^{14}C organic (131 Bq kg^{-1} C)
313	37	776	643

3.4.8 Radionuclide trends in Cores 1 to 7

While each core was presented individually in Sections 3.4.1. to 3.4.7, it is also important to investigate any trends between the cores. It must be noted that the cores were not collected on a north-south transect and are of differing Longitude, most notably Cores 1 and 5. Also the cores were collected from areas of differing sediment type which may influence the distribution of radionuclides in the sediments. Cores 3 and 4 were collected from areas of mud, Cores 1, 6 and 7 were collected from areas of sandy mud and Cores 2 and 5 were collected from areas of muddy sand (Institute of Geological Studies; Sheet number 54N 03W). Figure 3.34 plots the surface (0 - 2 cm) ^{137}Cs and ^{241}Am specific activities in the bulk sediment and ^{14}C specific activities (Bq kg^{-1} C) in the inorganic and organic carbon fraction of the sediment for Cores 1 to 7 against latitude. It is clear from Figure 3.34(a) that there is a trend of increasing activity with latitude for ^{137}Cs, ^{241}Am and organic ^{14}C activities, however, the increase in inorganic ^{14}C can only be clearly seen in Figure 3.34(b). It is clear from this that the basic trends in specific activity with latitude are broadly similar for all four radionuclides, despite the differences in biogeochemistry and transfer routes into the sediments. While the overall increase in activity with latitude is readily apparent, the organic ^{14}C specific activity for Core 1 does not follow the trend and the activities for radionuclides in Core 5 do not seem to follow this trend. As Core

Figure 3.34 (a) ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1}) and inorganic and organic ^{14}C specific activities (Bq kg^{-1} C) in the surface (0 - 2 cm) sediments of Cores 1 to 7 and (b) inorganic ^{14}C activities in the surface (0 - 2 cm) sediments of Cores 1 to 7.



5 was collected from an area of coarser material (muddy sand instead of sandy mud) a decrease in the % clay in this core relative to the other cores may be the reason. Of the radionuclides, ^{241}Am shows the greatest increase with latitude, with the specific activity of Core 7 being approximately 6 times that of Core 1. In comparison the ^{137}Cs activities are highest in Core 6, there is an increase of approximately 2.4 between Core 1 and Core 6 (the lowest and highest activities for ^{137}Cs). For the organic ^{14}C, Core 2 has the lowest specific activity, there is an increase in activity of approximately 1.8 between Cores 2 and 7 (lowest and highest activities for organic ^{14}C). The inorganic ^{14}C shows the smallest rise in activity with an increase in activity from Core 1 to Core 7 of approximately 1.4.

Plotting the ^{137}Cs, ^{241}Am, inorganic ^{14}C (above 0 Bq kg^{-1}C) and organic ^{14}C (above 98 Bq kg^{-1} C) activity inventories (Bq m^{-2}) against latitude shows an increase in ^{137}Cs, ^{241}Am, and organic ^{14}C (above 98 Bq kg^{-1}C) activity inventories (Bq m^{-2}) inventories with latitude (Figure 3.35). (As the trends in inventories for the upper and lower estimates of inventories are similar, the upper limits were chosen to illustrate the trends in ^{14}C inventory with latitude).

The inventories in Core 2 are lower than those in Core 1, possibly due to either, the difference in length or the difference in sediment type between these cores. This discontinuity is most pronounced for the organic ^{14}C inventories. The inorganic ^{14}C inventories do not follow this trend showing a decrease between Core 1 and 2, an increase between Cores 2 and 5, followed by decreasing activities for Cores 6 and 7. The decrease in ^{137}Cs and ^{241}Am inventories between Cores 1 and 2, is probably due to the fact that Core 2 was shorter than the other cores. Again, for ^{137}Cs and ^{241}Am inventories there is a decrease in activity between Cores 4 and 5, probably due to changes in sediment composition. The overall increase in activities and inventories with increasing latitude is consistent with the suggestion of net northwards movement of contaminated sediment.

Figure 3.35 ^{137}Cs, ^{241}Am, inorganic ^{14}C and organic ^{14}C inventories (Bq m^{-2}) for Cores 1 to 7

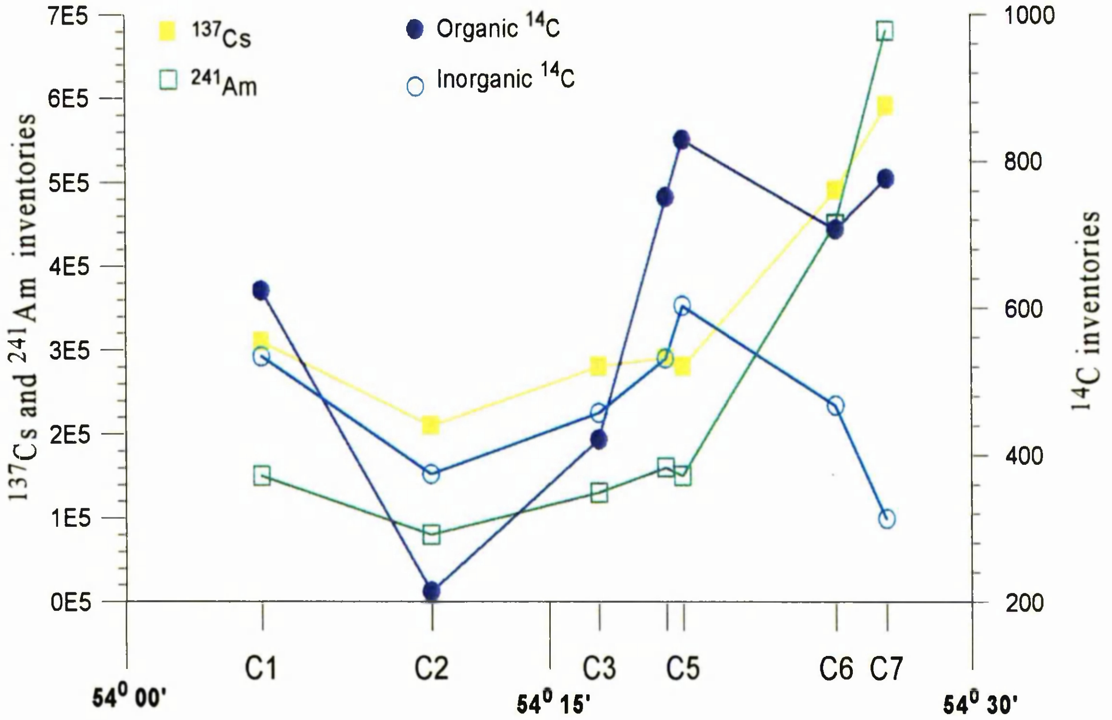
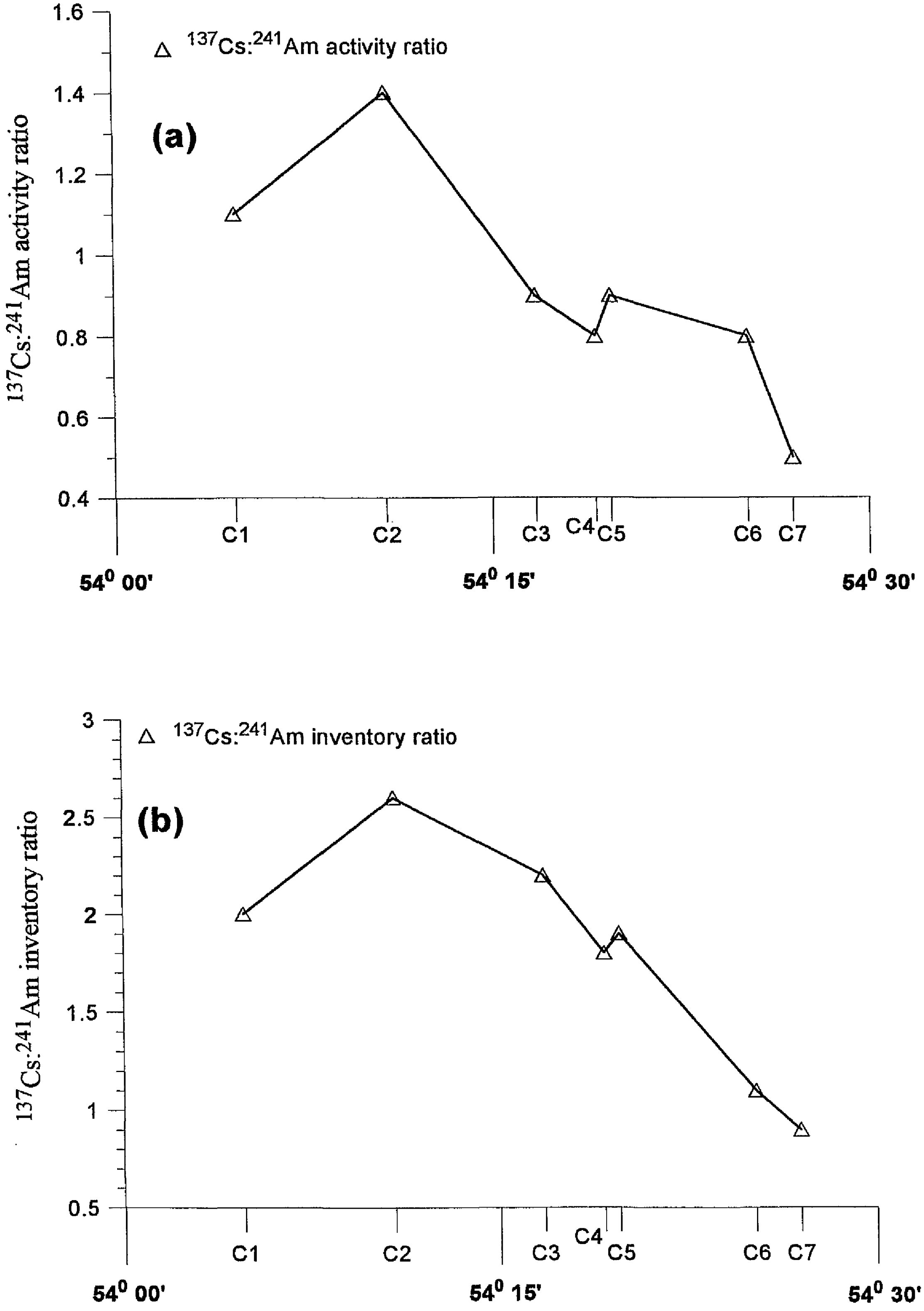


Figure 3.36(a) shows the ^{137}Cs:^{241}Am activity ratios for surface sediments (0 -2 cm) for Cores 1 to 7 with increasing latitude. Overall, the ratios exhibit an inverse pattern to that of the surface activities (0- 2 cm) and inventories with latitude. There is a sharp increase in ^{137}Cs:^{241}Am activity ratios between Core 1 and Core 2, possibly due to the differences in longitude or sediment type, followed by a general decrease from Core 2 to Core 6, with a slight discontinuity in the trend at Core 4. Core 7 shows a sharp drop in activity ratio. The ^{137}Cs:^{241}Am inventory ratios (Figure 3.36b) follow a similar pattern to that of the activity ratios, with sharp increases in values between Core 1 and 2, followed by a gradual decrease in values between Cores 2 and 5. The discontinuity in trend at Core 4 is more pronounced for the activity ratios. There is a sharp decrease in activity between Cores 5 and 6.

MacKenzie *et al.* (1998) noted that ^{137}Cs:^{241}Am activity ratios of <1 are due to prolonged exposure to seawater. This is consistent with the concept of a northwards movement of the contaminated sediment, with lower ^{137}Cs:^{241}Am activity ratios of the more northerly cores reflecting a greater distance of transport and a corresponding greater contact time with seawater.

Figure 3.36 (a) ^{137}Cs:^{241}Am activity ratios in surface (0 - 2 cm) sediments of Cores 1 to 7 and (b) ^{137}Cs:^{241}Am inventory ratios of Cores 1 to 7.



This apparent decrease in ^{137}Cs:^{241}Am activity ratios during transport has significant implications for the use of activity ratios to define mixing zones as employed by Mackenzie *et al.* (1998) and adopted here since the addition of sediment with low ^{137}Cs:^{241}Am activity ratios could give apparently greater depths of intense mixing than apply in reality. Correspondingly, removal (by northwards transport) of surface sediment with a low ^{137}Cs:^{241}Am activity ratio from southern locations could lead to underestimation of the intensity of surface mixing.

3.4.9 Total ^{137}Cs, ^{241}Am ^{238}Pu and ^{239,240}Pu inventories (Bq) and inorganic and organic ^{14}C inventories (Bq) in the sediments of the NE Irish Sea

Total inventories (Bq) were calculated, based on the core inventories (Bq m^{-2}) and sediment types that the cores were collected from (Appendix 6), giving overall activities of 6.2 x 10^{14} Bq (620 TBq) for ^{137}Cs, 4.1 x 10^{14} Bq (410 TBq) for ^{241}Am, upper and lower limits for inorganic ^{14}C of 917 GBq and 69 GBq, respectively, and upper and lower limits for organic ^{14}C of 1,132 and 910 GBq, respectively.

In order to account for the overall increase in inventory (Bq m^{-2}) with latitude, cores should represent both the southern and northern latitudes of each area of sediment. This is true for the distribution of cores analysed for ^{137}Cs, ^{241}Am and ^{14}C, but is not true of the distribution of cores analysed for ^{238}Pu and ^{239,240}Pu so these data are not considered here. The cumulative decay corrected discharge inventories from Sellafield to the Irish Sea (1952 - 1998) are 41 x 10^3 TBq for ^{137}Cs, 1,032 TBq for ^{241}Am (including ingrowth of ^{241}Pu) and 92 TBq for ^{14}C. In discussing the overall inventories in relation to the total discharges activity from Sellafield from 1952 to 1998, it must be taken into account that this study has not included intertidal or coarse grained sub-tidal sediments in the inventory calculation. Therefore, the overall inventories presented in this study apply only to the area and sediment types specified and should not be applied to the whole of the Irish Sea. From the data presented here it appears that approximately 1.5 % of the ^{137}Cs remains in the sediments of the area investigated, which is consistent with the initial uptake of 10% of the discharges to the fine grained sediments of the Sellafield "mud patch" followed by redistribution of these sediments and subsequent re-dissolution of the ^{137}Cs during sediment transport. Approximately 40 % of the discharged ^{241}Am remains in the sediments of the area investigated during this study, consistent with uptake of

90% of the discharged activity in the fine grained sediments of the Sellafield "mud patch" followed by redistribution of the contaminated sediment.

The upper limit inorganic and organic ^{14}C inventories calculated during this study are approximately 1 and 1.2 %, respectively, of the cumulative discharge of 92 TBq while the lower limit ^{14}C inventories are approximately 0.08 and 1 %, respectively, of the cumulative ^{14}C discharge. These values are consistent with the conclusion from Section 3.2 that ^{14}C discharged from Sellafield to the Irish Sea is rapidly removed in solution through the North Channel.

3.4.10 ^{137}Cs and ^{241}Am specific activities in bulk sediments (Bq kg^{-1} dry sediment) and ^{14}C specific activities in the inorganic and organic carbon fraction of sediments collected from outwith the Sellafield "mud patch".

Van Veem grab samples were collected from sandier locations relative to the Sellafield "mud patch" (Section 2.1.5) and were analysed for ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight) in the bulk sediment and bulk ^{14}C specific activities (Bq kg^{-1} C) in the inorganic and organic carbon fractions of the sediment.

^{137}Cs and ^{241}Am specific activities in Grabs 1 to 5

The ^{137}Cs and ^{241}Am specific activities and ^{137}Cs:^{241}Am activity ratios for Grabs 1 to 5 are presented in Table 3.40 and Figure 3.37. The ^{137}Cs and ^{241}Am specific activities ranged from 11.2 ± 0.05 to 322 ± 1 Bq kg^{-1} and 12.8 ± 0.05 to 589 ± 2 Bq kg^{-1}, respectively, for Grabs 1 to 5. ^{137}Cs and ^{241}Am specific activities exhibit similar trends with latitude between Grab 1 and 5,. There is an overall increase in activity with latitude, with ^{137}Cs and ^{241}Am activities in Grab 5 being 15 and 17 times higher, respectively, than in Grab 1. However, highest ^{137}Cs and ^{241}Am activities are found in Grab 3. As all the ratios are < 1.0. this shows that the sediments of each grab have undergone prolonged exposure to seawater (probably during sediment transport) resulting in re-dissolution of ^{137}Cs. There appears to be no relationship between sediment type, activity ratio and latitude as Grabs 1, 3 and 5 were collected from areas of sand while Grabs 2 and 4 were collected from areas of muddy sand (Institute of Geological Sciences; Sheet 54N 04W), with the ^{137}Cs:^{241}Am activity ratios for Grabs 2 to 4 being lower than those of Grabs 1 and 5.

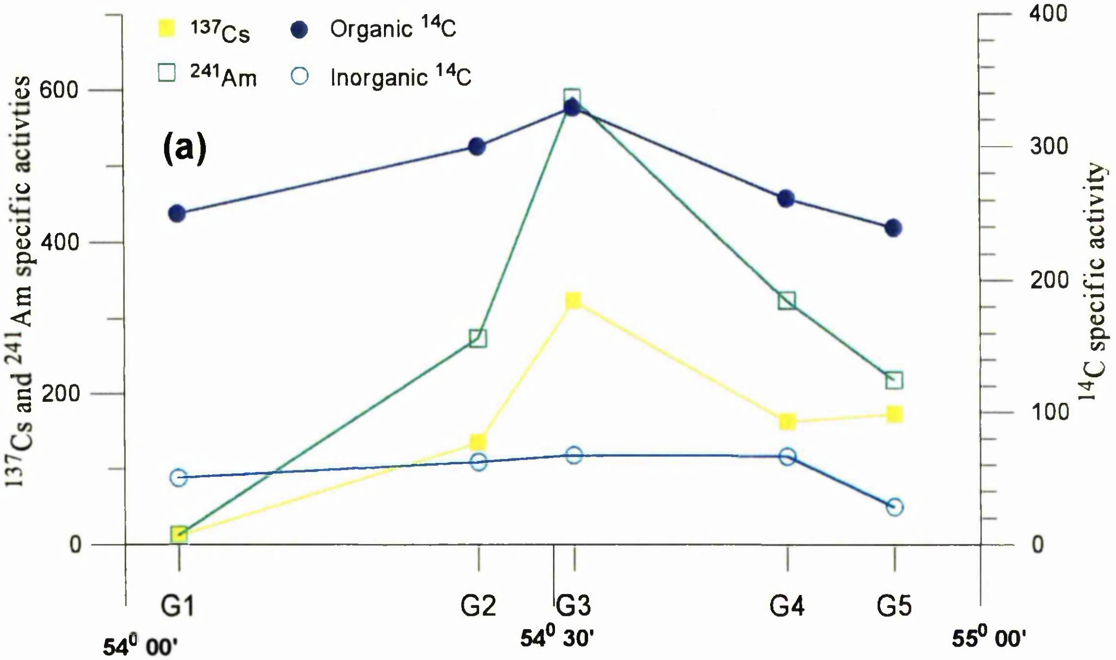
Table 3.40 ^{137}Cs and ^{241}Am activities (Bq kg^{-1} dry weight ± 1σ) and ^{137}Cs:^{241}Am activity ratio in sediment from Grabs 1 to 5.

Grab No.	**Location**	**^{137}Cs**	**^{241}Am**	**^{137}Cs:^{241}Am**
Grab 1 (PC190)	54^0 03' N 03^0 50' W	11.2 ± 0.05	12.8 ± 0.05	0.9 ±0.004
Grab 2 (PC187)	54^0 20' N 03^0 33' W	133 ± 1	273 ± 1	0.5 ± 0.004
Grab 3 (PC189)	54^0 25' N 03^0 58' W	322 ± 1	589 ± 2	0.5 ± 0.002
Grab 4 (PC188)	54^0 37' N 03^0 46' W	161 ± 0.2	323 ± 1	0.5 ± 0.006
Grab 5 (PC192)	54^0 ' 42N 03^0 43' W	171 ± 1	217 ± 1	0.8 ± 0.005

^{14}C specific activities in the inorganic and organic carbon fraction of Grabs 1 to 5

Inorganic and organic ^{14}C specific activities are presented in Table 3.41 and Figure 3.37. Inorganic ^{14}C specific activities (Bq kg^{-1} C) increase with latitude from Grabs 1 to 4, but there is a marked decrease in specific activity between Grabs 4 and 5, with Grab 5 having 0.56 times the specific activity of Grab 1. δ^{13}C values for of Grabs 1 to 5 range from + 1.2 to + 0.5 ‰ (relative to PDB) indicating a marine origin for the inorganic carbon fraction of Grabs 1 to 5. Organic carbon specific activities ranged from 240 ± 1 to 300 ± 3, with highest activities in Grab 2 and lowest in Grab 5. With the exception of Grab 5, the specific activities of the organic carbon fraction of the sediment are above modern marine background and, as with the surface activities of Cores 1 to 7, contain ^{14}C enhanced (Sellafield derived) organic material. δ^{13}C values for Grabs 1 to 5 range from - 15.2 to -28.3 ‰ (relative to PDB), indicating both marine and terrestrial inputs of organic material to the sediments.

Figure 3.37 (a) ^{137}Cs and ^{241}Am specific activities (Bq kg^{-1} dry weight) and ^{14}C specific activities (Bq kg^{-1} C) in the inorganic and organic carbon fractions of Grabs 1 - 5. (b) ^{137}Cs:^{241}Am activity ratios in Grabs 1-5.



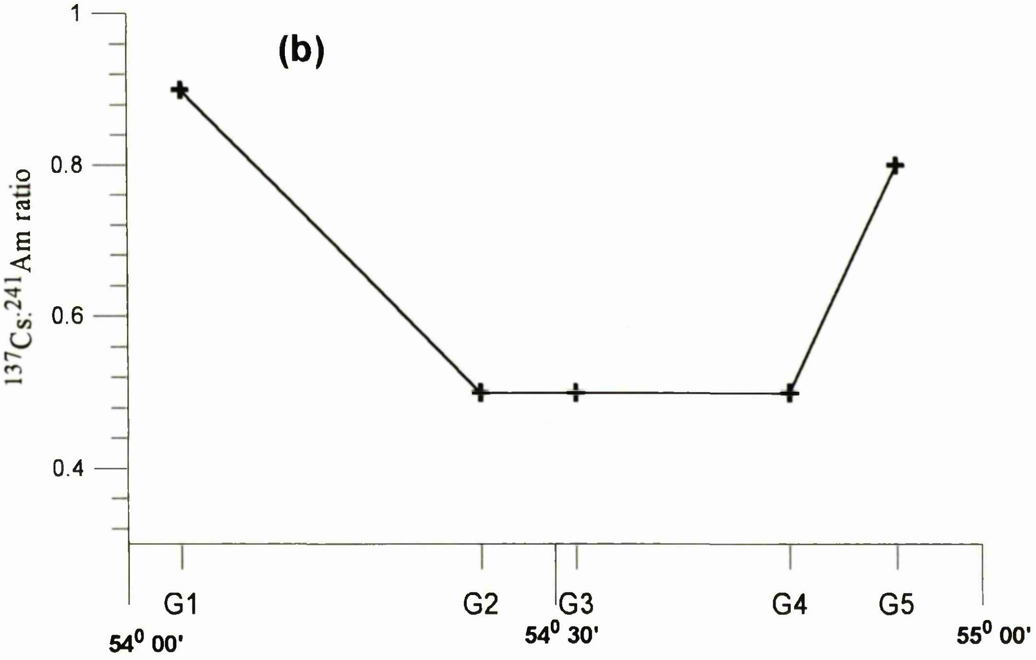


Table 3.41 Inorganic and organic carbon ^{14}C specific activities (Bq kg^{-1} C ± 1σ) and $\delta^{13}C$ values (‰ relative to PDB) in Grabs 1 to 5

Grab No.	**Location**	**$^{14}C_{(inorg)}$ activity**	**$\delta^{13}C_{(inorg)}$ (‰) value**	**$^{14}C_{(org)}$ activity**	**$\delta^{13}C_{(org)}$ (‰) value**
Grab 1 (PC190)	54^0 03' N 03^0 50' W	50 ± 1	+ 1.2	250 ± 1	- 21.0
Grab 2 (PC187)	54^0 20' N 03^0 33' W	62 ± 1	+ 0.8	300 ± 3	- 28.3
Grab 3 (PC189)	54^0 25' N 03^0 58' W	67 ± 1	+ 1.0	329 ± 3	- 15.2
Grab 4 (PC188)	54^0 37' N 03^0 46' W	66 ± 1	+ 0.6	261 ± 3	- 23.7
Grab 5 (PC192)	54^0 ' 42N 03^0 43' W	28 ± 1	+ 0.5	239 ± 1	- 21.5

In order to investigate any effect of the addition of coarse inter-tidally derived shell material with enhanced ^{14}C activities (Section 3.3) to the coarse fraction of the sediments, Grabs 2 and 3 were wet sieved into size fractions of > 500 μm, 500 - 63 μm and < 63 μm, and the sediment in each size fraction was analysed for inorganic ^{14}C activities (Table 3.42). The bulk of the sediment in both grabs was found in the 500 - 63 μm size fraction. However, this size fraction exhibited lower ^{14}C activities than the > 500 μm or < 63 μm size fractions in both grabs. The highest activities for both grabs was found in the largest size fraction although both activities were lower than the current marine background. As with the Cores 1 to 7 and Grabs 1 to 5 the $\delta^{13}C$ values for the different size fractions show that the inorganic material in the sediment, in the size separated fractions are of marine origin.

Table 3.43 ^{14}C specific activities (Bq kg^{-1} C ± 1σ) in size separated fractions of the inorganic carbon component of Grabs 2 and 3.

Sample	**Location**	**Size fraction**	**% of weight**	**^{14}C activity**	**δ^{13}C (‰)**
Grab 2 (PC187)	54^{0} 20' N 03^{0} 33' W	> 500µm	1%	182 ± 2	+ 0.9
Grab 2 (PC187)	54^{0} 20' N 03^{0} 33' W	500µm - 63 µm	80%	28 ± 1	+ 1.0
Grab 2 (PC187)	54^{0} 20' N 03^{0} 33' W	<63 µm	19%	80 ± 1	+ 0.5
Grab 3 (PC189)	54^{0} 25' N 03^{0} 58' W	> 500µm	1%	200 ± 2	+ 0.9
Grab 3 (PC189)	54^{0} 25' N 03^{0} 58' W	500µm - 63 µm	94%	60 ± 1	+ 1.1
Grab 3 (PC189)	54^{0} 25' N 03^{0} 58' W	<63 µm	5%	102 ± 1	+ 0.6

DISCUSSION AND CONCLUSIONS

❑ Analysis of DIC and sessile organisms collected on an annual basis from Burtonport is consistent with a site remote from the influence of Sellafield discharges. Ambient background values of 252 ± 1 Bq kg^{-1} C for the DIC, 253 ± 1 Bq kg^{-1} C for seaweed, 246 ± 2 Bq kg^{-1} C for mussels, 246 ± 2 Bq kg^{-1} C for flatfish, 252 ± 2 Bq kg^{-1} C for roundfish and 267 ± 5 Bq kg^{-1} C for crab were determined.

❑ Trends in ^{14}C activities in the DIC fraction of seawater and dissolved ^{137}Cs in seawater from Nethertown show that seawater at this site is not well mixed with respect to the Sellafield discharge. This renders the site unsuitable for use in relating the temporal variations in the ^{14}C specific activity of the DIC fraction of the water column with changes in the activity of the monthly ^{14}C discharges from Sellafield.

❑ Contrastingly , temporal variations in the ^{14}C activities of the DIC and POC at the St. Bees Head Site bear a strong qualitative resemblance to those of the monthly discharges, indicating that the water column is well mixed at this point. From these results it would appear that at this site, both the DIC and POC fractions of the water column respond rapidly (within weeks) to changes in the discharge activity.

❑ While ^{14}C activities in the DIC fraction of seawater from Portpatrick were lower than those at Nethertown or the St. Bees Head site, trends in ^{14}C activities in the DIC bear a qualitative resemblance to temporal variations in the monthly discharge activities, although an there is an apparent transit time of two months between the peak discharges of ^{14}C from Sellafield and the appearance of a peak in net ^{14}C activity in the DIC at Portpatrick. In contrast, trends in the ^{14}C activities in the other biogeochemical fractions (DOC, PIC and POC) bear no resemblance to temporal variations in the monthly discharge activities.

❑ Both at the St. Bees Head site and at Portpatrick, there is conclusive evidence of transfer of ^{14}C from the phase in which it is discharged from Sellafield (DIC) to the other biogeochemical phases of the water column (DOC, POC, PIC).

❑ Both an empirical and a simple modelling approach (using varying halving times for ^{14}C activity in the NE Irish Sea) indicate that close to 100% of the Sellafield ^{14}C discharges are dispersed beyond the Irish Sea, in the form of DIC. This is occurring on a time-scale of months and indicates that the 'dilute and disperse' mechanism is operating well, with the a large percentage of radionuclides in the dissolved phase being removed rapidly from the Irish Sea.

❑ ^{14}C analysis of mussel flesh and shells at Nethertown shows a reasonably rapid response to either changes in the discharge activities or DIC activities. However, the increases in ^{14}C specific activities of flesh and shell material occur at different times, with the highest shell activity occurring six months after that of the flesh activity.

❑ Using these ^{14}C data, dose calculations show that (based on the SEPA, RIFE report 1999) ingestion of ^{14}C *via* consumption of mussel flesh by members of the Sellafield fishing group is small in comparison to the overall dose from ^{14}C calculated by SEPA (1999) to this critical group.

❑ ^{14}C analysis of mussel flesh at Portpatrick does not show any apparent response to changes in either the ^{14}C discharges or DIC activities.

❑ Analysis of shell fragments collected from intertidal areas (Nethertown and Sandyhills Bay) suggests that such material could be a significant source of the ^{14}C present in the inorganic carbon fraction of the sediments.

❑ The use of ^{137}Cs:^{241}Am nuclide ratios to determine rates of mixing in the sediment was preposed by Mackenzie *et al.* (1999) according to the theory that rapidly mixed sediments would have low nuclide ratios (<2) due to the frequent exposure of the sediment to the overlying water column, resulting in re-dissolution of ^{137}Cs (hence lowering the ^{137}Cs:^{241}Am nuclide ratio), less rapidly mixed sediments would have a higher nuclide ratio (2-6) and slowly mixed sediments would have a ratio of >6. Following the work of Wolstenholme (1999), this approach was adopted in this study in order to identify zones of differing mixing intensities within the sediment column in order to relate the incorporation of Sellafield derived ^{14}C to the physical mixing characteristics of these sediments. However, despite the differences in biogeochemistry and transfer routes into the sediments a trend of increasing radionuclide specific activities and inventories (^{137}Cs, ^{241}Am, inorganic ^{14}C and organic ^{14}C) with increasing latitude is seen. This indicates that there is a northwards movement of contaminated fine sediment.

☐ If this is so, then ^{137}Cs:^{241}Am nuclide ratios are inappropriate for use as proxies for the identification of zones of differing mixing intensity within the sediments, as the northwards movement of sediment would also result in low ^{137}Cs:^{241}Am nuclide ratios due to re-dissolution of ^{137}Cs during sediment transport. Mixing zones determined using ^{137}Cs:^{241}Am nuclide ratios would therefore be based on the physical transport of the sediment combined with actual mixing characteristics of the sediment, giving apparently greater depths of mixing than apply in reality in northern locations due to addition of sediment with a low ^{137}Cs:^{241}Am nuclide ratio. Correspondingly, removal (by northwards transport) of surface sediment with a low ^{137}Cs:^{241}Am nuclide ratio from southern locations could lead to underestimation of the intensity of surface mixing. It is therefore difficult to relate the depth of penetration of Sellafield derived ^{14}C into the sediments to the physical mixing characteristics of the sediment based on the ^{137}Cs and ^{241}Am data presented here.

☐ While the ^{137}Cs and ^{241}Am activity inventories and ^{137}Cs:^{241}Am nuclide ratios indicate that there is a northwards movement of fine grained sediment in the Irish Sea, these nuclides exhibit different environmental behaviours in the marine environment which could cause the distributions of activity and activity ratios to be interpreted as due to their differing behaviour and not to sediment movement. Analysis of Sellafield derived radioisotopes (in this case ^{238}Pu and ^{239,240}Pu), which have identical behaviour in the marine environment, should also show increased activity inventories with latitude if there is a northwards movement of fine grained sediment.

☐ In order to investigate this a small number of plutonium isotope analysis were carried out. Due to a shortage of time and financial restrictions analyses only a limited number of analyses could be carried out (Core 2, Core4 and Core7). While such a limited data set is not conclusive, the trends of increasing inventories with latitude shown supports the theory of northwards movement of fine grained sediment in the NE Irish Sea.

- Choosing suitable ^{14}C background activities for the inorganic and organic carbon fraction of the sediment (see Section 3.1) is problematical and so background activities representing upper and lower limits for background activities have been used to calculate inventories for Sellafield derived ^{14}C for each core (Bq m^{-2}) and from these a total inventory for Sellafield derived ^{14}C within the area studied. It is calculated that a small percentage (approximately 1 - 2 %) of the ^{14}C discharges (1952 - 1998) is retained in the sediments of the NE Irish Sea. This is mainly contained in the organic carbon fraction and to a lesser extent in the inorganic form. This is consistent with rapid removal of Sellafield derived ^{14}C through the North Channel.

- The upper limit for the total inventory of ^{14}C retained in the inorganic carbon fraction (assumed background of 0 Bq kg^{-1} C) of fine NE Irish Sea sediment was estimated to be 917 GBq which corresponds to approximately 1% of the integrated Sellafield discharges to the time of this study.

- The lower limit for the total inventory of ^{14}C retained in the inorganic carbon fraction (assumed background of 45 Bq kg^{-1} C) of fine NE Irish Sea sediment was estimated to be 69 GBq which corresponds to approximately 0.08 % of the total Sellafield discharges.

- The upper limit for the total inventory of ^{14}C retained in the organic carbon fraction (assumed background of 98 Bq kg^{-1} C) of fine NE Irish Sea sediment was estimated to be 1.2 x 10^{3} GBq which corresponds to approximately 1.2% of the total Sellafield discharges.

- The lower limit for the total inventory of ^{14}C retained in the organic carbon fraction (assumed background of 131 Bq kg^{-1} C) of fine NE Irish Sea sediment was estimated to be 910 GBq which corresponds to approximately 1% of the total Sellafield discharges.

- ☐ Approximately 1.5 % of the environmental inventory of discharged ^{137}Cs (1952 - 1998) remains in the area investigated, consistent with initial uptake of 10% of the discharges into the fine grained sediments of the Sellafield "mud patch", followed by redistribution of the contaminated sediments and re-dissolution of ^{137}Cs from these sediments.

- ☐ Approximately 40 % of the discharged ^{241}Am (allowing for ingrowth from ^{241}Pu) remains in the area investigated. This is consistent with the initial uptake of 90 % of the discharged ^{241}Am into the fine grained sediments of the Sellafield "mud patch" followed by redistribution of this contaminated material.

- ☐ Currently, there is insufficient data to comment on the distribution of ^{14}C (and other radionuclides) in the coarse sediments recovered by grab sampling.

In conclusion it would seen that further investigation of the trend of northwards movement of contaminated fine grained sediments is warranted. It would be recommended that such a study should cover a larger area than this project and should include sediment size analysis and other sedimentary characteristics in addition to radionuclide analysis.

Furthermore, with a more intensive sampling program, it could be determined whether anthropogenic ^{14}C can act as a tracer of carbon transfer between different biogeochemical fractions. For example, it could be used in studies of the rate of uptake of Sellafield derived ^{14}C by phytoplankton in the Irish Sea in order to establish rates of carbon cycling between phytoplankton and filter feeding organisms in the Irish Sea.

References

Aarkrog, A., H. Dahlgaard, et al. (1999). "Marine radioactivity in the Arctic: a retrospect of environmental studies in Greenland waters with transport of ^{90}Sr and ^{137}Cs with the East Greenland current." The Science of the Total Environment **237/238**: 143 - 151.

Adams, J. L., H. Faure, et al. (1990). "Increases in terrestrial carbon storage from the last glacial maximum to the present." Nature **348**: 711-714.

Allen, J. R., E. G. Jones, et al. (1996). The distribution of nutrients and phytoplankton in the north-west Irish Sea., National Rivers Authority (NW Region).

Armstrong, F. A. J., P. M. Williams, et al. (1966). "Photo-oxidation of organic matter in seawater by ultra-violet radiation, analytical and other applications." Nature **211**: 481-483.

Arrol, W. J. and r. Glascock (1947). "Conversion of carbon dioxide to acetylene on a micro scale." Nature **159**: 810.

Aston, S. R., D. A. Assinder, et al. (1981). "Plutonium occurrence and phase distribution in sediments of the Wyre Estuary, north-west England." Marine Pollution Bulletin **12**: 308-314.

Aston, S. R. and D. A. Stanners (1982). "The transport and deposition of americium in intertidal sediments of the Ravenglass estuary and its relationship to plutonium." Environmental pollution, Series B **3**: 1-9.

Baes, J., A. Bjorkstrom, et al. (1985). Uptake of carbon dioxide by the oceans. Atmospheric Carbon Dioxide and the Global Carbon Cycle, US Department of Energy Report DOE/ER-0239. J. R. Trabacka, NTIS. Springfield, Virginia.

Barker, H. (1953). "Radiocarbon dating: large-scale production of acetylene from organic material." Nature **221**: 49-50.

Barker, H., R. Burliegh et al. (1969). New method for the combustion of samples for radiocarbon dating" Nature **221**, 49-50.

Barnes, R. D. (1987). Invertebrate Zoology. 6th edition. Saunders College Publishing, Pennsylvania, USA

Baxter, M. S. and J. G. Farmer (1973). "Radiocarbon: short-term variations." Earth and Planetary Science Letters **20**: 295.

Baxter, M. S., I. G. McKinley, et al. (1979). "Windscale radiocaesium in the Clyde Sea area." Marine Pollution Bulletin **10**: 116-120.

Baxter, M. S. and A. Walton (1971). "Fluctuations of atmospheric carbon-14 concentrations during the past century." Proceedings of the Royal Society of London, Series A. **321**: 105-127.

Begg, F. H. (1992). Anthropogenic ^{14}C in the natural aquatic environment. Physical Sciences. Glasgow, University of Glasgow.

Begg, F. H., M. S. Baxter, et al. (1991). Anthropogenic ^{14}C as a tracer in western UK coastal waters. Radionuclides in the Study of Marine Processes. P. J. Kershaw and D. S. Woodhead. London, Elsevier Applied Science.

Begg, F. H., G. T. Cook, et al. (1992). "Anthropogenic radiocarbon in the Eastern Irish Sea and Scottish coastal waters." Radiocarbon **34**(3): 707-716.

Belderson, R. H. (1964). "Holocene sedimentation in the western half of the Irish Sea." Marine Geology **2**: 147-163.

Belderson, R. H. and A. H. Stride (1969). "Tidal currents and sand wave profiles in the north-eastern Irish Sea." Nature **222**: 74-75.

Berger, W. H., K. Fischer, et al. (1988). Ocean carbon dioxide flux: Maps of primary production and export production. In: Biogeochemical Cycling and Fluxes Between the Deep Euphotic Zone and Other Oceanic Realms., NoAA, Washington D.C.

Berger, W. H., V. S. Smetacek, et al. (1989). Productivity of the ocean: Present and past. Dahlem Workshop Report. New York, John Wiley and Sons.

Berner, R. A. (1982). "Burial of organic matter and pyrite sulfur in the modern ocean: Its geochemical and environmental significance." American Journal of Science **282**: 451-473.

BNFL, (1976 - 1999). Annual report on Radioactive discharges and monitoring of the Environment. Safety, Health and Environment Directorate, Risley, BNFL Publications

BNFL (1992a). Nuclear fuel reprocessing technology. Risley, BNFL Publications.

BNFL (1992b). The thermal oxide reprocessing plant (THORP). Risley, BNFL Publications.

BNFL (1996). THORP: A world leader for the reprocessing and recycling of used nuclear fuel. Risley, BNFL Publications.

Bonaka, H. (1980). Produktion und freisetung von tritium und kohlenstof-14 durch kernwaffenversuche, testexplosionen und kerntechnische Anlagen, einschliealich Weideraufbereitungsanlagen. Strahlenschutzprobleme im Zusammenhang mit der Verwendung von Tritium und Kohlenstoff-14 und Ihren Verbindungen. F. Strieve and G. Kistner, institute fur Strahlenhygiene des Bundesgesundheitsamtes.

Bowden, K. F. (1950). "Processes affecting the salinity of the Irish sea." Monthly notices of the Royal Astronomical society -Geophysics supplement **6**: 63 - 89.

Bradley, P. E., E. M. Scott, et al. (1991). Radiocaesium in local and regional coastal water modelling exercises. Radionuclides in the Study of Marine Processes. P. J. Kershaw and D. S.

Woodhead. London and New York, Elsevier applied science.

Broecker, W. S., T. H. Peng, et al. (1985). "The distribution of bomb radiocarbon in the ocean." Journal of Geophysical Research **83**: 6179-6970.

Broeker, W. S. and T. H. Peng (1982). Tracers in the Sea., Eldigio Press.

Brown, J. E., P. McDonald, et al. (1995). "Discharge patterns of metals and radionuclides in the Ribble Estuary saltmarshes." Proceedings of 10th international Conference; Heavy metals in the environment. **1**.

Bruns, M., K. O. Munnich, et al. (1980). "Natural radiocarbon variations from AD200 to 800." Radiocarbon **22**: 273 -277.

Bush, R. P., G. M. Smith, et al. (1984). "Carbon-14 waste management." Commission of the European Communities Nuclear Science and Technology, Luxembourg, EUR 8749 EN.

Bush, R. P., I. F. White, et al. (1983). Carbon-14 waste management. UK Atomic Energy Report R10543- Harwell., Research Establishment.

Calvert, S. E., R. E. Karlin, et al. (1991). "Low organic carbon accumulation rates in Black Sea sediments." Nature **351**: 692-695.

Carlson, C. A., H.W. Ducklow et al. (1994) Annual flux of dissolved organic carbon from the photic zone in the northwestern Sargasso Sea. Nature **371** 405-408.

Carter, M. N. and A. A. Moghissi (1977). "Three decades of nuclear testing." Health Physics **33**: 55-71.

Chester, R. (1990). Marine Geochemistry. London, Unwin Hyman.

Cleveland, J.M., (1979). "Critical review of plutonium equilibrium of environmental concern. In: Chemical Modelling in Aqueous Systems. E. A. Jenne (eds) American Chemistry Society 321-338.

Cleveland, J.M. (1970a). "The Chemistry of Plutonium". Gordon and Breach, New York.

Cleveland, J.M., (1970b). "Aqueous coordination complexes of plutonium. Coordination Chemistry Review **5** 101-137.

Cook, G. T., F. H. Begg, et al. (1995). "Anthropogenic ^{14}C marine geochemistry in the vicinity of a nuclear fuel reprocessing plant." Radiocarbon **37**(2): 459-467.

Cook, G. T., A. B. MacKenzie, et al. (1997). "Remobilisation of Sellafield-derived radionuclides and transport from the North East Irish Sea." Journal of Environmental Radioactivity **40**(1): 227 - 341.

Cook, G. T., A. B. MacKenzie, et al. (1998). "Natural and anthropogenic ^{14}C in the UK marine environment." Journal of Environmental Radioactivity **40**(1): 89-111.

Dahlgaard, H. (1995). "Transfer of European coastal pollution to the Arctic: Radioactive tracers." Marine Pollution Bulletin **31**: 3-7.

Damon, P. E., A. Long, et al. (1973). "On the magnitude of the 11-year radiocarbon cycle." Earth and Planetary Science Letters **20**: 300-306.

Davies, A. M. and P. Hall (2000). "The response of the North Channel of the Irish Sea and Clyde Sea to wind forcing." Continental Shelf Research **20**: 897 - 940.

Day, J. P. and J. E. Cross (1981). "^{241}Am from the decay of ^{241}Pu in the Irish Sea." Nature **292**: 43-45.

de Jong, A. F. M., W. G. Mook, et al. (1979). "Confirmation of the Suess wiggles: 3200-3700

BC." Nature **280**: 48-49.

Degens, E. T. and K. Mooper (1976). Factors controlling the distribution and early digenesis of organic matter in marine sediments. Chemical Oceanography, Vol. 5. J. P. Riley and R. Chester. London, Academic Press.

Dickson, R. R. and R. G. V. Boelens (1988). The status of the current knowledge on anthropogenic influences in the Irish Sea., International Council for the Exploration of the Sea.

Duce, R. A. and E. K. Duursma (1977). Inputs of organic matter to the ocean. Marine Chemistry. **5:** 319-339.

Dunster, H. J. (1998). "An historical perspective of radioactive effluents: discharges from Sellafield to the Irish Sea." Radiation Protection Dosimetry **1-4**: 15-21.

Duplessy, J. C. (1986). "Carbon Dioxide and other greenhouse gases: Climatic and associated impacts." Proceedings of a symposium organised by the Commission of the European Communities, Directorate-General for Science, Research and development.

Dyer, K. R. (1986). Review of oceanographic processes influencing radioactive waste disposal in the Irish Sea. IOS Report No. 232. Goldmaning, UK, Institute of Oceanographic Sciences.

Eadie, B. J., L. M. Jeffrey, et al. (1978). "Some observations on the stable carbon isotope composition of dissolved and particulate organic carbon in the marine environment." Geochimica et Cosmochimica Acta **42**: 1265-1269.

Eakins, J. D., A. Morgan, et al. (1990). "Measurements of α-emitting Plutonium and Americium in the intertidal sands of west Cumbria, UK." Journal of Environmental Radioactivity **11**: 37-54.

Eisenbud, M. (1989) "Management strategies for low-level radioactive waste disposal" B New York State Journal of Medicine **65** (4) 451-460

Elsasser, W. R., E. P. Nay, et al. (1956). "Cosmic ray intensity and geomagnetism." Nature **178**: 1226-1227.

Erlenkeuser, H. (1980). "^{14}C age and vertical mixing of deep-sea sediments." Earth and Planetary Science Letters **47**: 319-326.

Fogg, G. E. (1975). Primary productivity. Chemical Oceanography. J. P. Riley and G. Skirrow. New York, Academic Press.

Fry, B., E.T. Peltzer, et al. (1996) Analysis of marine DOC using a dry combustion method. Marine Chemistry **54** 191-201.

Godwin, H. (1962). "Half-life of carbon." Nature **195**: 984.

Gowen, R. J., B. M. Steward, et al. (1995). "Regional differences in stratification and its effect on phytoplankton production and biomass in the northwestern Irish Sea." Journal of Plankton Research **17**(4): 753 - 769.

Gray, J., S. R. Jones, et al. (1995). "Discharges to the environment from the Sellafield site, 1951-1992." Journal of Radiological Protection **15**(2): 99-131.

Gross, M. G. (1990) Oceanography. 6th edition . Merrill Publishing Company, Columbus.

Gulliver, P., Cook G.T. et al. (2001) "Transport of Sellafield derived ^{14}C from the Irish Sea through the North Channel" Proceedings of the 17th International Radiocarbon Conference, Jerusalem 1999, Radiocarbon In Press.

Gupta, S. K. and H. A. Polach (1985). Radiocarbon dating practices at ANU. Handbook, Radiocarbon Laboratory, research School of Pacific Studies, ANU, Canberra.

Hallberg, L., H. Brise, et al. (1960). Determination of ^{55}Fe and ^{59}Fe in blood" Int. J. Appl. Radiat. Isotopes **9** 100-108.

Hamilton, E. I. and K. R. Clarke (1984). "The recent sedimentation history of the Esk estuary, Cumbria, UK: the application of radiochronology." Science of the Total Environment **35**: 325 - 386.

Harkness, D. D. (1983). "The extent of natural ^{14}C deficiency in the coastal environment of the United Kingdom" Proceedings of the 1st International Symposium on ^{14}C and Archaeology, Groningen, European Council.

Hetherington, J. A. (1975). The behaviour of plutonium nuclides in the Irish Sea. Environmental toxicisity of aquatic radionuclides: Models and mechanisms. M. W. Miller and J. N. Stannard. Michigan, USA, Ann Arbour Science.

Hill, A. E., J. Brown, et al. (1997). "The summer gyre in the Western Irish Sea: Shelf sea paradigms and management implications." Estuarine, Coastal and Shelf Science **44A**: 83-95.

Hill, A. E. and J. H. Simpson (1986). "Low frequency variability of the Scottish Coastal Current induced by along-shore pressure gradients." Estuarine, Coastal and Shelf Science **27**: 163 - 180.

Hills-Colinvaux, L. (1980). " Ecology and taxonomy of Halimesa: primary producer of coral reefs." Adv. Marine Biology **17**: 1-327.

Howarth, M. J. (1982). Non-tidal flow in the North Channel of the Irish Sea. Hydrodynamics of Semi-enclosed Shelf Seas. J. C. J. Nihoul. Amsterdam, Elsevier: 205 - 241.

Hunt, G. J. (1985). Timescales for dilution and dispersion of transuranics in the Irish Sea near Sellafield. Science of the Total Environment **46**, 261-278.

Hunt, G. J. and P. J. Kershaw (1990). "Remobilisation of artificial radionuclides from the sediment of the Irish Sea." Journal of Radiological Protection **10**: 147-151.

International Atomic Energy Agency (1991a). IAEA Bulletin, **33** (4). Quarterly Journal of the

IAEA, Vienna.

International Atomic energy Agency (1991b).Report on Consultants Group meeting on ^{14}C reference materials for Radiocarbon Laboratories. February 18-20, 1991, Vienna.

Irish Sea Study Group. (1990) The Irish Sea: An environmental review. Volumes I to V, Liverpool University Press.

Jefferies, D.F. and A.K. Steele (1989) "Observed and predicted concentrations of ^{137}Cs in seawater of the Irish Sea 1970-1985" Journal of Environmental Radioactivity **10** (2) 172-189.

Jefferies, D. F., A. Preston, et al. (1973). "Distribution of caesium-137 in British Coastal Waters." Marine Pollution Bulletin **4**: 118 - 122.

Jefferies, D. F., A. K. Steele, et al. (1982). "Further studies on the distribution of ^{137}Cs in British Coastal waters -1. Irish Sea." Deep -Sea Research **29**(6A): 713 - 738.

Jensen, P. R., R. A. Gibson, et al. (1985). " Photosynthesis and calcification in four deep water Halimeda species (Chlorophyceae, Caulerpales)." Deep Sea Research **32**: 451-464.

Johnson, L. R. (1983). "The transport mechanisms of clay and fine silt in the North Irish Sea." Marine Geology **52**: M33-M41.

Jones, P. G. W. and A. R. Folkard (1970). "Hydrographic observations in the eastern Irish Sea with particular reference to the distribution of nutrient salts." Journal of the Marine Biological Association of the United Kingdom **51**: 159 - 182.

Keeling, C. D., R. B. Bacastow, et al. (1982). Measurements of the concentration of carbon dioxide at Mauna LOA Observatory, Hawaii. Carbon Dioxide Review. W. C. Clarke. New York, Oxford University Press: 377-385.

Kelly, G. N., J. A. Jones, et al. (1975). The predicted radiation exposure of the population of the European Community resulting from discharges of krypton-85, tritium, carbon-14 and iodine-129 from the nuclear power industry to the year 2050. V/2676/75. Luxembourg, Commission of the European Communities.

Kemp. A. I. W., R. I. Thomas et al. (1976). Fish Resources Board, Canada. **33**, 440.

Kennington, K., J. R. Allen, et al. (1999). "Phytoplankton and nutrient dynamics in the north-east Irish Sea." Hydrobiologia **393**: 57-67.

Kershaw, P. J. (1986). "Radiocarbon dating of Irish Sea Sediments." Estuarine, Coastal and Shelf Science **23**: 295 - 303.

Kershaw, P. J. and A. Baxter (1995). "The transfer of reprocessing wastes from north-west Europe to the Arctic." Deep -Sea Research II **42**(6): 1413-1448.

Kershaw, P. J., D. McCubbin, et al. (1999). "Continuing contamination of north Atlantic and Arctic waters by Sellafield radionuclides." The Science of the Total Environment **237/238**: 119 - 132.

Kershaw, P. J., R.J. Pentreath, et al. (1992) A review of radioactivity in the Irish sea. A report prepared for the Marine Pollution Monitoring Management Group. Ministry of Agriculture, Fisheries and Food aquatic environment monitoring report number 32. Lowestoft.

Kershaw, P. J., D. S. Woodhead et al. (1990) A sediment history of Sellafield discharges. Journal of Environmental Radioactivity **12**, 201-241.

Kershaw, P. J., D. J. Swift, et al. (1988). "Evidence of recent sedimentation in the Eastern Irish Sea." Marine Geology **85**: 1 - 14.

Kershaw, P. J., D. J. Swift, et al. (1984). "The incorporation of plutonium, americium and curium into the Irish Sea seabed by biological activity." Science of the Total Environment **40**: 61 - 81.

Kershaw, P. J., D. J. Swift, et al. (1983). "Plutonium redistribution by biological activity in Irish Sea sediments." Nature **306**: 774 - 775.

Kirby, R., W. R. Parker, et al. (1983). Part 3. An evaluation of possible mechanisms for the incorporation of radionuclides in to marine sediments. Sedimentation studies relevant to low-level radioactive effluent dispersal in the Irish Sea.

Knight, P. J. and M. J. Howarth (1999). "The flow through the North Channel of the Irish Sea." Continental Shelf Research **19**: 693 - 716.

Lassey, K. R., M. R. Manning, et al. (1988). Assessment of the inventory of carbon-14 in the oceans: an overview. Inventories of selected radionuclides in the oceans. IAEA-TECDOC-481. Vienna, IAEA.

Le Clercq, M., J. Van der Plicht, et al. (1997) Radiocarbon in marine dissolved organic carbon (DOC) Nuclear Instruments and Methods in Physics B **123** 443-446.

Leonard, K. S., D. McCubbin, et al. (1997). "Distribution of Technetium-99 in UK coastal waters." Marine Pollution Bulletin **34**(8): 628-636.

Leonard, K. S., D. McCubbin, et al. (1998). "^{137}Cs/^{90}Sr ratios in the Irish Sea and adjacent waters: A source term for the Arctic." Radiation Protection Dosimetry **75**(1-4): 207-212.

Libby, W. F. (1946). "Atmospheric helium-three and radiocarbon from cosmic radiation." Physical review **69**: 671-772.

Libes, S. M. (1992). An introduction to Marine Biogeochemistry. New York, John Wiley and Sons.

Light, E. S., M. Merker, et al. (1973). "Time dependence worldwide distribution of atmospheric neutrons and their products 2: Calculation." Journal of Geophysical Research **78**: 2741-2762.

Maberly, S. C. and T. V. Madsen (1990). "Contribution of air and water to the carbon balance of *Fucus spiralis*." Marine Ecology Progress Series **62**: 175 - 183.

MacKenzie, A. B., G. T. Cook, et al. (1999). Radionuclide distributions and particle size associations in Irish Sea surface sediments: implications for actinide dispersion. Journal of Environmental Radioactivity **44** 275-296

MacKenzie, A. B., G. T. Cook, et al. (1998). "The influence of mixing timescales and re-dissolution processes on the distribution of radionuclides in northeast Irish Sea sediments." Journal of Environmental Radioactivity **39**(1): 35-53.

MacKenzie, A. B. and R. D. Scott (1993). "Sellafield waste radionuclides in Irish Sea intertidal and salt marsh sediments." Environmental Geochemistry and Health **15**: 173-184.

MacKenzie, A. B., R. D. Scott, et al. (1994). "Sediment Radionuclide Profiles: Implications for mechanisms of Sellafield waste dispersal in the Irish Sea." Journal of Environmental Radioactivity **23**: 39 -69.

MacKenzie, A. B., R. D. Scott, et al. (1987). "Mechanisms for northwards dispersal of Sellafield waste." Nature **329**(6134): 42-45.

MacKenzie, A. B., M.S. Baxter, et al. (1979). "The determination of ^{134}Cs, ^{137}Cs, ^{210}Pb, ^{226}Ra and ^{228}Ra in nearshore marine sediments and seawater" Journal of Radioanalytical Chemistry **48** 29-47

MAFF (1990 - 1999). Radioactivity in food and the environment, Ministry of Agriculture, Fisheries and Food, Lowestoft, UK.

Mantoura, R. F. C. and E. M. S. Woodward (1983). "Conservative behaviour of riverine dissolved organic carbon in the Severn Estuary: chemical and geochemical implications." Geochemica et Cosmochemica Acta **47**: 1293-1309.

Martin J. H., D.M Knauer. et al. (1987). VERTEX: carbon cycling in the northeast Pacific. Deep Sea Research **34**, 474-478

Mauchline, J. (1980). Artificial radioisotopes in the marginal seas of north-western Europe. The North-West European Shelf Seas: the Sea Bed and the Sea in Motion. II. Physical and Chemical Oceanography, and Physical Resources. F. T. Banner, M. B. Collins and K. S. Massie. Amsterdam, Elsevier: 517-542.

Mazaud, A., C. Laj, et al. (1991). "Geomagnetic field control of ^{14}C production over the last 80KY: Implications for the radiocarbon timescale." Geophysical research Letters **18**(10): 1885-1888.

McCartney, M., P. J. Kershaw, et al. (1994). "Artificial radionuclides in the surface sediments of the Irish Sea." Science of the Total Environment **141**: 103-138.

McDonald, P., G. T. Cook, et al. (1990). "Radionuclide transfer from Sellafield to South-west Scotland." Journal of Environmental Radioactivity **12**: 285-298.

McKay, W. A. and M. S. Baxter (1986). "Radiocaesium and circulation patterns West of Scotland." Journal of Environmental Radioactivity **4**: 205 - 232.

McNamara, N., McCartney et al. (1998) "A review of ^{14}C waste arising from the nuclear industry in the United Kingdom" Proceedings of the 16th International Radiocarbon Conference, Groningen, 1996. Radiocarbon **40** (1) 425 - 432.

McNichol, A. P., G. A. Jones, et al. (1994). "The rapid preparation of seawater $\sum CO_2$ for radiocarbon analysis at the National Ocean Sciences AMS facility." Radiocarbon **36**(2): 237-246.

Menzel, D. W. and R. Vaccaro (1964). "Measurement of dissolved organic and particulate carbon in seawater." Limnology et Oceanography **9**: 138-142.

Meybeck, M. (1982). "Carbon, nitrogen and phosphorus transport by world rivers." American Journal of Science **282**: 401-450.

Meyers-Schulte, K. J. and J. I. Hedges (1986). "Molecular evidence for a terrestrial component of organic matter dissolved in ocean water." Nature **321**: 61-63.

Michener, R. H. and D. M. Schell (1994). "Stable isotope ratios as tracers in marine aquatic food webs." Stable Isotopes in Ecology and Environmental Science. K. Lajtha and R. H. Michener. Oxford, Blackwell Scientific Publications.

Miller, J. M., B. W. Thomas, et al. (1982). "Measurement of marine radionuclide distribution using a towed sea-bed spectrometer." Marine Pollution Bulletin **13**: 315-319.

Milliman, J. D. (1993). "Production and accumulation of calcium carbonate in the ocean: budget of a non-steady state." Global Biogeochemical Cycles **7**: 927-957.

Milliman, J. D. and A. W. Droxler (1995). "Calcium carbonate sedimentation in the global ocean: linkages between the neritic and pelagic environments." Oceanography **8**: 92-94.

Munnich, K. O. and W. Roether (1967). Transfer of bomb ^{14}C and tritium from the atmosphere to the ocean. Radioactive Dating and Methods of Low-Level Counting. Vienna, IAEA: 93-104.

Murray, C. N., H. Kautsky, et al. (1978). "Actinide activities in water entering the North Sea." Nature **276**: 225-230.

NEA (1980). The radiobiological significance and management of tritium, carbon-14, krypton-85 and iodine-129 arising from the fuel cycle. Report by NEA Group of Experts, Nuclear Energy Agency.

Neinhuis, P. H. (1981). Distribution of organic matter in living marine organisms. Marine Organic Chemistry. E. K. Duursma and R. Dawson. Amsterdam, Elsevier: 31-69.

Nelson, D. M. and M. B. Lovett (1978). "Oxidation state of plutonium in the Irish Sea." Nature **276**: 599-601.

Noakes, J. E., I. F. Isbell, et al. (1963). "Benzene synthesis by low temperature catalysis for radiocarbon dating." Geochimica et Cosmochimica Acta **27**: 797-804.

Noakes, J. E., S. M. Kim, et al. (1965). Chemical and counting advances in liquid scintillation age dating. Radiocarbon and Tritium dating, proceedings of the 6th international conference, Us atomic energy commission.

Otlet, R. L., A. J. Walker, et al. (1997). "Background carbon-14 levels in UK foodstuffs 1981 - 1995, based on a 1992 survey." Journal of environmental radioactivity **34**: 191 - 196.

Pantin, H. M. (1977). Quaternary sediments of the northern Irish Sea. The Quaternary History of the Irish Sea. C. Kidson and M. J. Tooley. Liverpool, Seel House Press: 27-54.

Pantin, H. M. (1978). "Quaternary sediments from the north-east Irish Sea; Isle of Man to Cumbria." Bulletin of the geological Society of great Britain **64**: 43.

Parsons, T. R. (1975). Particulate organic carbon in the sea. In: Chemical Oceanography. J. P. Riley and G. Skirrow (eds). Volume 2, 365-383. Academic Press, London.

Pentreath, R. J., M. B. Lovett, et al. (1984). Impact on public radiation exposure of transuranium nuclides discharged on liquid wasted from fuel element reprocessing at Sellafield, United Kingdom. Vienna, International Atomic Energy Association.

Pietig, F. and H. W. Scharoenseel (1966). "Determination of age by liquid scintillation spectrometry: a new catalyst for the synthesis of benzene." Atompraxis **12**: 95-97.

Pilson, M. E. Q. (1998). An Introduction to the Chemistry of the Sea. New Jersey, USA, Prentice Hall.

Prandle, D. (1976). "Research note. Wind induced flow through the North Channel of the Irish Sea." Geophysical Journal of the Royal Astronimical Society **45**: 437 - 442.

Prandle, D. (1984). "A modelling study of the mixing of ^{137}Cs in the seas of the European continental shelf." Philosophical Transactions of the Royal Society of London **A310**: 407 - 436.

Pulford, I. D., R. L. Allen et al. (1998). " Geochemical associations of Sellafield derived radionuclides in saltmarsh deposits if the Solway Firth" Environmental Geochemistry and Health **20** 95-101

Putten, E. A., D. F., et al. (2000). "High resolution distribution of trace metals in the calcite shell layer of modern *Mytilus edulis*: Environmnetal and biological controls." Geochimica et Cosmochimica Acta **64**(6): 997-1011.

Quay, P. D. and M. Stuiver (1980). "Vertical advection-diffusion rates in the oceanic thermocline determined from ^{14}C distributions." Radiocarbon **22**: 607-625.

Ramster, J. W. and H. W. Hill. (1969). "The current system in the northern Irish Sea." Nature **224**: 59 - 61.

Raymond, P.A. and J. E. Bauer. (2001) "DOC cycling in a temperate estuary: A mass balance approach using natural ^{14}C and ^{13}C isotopes" Limnology and Oceanography **46** (3) 655-667

Richey, J. E., J. T. Brock, et al. (1980). "Organic carbon: Oxidation and transport by the Amazon river." Science **207**: 1348-1351.

Rotty, R. M. and C. D. I. Masters, (1985). Carbon dioxide from fossil fuel combustion: trends, resources and technological implications. Atmospheric Carbon Dioxide and the global carbon cycle, US Department of Energy Report, DOE/ER-0239. Ed. J. R. E. Trabacka, NTIS, Springfield, Virginia.: 63-80.

Schlesinger, W. H. and J. M. Melack (1981). "Transport of organic carbon in the world's rivers." Tellus **33**: 172-187.

Scott, E. M., D.D. Harkness, et al. (1998) "Interlaboratory comparisons: Lessons learned" Proceedings of the 16th International Radiocarbon Conference, Groningen, 1997. Radiocarbon **40** (1) 331-240

Seligman, H. (1955). The disposal of waste products in the Irish Sea. Part 1. First experiments for the study of movement and dilution of released dye in the sea. International Conference on the Peaceful Uses of Atomic Energy, Geneva.

Seligman, H. and J. M. C. Scott (1948). The dissipation of effluent in the Irish Sea., Atomic Energy Research Establishment, Harewell.

SEPA (1995 - 1999) "Radioactivity in Food and the Environment." In association with MAFF, Lowestoft, UK.

Sharpe, J. H. (1973). "Total organic carbon in seawater -comparison of measurements using persulphate oxidation and high temperature combustion." Marine Chemistry **1**: 211-229.

Sugimura, N. and Y. Suzuki (1988). "A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample." Marine Chemistry **24**: 105-131.

Simpson, J. H. and J. R. Hunter (1974). "Fronts in the Irish Sea." Nature **250**: 404 - 406.
Solomon, A. M., J. R. Trabalka, et al. (1985). The global carbon cycle. In: Atmospheric Carbon Dioxide and the Global Carbon Cycle. Department of Energy report DOE/ER-0239. T. J.R. Springfield, Virginia, NTIS: 1-14.

Stanners, D. A. and S. R. Aston (1981). "^{134}Cs:^{137}Cs and ^{106}Ru:^{137}Cs ratios in intertidal sediments from the Cumbria and Lancashire coasts, England." Estuarine, coastal and shelf science **13**: 409 - 417.

Strickland, J. D. H. (1965). Production of organic matter in the primary stages of the marine food chain. Chemical Oceanography. J. P. Riley and G. Skirrow. London, Academic Press.

Stuiver, M. (1961). "Variations in radiocarbon concentrations and sunspot activities." Journal of Geophysical Research **66**: 273.

Stuiver, M. (1980). "^{14}C distributions in the Atlantic Ocean." Journal of Geophysical Research **85**: 2711-2718.

Stuiver, M. (1982). "A high-precision calibration of the AD radiocarbon timescale." Radiocarbon **24**: 1-26.

Stuiver, M. and H. A. Polach (1977). "Discussion reporting of ^{14}C data." Radiocarbon **19**: 355-363.

Stuiver, M. and P. D. Quay (1981). "Atmospheric ^{14}C changes in resulting from fossil fuel CO_2 release and cosmic ray variability." Earth and Planetary Science Letters **53**: 349-362.

Suess, H. E. (1953). Natural radiocarbon and the rate of exchange of carbon dioxide between the atmosphere and the sea. Nuclear Processes in Geologic Settings. W. Aldrich. Chicago, University of Chicago Press**:** 52-56.

Suess, H. E. (1955). "Radiocarbon concentration in modern wood." Science **122**: 415-417.

Suess, H. E. (1970a). Brittlecone pine calibration of the radiocarbon timescale. 2500BC to the present. In: Radiocarbon variations and absolute chronology. Proceedings of the of the 12th Nobel Symposium, Upsalla, Sweden.

Suess, H. E. (1970b). Three causes of the secular ^{14}C fluctuations, their amplitudes and time constants. Proceedings of the of the 12th Nobel Symposium, Uppasala, Sweden.

Sugimura, N. and Y. Suzuki (1988). "A high-temperature catalytic oxidation method for the determination of non-volatile dissolved organic carbon in seawater by direct injection of a liquid sample." Marine Chemistry **24**: 105-131.

Sundquist, E. T. (1993). "The global carbon dioxide budget." Science **259**: 934-941.

Tamers, M. A. (1960). "Carbon-14 dating with the liquid scintillation counter: total synthesis of the benzene solvent." Science **132**: 668-669.

Tanaka, N., M. C. Monaghan, et al. (1986). "Contribution of metabolic carbon to mollusc and barnacle shell carbonate." Nature **320**: 520-523.

Taylor, D. M., J. P. Moroni, et al. (1990). "The metabolism of ^{3}H and ^{14}C with special reference to radiation protection." Radiation Protection Dosimetry **30**(2): 87-93.

Turrell, W. R. and E. W. Henderson (1990). "Transport events within the Fair Isle Current during the autumn circulation experiment (ACE)." Estuarine, Coastal and Shelf Science **31**: 25 - 44.

UNSCEAR (1977). Sources and effects of ionizing radiation. United National Scientific Committee on the Effects of Atomic Radiation 1977. New York, Report to the General Assembly, United Nations, .

UNSCEAR (1993). Sources and effects of ionizing radiation. United National Scientific Committee on the Effects of Atomic Radiation 1993. New York, Report to the General Assembly, United Nations.

Watson, D. C. and T. A. Norton (1985). "Dietary preference of the common periwinkle, *Littorina littorea (L)*." Journal of Experimental Marine Biology Ecology **88**: 193.

Williams, P. M. (1975). Biological and chemical aspects of dissolved organic material in sea water. Chemical Oceanography. J. P. Riley and G. Skirrow. London, Academic Press. **2:** 301 -363.

Williams, P. M. and E. R. M. Druffel (1988). "Dissolved organic matter in the ocean: comments on a controversy." Oceanography **1**: 14-17.

Williams, P. M. and E. R. M. Druffel (1987). "Radiocarbon in dissolved organic matter in the central North Pacific Ocean." Nature **330**: 246-248.

Williams, S. J., R. Kirby, et al. (1981). Sedimentation studies relevant to low-level radioactive effluent dispersal in the Irish Sea. Part II, Sea bed morphology, sediments and shallow sub-bottom stratigraphy of the eastern Irish Sea. Institute of Oceanographic Sciences, Wormley, Surrey, Report 120. (Unpublished manuscript)

Wilson, T. R. S. (1974). "Caesium-137 as a water movement tracer in the Irish Sea and St. Georges Channel." Nature **248**: 125 - 127.

Wong, K. M. (1971). "Radiochemical determination of plutonium in seawater, sediments and marine organisms" Annals of Chim Acta **56** 355-364.

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

Wolstenholme, A. (1999). The biogeochemistry of ^{14}C within the Irish Sea. Glasgow, University of Glasgow.

Wolstenholme, A., G. T. Cook, et al. (1999). "The behaviour of Sellafield derived ^{14}C in the NE Irish Sea." Radiocarbon **40**(1): 447-458.

Young, E. F., J. N. Alderidge, et al. (2000). "Development and validation of a three-dimensional curvilinear model for the study of fluxes through the North Channel of the Irish Sea." Continental Shelf Research **20**: 997-1035.

Young, J. R. and A. W. Fairhall (1968). "Radiocarbon from nuclear weapons tests." Journal of Geophysical Research **73**: 1185-1200.

Appendix 1 Conversion of ^{14}C activities (Bq kg^{-1} C) to ^{14}C activities mBq l^{-1} in the DIC, DOC, PIC and POC fractions of seawater

Calculation of average DIC concentration (mg C l^{-1}) where:

(a) = Volume of sample CO_2 (l) (Column 2; Table A1)
(b) = Volume of sample seawater (l) (Column 3; Table A1)
(c) = conversion factor of 1x 10^{-6}, for conversion from mg C l^{-1} kg C l^{-1}
(g) = conversion factor of 1000, for conversion from mBq l^{-1} to Bq l^{-1}
(j) = conversion factor of 1 x 10^{9}, for conversion from mBq l^{-1} to Bq km^{-3}
(k) = daily flux of water through the North Channel of 5 km^{3} d^{-1}
(l) = length of study period = 730.5 days

calculation for the removal of ^{14}C in the DIC fraction (August 1997 to July 1999) using data from Table A1 and Table 3.6:

1) $$\frac{\textbf{(a)} \times 12}{22.4} = \textbf{(c)}\ \text{g C}$$

2) $$\frac{\textbf{(c)} \times 1000}{\textbf{(b)}} = \textbf{(d)}\ (\text{mg C l}^{-1})$$

3) $$\textbf{(d)} \times \textbf{(e)} = \textbf{(f)}\ (\text{kg C l}^{-1})$$

4) **(f)** x net DIC activity (Bq kg^{-1} C) (Table 3.6) x **(g)** = **(h)** mBq l^{-1} (Table 3.11)
5) Sum $(\mathbf{h_1})..(\mathbf{h_{24}}) \div 24$ = **(i)** average monthly activity (mBq l^{-1}) during study period
6) **(i)** x **(j)** x **(k)** x **(l)** = **(m)** activity (Bq) removed between August 1997 and July 1999

Table A1 Volume (l) of CO_2 collected from Hydrolysis of seawater and Volume (l) of seawater used for hydrolysis used to calculate concentration of DIC (mg C l^{-1})

Collection date	(a) Vol. CO_2 (litre)	(b) Vol seawater (litre)	(d) DIC (mg C l^{-1})
August '97	3.21 ± 0.02	80 ± 4	22 ± 1.1
September '97	3.49 ± 0.02	80 ± 4	23 ± 1.2
October '97	3.96 ± 0.02	80 ± 4	27 ± 1.3
November '97	3.53 ± 0.02	80 ± 4	24 ± 1.2
December '97	3.84 ± 0.02	80 ± 4	26 ± 1.3
January '98	3.36 ± 0.02	80 ± 4	23 ± 1.1
February '98	3.92 ± 0.02	80 ± 4	26 ± 1.6
March '98	3.62 ± 0.02	80 ± 4	24 ± 1.2
April '98	3.70 ± 0.02	80 ± 4	25 ± 1.2
May '98	3.35 ± 0.02	80 ± 4	22 ± 1.1
June '98	3.75 ± 0.02	80 ± 4	25 ± 1.1
July '98	3.44 ± 0.02	80 ± 4	23 ± 1.2
August '98	3.79 ± 0.02	80 ± 4	25 ± 1.3
September '98	3.60 ± 0.02	80 ± 4	24 ± 1.2
October '98	3.84 ± 0.02	80 ± 4	26 ± 1.3
November '98	3.89 ± 0.02	80 ± 4	26 ± 1.3
December '98	3.92 ± 0.02	80 ± 4	26 ± 1.3
January '99	3.91 ± 0.02	80 ± 4	26 ± 1.3
February '99	3.89 ± 0.02	80 ± 4	26 ± 1.3
March '99	3.73 ± 0.02	80 ± 4	25 ± 2.1
April '99	3.83 ± 0.02	80 ± 4	26 ± 1.3
May '99	3.48 ± 0.02	80 ± 4	23 ± 1.2
June '99	3.16± 0.02	80 ± 4	21 ± 1.0
July '99	3.35 ± 0.02	80 ± 4	22 ± 1.1

Calculation for the removal of ^{14}C in the DOC, PIC and POC fractions (August 1997 to July 1999) using data from Table A2 and Table 3.8

Where:

(e) = conversion factor of 1 x 10^6 for conversion from mg C l^{-1} to kg C l^{-1}

(g) = conversion factor of 1000, for conversion from Bq l^{-1} to mBq l^{-1}

(j) = conversion factor of 1 x 10^9, for conversion from mBq l^{-1} to Bq km^{-3}

(k) = daily flux of water through the North Channel of 5 km^3 d^{-1}

(l) = length of study period = 730.5 days

(n), (o) and (p) = concentration of biogeochemical fraction in sample (mg C l^{-1}) (Table A2; Column 2, 3 and 4, respectively)

1) **(i)/(j)/(k)** x**(e)** = **(f)** kg C l^{-1} (Table A2)

2) **(f)** x net DOC/PIC/POC activity (Bq kg^{-1} C) (Table 3.8) x **(g)** = **(h)** mBq l^{-1} (Table 3.10)

3) **For DOC**

Sum **($h_{May\ 98}$)..($h_{Nov\ 98}$)** ÷ 3 = **(i)** average quarterly activity (mBq l^{-1})

4) **(i)** x **(j)** x **(k)** x **(l)** = activity removed in DOC (August 1997 to July 1999)

5) **For POC and PIC**

6) Sum **($h_{Nov\ 1997}$)...($h_{Feb\ 1999}$)** ÷ 6 = **(i)** average quarterly activty (mBq l^{-1})

7) **(i)** x **(j)** x **(k)** x **(l)** = activity removed in PIC and POC (August 1997 to July 1999)

Table A2 Volume (l) of CO_2 collected from Hydrolysis of seawater and Volume (l) of seawater used for hydrolysis used to calculate concentration of DOC (mg C l^{-1})

Collection date	(n) DOC (mg C l^{-1})	(o) PIC (mg C l^{-1})	(p) POC (mg C l^{-1})
November '97	F	0.09 ± 0.004	0.12 ± 0.006
February '98	0.098 ± 0.005	0.05 ± 0.003	0.11 ± 0.006
May '98	0.134 ± 0.007	0.03 ± 0.002	0.12 ± 0.006
August '98	0.116 ± 0.006	0.05 ± 0.003	0.11 ± 0.006
November '98	F	0.03 ± 0.003	0.06 ± 0.003
February '98	F	0.13 ± 0.007	0.21 ±0.011
Mean ± SE	0.116 ± 0.006	0.06 ± 0.003	0.12 ± 0.006

F Analysis failed

Appendix 2 Removal of ^{14}C and ^{137}Cs from the NE Irish Sea using a simple model

$A_r = A_m - A_{m1}$ where

A_r is the activity removed; A_m is the activity in the NE Irish Sea for a given month and A_{m1} is the residual activity in the NE Irish Sea the following month.

A_m = Discharge activity for that month + residual activity from previous discharges

Table A3 Activity of ^{14}C removed from the Irish Sea using a halving time of one month

Date	A_m	A_{m1}	A_r
July '97	63.4	37.9	25.5
August '97	51.4	25.4	26
Sept. '97	481.3	238.1	243.2
Oct '97	1119.9	554.1	565.8
Nov. '97	2305.0	1140.6	1164.4
Dec. '97	2291.9	1134.1	1157.8
Jan. '98	1978.8	979.2	999.6
Feb. '98	1324.9	655.6	669.3
March '98	1196.1	591.9	604.2
April '98	1287.2	637.0	650.2
May '98	999.6	494.6	505
June '98	736.6	364.5	372.1
July '98	747.2	369.7	377.5
August '98	408.7	202.3	206.4
Sept. '98	229.9	113.7	116.2
Oct. '98	149.9	74.1	75.8
Nov. '98	204.8	101.4	103.4
Dec. '98	192.7	95.4	97.3
Jan. '99	747.0	369.6	377.4

Feb. '99	946.0	468.1	477.9
March '99	1004.0	496.8	507.2
April '99	1147.0	567.6	579.4
May '99	796.9	394.3	402.6
June '99	535.9	265.2	270.7

Table A4 Activity of ^{14}C removed from the Irish Sea using variable halving times

Date	A_m	A_{m1}	A_r
July '97	358.2	252.0	106.2
August '97	270.0	191.4	80.6
Sept. '97	647.2	300.2	346.7
Oct '97	1182.3	554.1	628.2
Nov. '97	2305.0	1140.6	1164.4
Dec. '97	2291.9	1134.1	1157.8
Jan. '98	1978.8	522.7	1456.1
Feb. '98	868.4	302.3	566.1
March '98	842.8	266.0	576.8
April '98	806.5	344.2	462.3
May '98	706.8	494.6	212.2
June '98	736.6	364.5	372.1
July '98	747.2	369.7	377.5
August '98	408.7	202.3	206.4
Sept. '98	229.9	113.7	116.2
Oct. '98	149.9	227.5	-
Nov. '98	408.2	392.2	16.0
Dec. '98	483.5	154.5	229.0
Jan. '99	806.1	80.5	725.6
Feb. '99	654.9	79.6	575.3
March '99	615.5	74.7	560.8
April '99	724.8	786.2	-

May '99	1015.5	193.2	822.3
June '99	334.8	437.0	-

Table A5 Activity of ^{137}Cs removed from the Irish Sea using a one month halving time

Date	A_m	A_{ml}	A_r
July '97	1495.2	520.5	974.7
August '97	1044.0	363.4	680.6
Sept. '97	677.8	235.9	441.9
Oct '97	856.1	298.0	558.1
Nov. '97	1283.5	446.8	836.7
Dec. '97	1292.5	449.9	842.6
Jan. '98	960.6	334.4	626.2
Feb. '98	1050.0	365.5	684.5
March '98	1181.3	411.2	770.1
April '98	1097.5	382.0	715.5
May '98	839.4	292.2	547.2
June '98	648.2	225.6	422.6
July '98	627.6	218.5	409.1
August '98	527.5	183.6	343.9
Sept. '98	502.3	174.9	327.4
Oct. '98	646.7	225.1	421.6
Nov. '98	1082.4	376.8	705.6
Dec. '98	2014.8	701.3	1313.5
Jan. '99	1810.3	630.1	1180.2
Feb. '99	1260.1	438.6	821.5
March '99	781.6	272.1	509.5
April '99	792.5	275.9	516.6
May '99	1297.8	451.8	846
June '99	1141.2	397.2	744

Table A6 Activity of ^{137}Cs removed from the NE Irish Sea using variable halving times

Date	A_m	A_{m1}	A_r
July '97	2544.8	1790.1	754.7
August '97	2313.7	1627.6	686.1
Sept. '97	1942.0	776.7	1165.3
Oct '97	1397.0	551.4	845.6
Nov. '97	1536.9	760.5	776.4
Dec. '97	1606.2	794.8	811.4
Jan. '98	1305.5	334.3	971.2
Feb. '98	1050.0	365.5	684.5
March '98	1181.3	354.6	826.7
April '98	1170.5	382.0	788.5
May '98	839.4	574.8	264.6
June '98	930.9	460.6	470.3
July '98	862.6	426.8	435.8
August '98	735.9	364.1	371.8
Sept. '98	682.9	337.9	345
Oct. '98	809.8	795.7	14.1
Nov. '98	1653.0	1319.0	334
Dec. '98	2957.0	1470.2	1486.8
Jan. '99	2579.1	160.0	2419.1
Feb. '99	790.0	95.7	694.3
March '99	438.7	53.2	385.5
April '99	573.6	868.3	-
May '99	1890.3	451.8	1438.5
June '99	1141.2	1064.7	76.5

Appendix 3 Wet and dry weights (g) for Cores 1 to 7

Table A7 Wet weights for cores 1 to 7

Depth (cm)	Core 1 (weight g)	Core 2 (weight g)	Core 3 (weight g)	Core 4 (weight g)	Core 5 (weight g)	Core 6 (weight g)	Core 7 (weight g)
0-2	119	88	148	63	135	172	94
2-4	161	161	128	151	224	176	212
4-6	176	200	159	170	217	177	239
6-8	225	163	185	196	223	186	216
8-10	208	194	189	236	215	213	435
10-15	465	480	431	500	485	440	504
15-20	526	503	489	477	496	479	510
20-25	469	483	434	462	511	491	544
25-30	497	487	464	458	600	467	504
30-35	476	498	521	444	492	471	494
35-40	485	531	513	428	502	514	532
40-45	469	501	552	366	511	507	493
45-50	487	520	514	463	472	482	524
50-55	494	504	479	449	557	493	196
55-60	484	317	485	450	520	491	201
60-65	486		472	492	524	481	
65-70	498		497	544	518	528	
70-75	485		493	473	516	460	
75-80	553		478	497	533	489	
80-85	311		288	496	270	436	
85-90	432		346	319	538	169	
90-95				310			

Table A8 Dry weights for cores 1 to 7

Depth (cm)	Core 1 (weight g)	Core 2 (weight g)	Core 3 (weight g)	Core 4 (weight g)	Core 5 (weight g)	Core 6 (weight g)	Core 7 (weight g)
0-2	82	45	78	26	75	92	48
2-4	107	92	70	76	143	100	129
4-6	124	120	90	194	141	102	161
6-8	160	99	108	108	149	107	142
8-10	120	119	133	127	148	129	140
10-15	336	310	255	259	331	270	334
15-20	388	321	300	285	337	313	345
20-25	347	308	265	285	364	314	358
25-30	369	316	282	281	413	299	336
30-35	356	325	331	271	352	300	336
35-40	356	353	328	267	354	336	363
40-45	338	337	354	295	370	330	342
45-50	361	313	337	296	344	320	366
50-55	372	344	312	280	412	328	162
55-60	361	226	320	273	386	343	
60-65	360		297	318	383	326	
65-70	377		322	278	377	360	
70-75	369		326	298	379	312	
75-80	426		310	293	397	328	
80-85	248		191	323	203	300	
85-90	344		326	210	406	118	
90-95				222			

Appendix 4 Calculation of ^{137}Cs and ^{241}Am inventories in Cores 1 to 7

Where:

(a) = Specific activity on core segment (Bq kg^{-1}) (Tables 3.16, 3.19, 3.23, 3.26, 3.30, 3.33 and 3.36)

(b) = dry weight (kg) (Table A8; Appendix 3)

(d) = internal area of core tubing (m^2) = 0.00535 m^2

VHIMZ = Very high intensity mixing zone

HIMZ = High intensity mixing zone

MIMZ = Medium intensity mixing zone

LIMZ = Low intensity mixing zone

Calculation:

1) **(a)** x**(b)** = **(c)** activity in segment (Bq)
2) **(c)** ÷ **(d)** = **(e)** inventory in segment (Bq m^{-2})
3) Sum **(e_1)..(e_n)** = **(f)** inventory on mixing zone (Bq m^{-2})
4) **(f_{HIMZ})** + **(f_{MIMZ})** + **(f_{LIMZ})** = Total inventory in core (Bq m^{-2})

For Cores 6 and 7, Step 6 would be **(f_{VHIMZ})** + **(f_{HIMZ})** + **(f_{MIMZ})** = Total inventory in core (Bq m^{-2})

Appendix 5 Calculation of ^{14}C (inorganic/organic), ^{238}Pu and $^{239,240}Pu$ activity inventories in Cores 1 - 7

Table A9 Core 1 (PC186)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.3	2.7	1.1	0.8
Medium	1.4	2.4	1.0	0.6
Low	1.3	3.2	0.9	0.4

Table A10 Core 2 (PC85)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.7	0.8	1.1	0.8
Medium	1.6	2.5	1.2	0.5
Low	1.5	2.4	1.2	0.5

Table 11 Core 3 (PC87)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.7	2.2	0.9	0.8
Medium	1.6	4.5	1.1	0.5
Low	1.5	1.6	1.0	0.4

Table 12 Core 4 (PC89)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.7	2.7	1.1	0.8
Medium	1.5	2.6	1.1	0.6
Low	1.6	3.1	1.1	0.5

Table 13 Core 5 (PC185)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.5	4.1	1.1	0.8
Medium	1.4	2.6	1.0	0.6
Low	1.3	2.4	0.9	0.4

Table 14 Core 6 (PC92)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.6	3.3	1.0	0.8
Medium	1.5	2.0	0.6	0.5
Low	1.5	3.1	1.0	0.4

Table 15 Core 7 (PC86)

Mixing zone	average wet:dry ratio	total wet weight (kg)	% inorganic carbon	% organic carbon
High	1.7	2.2	1.0	0.8
Medium	1.5	3.1	0.9	0.5
Low	1.2	0.2	0.9	0.4

Calculation of upper and lower limits for inorganic and organic ^{14}C inventories in Cores 1 - 7

Where:

(a) = gross activity (Bq kg^{-1} C) (Tables 3.17, 3.20, 3.24, 3.27, 3.31, 3.34 and 3.37)

(b) = upper and lower limits for background activity (0 and 45 Bq kg^{-1} C for inorganic: 98 and 131 Bq kg^{-1} C for organic)

(d) = number of measurements for each mixing zone

(f) = average % carbon for mixing sone (Tables A9 to A15)

(g) = average wet:dry weight ratio fro mixing sone (Tables A9 to A15)

(i) = total wet weight of sediment in mixing zone (Tables A9 to A15)

(k) =internal area of core tubing (m^2) = 0.00535 m^2

VHIMZ = Very high intensity mixing zone

HIMZ = High intensity mixing zone

MIMZ = Medium intensity mixing zone

LIMZ = Low intensity mixing zone

Calculation:

1) **(a)** - **(b)** = **(c)** net activity (Bq kg^{-1} C)

2) $\dfrac{\underline{\textbf{Sum }(\mathbf{c_1 \ldots c_n})}}{\textbf{(d)}}$ = **(e)** average activity in mixing zone (Bq kg^{-1} C)

3) $\dfrac{\underline{\textbf{(e) x (f)}}}{\textbf{(g)}}$ = **(h)** activity (Bq kg^{-1} wet weight)

4) **(h)** x **(i)** = **(j)** ^{14}C activity in mixing zone (Bq)

5) **(j)** ÷ **(k)** = **(l)** ^{14}C inventory in mixing zone (Bq)

6) ($\mathbf{l}_{HIMZ}$) + ($\mathbf{l}_{MIMZ}$) + ($\mathbf{l}_{LIMZ}$) = Total inventory in core (Bq m^{-2})

For Cores 6 and 7, Step 6 would be ($\mathbf{l}_{VHIMZ}$) + ($\mathbf{l}_{HIMZ}$) + ($\mathbf{l}_{MIMZ}$) = Total inventory in core (Bq m^{-2})

Calculation of ^{238}Pu and 2$^{39, 240}$Pu inventories in Cores 1-7

Where:

(a) = Specific activity on core segment (Bq kg^{-1}) (Tables 3.21, 3.28 and 3.38)

(d) = number of measurements for each mixing zone

(g) = average wet:dry weight ratio fro mixing sone (Tables A9 to A15)

(i) = total wet weight of sediment in mixing zone (Tables A9 to A15)

(k) = internal area of core tubing (m^2) = 0.00535 m^2

VHIMZ = Very high intensity mixing zone

HIMZ = High intensity mixing zone

MIMZ = Medium intensity mixing zone

LIMZ = Low intensity mixing zone

Calculation:

1) $\dfrac{\mathbf{Sum}\ (\mathbf{c_1 \ldots c_n})}{\mathbf{(d)}}$ = **(e)** average activity in mixing zone (Bq kg^{-1})

2) $\dfrac{\mathbf{(e)}}{\mathbf{(g)}}$ = **(h)** activity (Bq kg^{-1} wet weight)

3) **(h)** x **(i)** = **(j)** plutonium activity in mixing zone (Bq)

4) **(j)** ÷ **(k)** = **(l)** inventory in mixing zone (Bq)

5) $(\mathbf{l}_{HIMZ}) + (\mathbf{l}_{MIMZ}) + (\mathbf{l}_{LIMZ})$ = Total inventory in core (Bq m^{-2})

For Cores 6 and 7, Step 6 would be $(\mathbf{l}_{VHIMZ}) + (\mathbf{l}_{HIMZ}) + (\mathbf{l}_{MIMZ})$ = Total plutonium inventory in core (Bq m^{-2})

Appendix 6

Based on the sediment distribution published by the Institute of Geological Sciences (Sheet 54N 04W) the area between 54^0 and 55^0 N; 03^0 15' and 04^0 20' W was divided into different sediment types and the areas each of these sediment types covered, calculated.

Mud; 54 km^2
Sandy mud; 595 km^2
Muddy sand; 1298 km^2

Cores 3 (PC87) and 4 (PC89) were collected from areas of mud.
Cores 1 (PC186), 6(PC92) and 7 (PC86) were collected from areas of sandy mud.
Cores 2 (PC85) and 5 (PC185) were collected from areas of muddy sand.

Average ^{137}Cs, ^{241}Am and upper and lower limits for ^{14}C inventories (Bq m^{-2}) were calculated for each sediment type **(a)**

These average inventories (Bq m^{-2}) were then converted to Bq km^{-2} **(b)**

(b) was multiplied by the area that the sediment type covered.

For example; ^{137}Cs from muddy sediments :

$(2.8 \times 10^5 + 2.9 \times 10^5) \div 2 = 2.85 \times 10^5$ Bq m^{-2}
$(2.85 \times 10^5) \times (1 \times 10^6) = 2.85 \times 10^{11}$ Bq km^{-2}
$(2.85 \times 10^{11}) \times (54) = 11.4 \times 10^{11}$ Bq of ^{137}Cs present in the muddy sediments of the NE Irish Sea.

This calculation was repeated for the sandy mud (2.8×10^{14} Bq) and muddy sand (3.2×10^{14} Bq) areas to give a total of 6.2×10^{14} Bq of ^{137}Cs in the sediments of the NE Irish Sea.

For the ^{238}Pu and ^{239,240}Pu calculations there was only one core for each type of sediment so no average was calculated.