

THE BEHAVIOR OF SELLAFIELD-DERIVED ^{14}C IN THE NORTHEAST IRISH SEA

ANNE WOLSTENHOLME,¹ G. T. COOK,¹ A. B. MacKENZIE,¹ PHILIP NAYSMITH¹
P. S. MEADOWS² and PAUL McDONALD³

ABSTRACT. Radiocarbon is an important constituent of the low level, liquid, radioactive effluent discharged from the Sellafield nuclear fuel reprocessing plant in northwest England, but despite the fact that it gives the highest collective dose commitment of all the nuclides in the waste, its behavior in the Irish Sea is poorly defined. There is therefore a clear requirement for an improved understanding of ^{14}C behavior in the Irish Sea, to assist with dose evaluation modeling and definition of the mixing and accumulation characteristics of the sediment in this area. In this context, results are presented here for a temporal study of ^{14}C activities in four geochemical fractions of seawater and in a sediment core from the vicinity of the Sellafield effluent outfall. Clear ^{14}C enrichments in the dissolved inorganic carbon (DIC) and particulate organic carbon (POC) components of seawater were observed, with temporal trends in activity that were related to variations in the Sellafield discharge. Smaller, but nevertheless detectable, enrichments were also observed for particulate inorganic carbon (PIC) and dissolved organic carbon (DOC) in the seawater. The distribution of ^{137}Cs and ^{241}Am revealed that the sediment core could be classified into three zones in which the intensity of mixing decreased discontinuously with depth. Bulk carbonate ^{14}C analyses of the core demonstrated the presence of glacial or pre-glacial carbonate in the system, but failed to show any evidence of contaminant ^{14}C input or provide information on sediment accumulation processes. In contrast, analysis of bulk organic matter from the sediment provided clear evidence of the recent perturbation of a well mixed system by input of younger material, consistent with the recent input of contaminant ^{14}C from Sellafield and possibly weapons testing fallout.

INTRODUCTION

Since 1952, low level, liquid, radioactive waste has been discharged, under authorization, into the northeast Irish Sea from the British Nuclear Fuels plc reprocessing plant at Sellafield in Cumbria, northwest England. For the majority of radionuclides (*e.g.*, ^{137}Cs , ^{238}Pu , $^{239,240}\text{Pu}$ and ^{241}Am), annual releases peaked in the early- to mid-1970s and from the mid-1980s onwards, they contributed only very small increments to the existing total environmental inventories (BNFL 1977–1994; Gray, Jones and Smith 1995). In contrast, the discharges of ^{14}C were relatively constant (*ca.* 1 to 2 TBq per annum) until the early 1990s when they increased substantially (12.4 TBq in 1995) (BNFL 1994; MAFF 1996). The total activity of ^{14}C that has been released from Sellafield is small relative to that of high yield fission products or transuranic activation products such as $^{239,240}\text{Pu}$. Nevertheless, as a consequence of its relatively long half life, high environmental mobility and propensity for entry into the food chain, ^{14}C has the highest estimated collective dose commitment to the UK population of all the radionuclides in the Sellafield liquid effluent discharge.

The offshore sediment is a key component of this system since it has acted as a major sink for Sellafield waste radionuclides. Indeed, it has been estimated that following discharge, almost all of the americium and plutonium and *ca.* 10% of the radiocaesium were initially incorporated into a deposit of silt and mud, off-shore from Sellafield (Smith, Parker and Kirby 1980; Miller *et al.* 1982; Pentreath *et al.* 1984; Jones, Roberts and Miller 1988), which forms part of a belt of fine sediment lying close to the Cumbrian coast and extending from Liverpool Bay in the south to the Solway Firth in the north (Fig. 1). The reduction in radionuclide concentrations in seawater, in response to reduced Sellafield discharges from the 1980s onwards, has resulted in significant redissolution of radiocaesium from the surface layers of the offshore sediment (Hunt and Kershaw 1990; McCartney *et al.* 1994; MacKenzie *et al.* 1994), as evidenced by $^{137}\text{Cs}/^{241}\text{Am}$ activity ratios for this material in the range 0.72 to 1.22 in 1992, relative to corresponding values of up to 8.5 in 1988–1989 (MacKenzie

¹Scottish Universities Research & Reactor Centre, Scottish Enterprise Technology Park, East Kilbride G75 0QF, Scotland

²Biosedimentology Unit, Institute of Biological and Life Sciences, University of Glasgow, Glasgow G12 8QQ, Scotland

³Westlakes Research Institute, Westlakes Science and Technology Park, Moor Row, Cumbria CA24 3LN, England

et al. 1998). In contrast, there has been very little redissolution of the less soluble actinides, Am and Pu (Hunt and Kershaw 1990; Cook *et al.* 1997a), resulting in a negligible reduction in the inventories of these species in the offshore sediment. Thus, in addition to the current discharges, this offshore sediment now constitutes a second, and major, potential source of radionuclides to the wider environment.

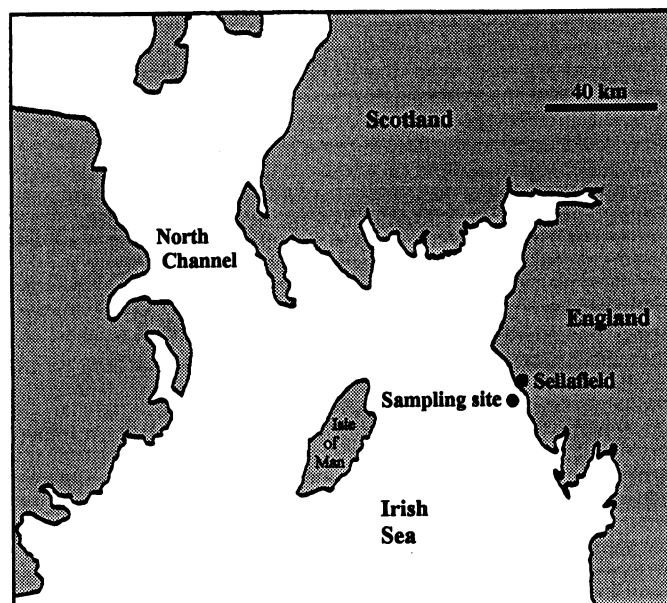


Fig. 1. Map of the northeast Irish Sea study area

Considerable research has been devoted to characterizing processes which affect the contaminated sediment, and it has been clearly established that this deposit is subject to intense physical and biological mixing (Kershaw *et al.* 1983, 1984, 1988). Although the mixing characteristics of the offshore sediment have been relatively well defined, it remains unclear whether or not the deposit is subject to long-term net accumulation. Cronan (1969) and Pantin (1977, 1978) concluded, on the basis of sedimentological evidence, that this was an area of active accumulation; however, Williams *et al.* (1981) and Kirby *et al.* (1983) contended that the area has a stable sedimentary regime, dominated by biological mixing processes. A number of attempts have been made to use ^{14}C to define the accumulation characteristics of this sediment, but the results of these investigations have been ambiguous. In an initial study of two cores from this area, Kershaw (1986) observed near constant bulk carbonate ^{14}C ages (*ca.* 12,500 \pm 1000 BP) from the surface to the base of the cores at 144 and 162 cm. In a further study, Kershaw, Swift and Denoon (1988) reported results for four more cores, one of which had an effectively constant age of 11,220 \pm 82 BP to a depth of 60 cm. However, the other three cores exhibited significant variations, with two having younger ages towards the surface, but no systematic progression of age with depth, while the third had a pronounced age minimum over the middle section of the core, with a value of 10,310 BP at 51–59 cm, but 15,330 BP at the surface and 14,710 BP at 110–119 cm. Kershaw, Swift and Denoon (1988) also determined ^{14}C ages for the shells of the gastropod *Turritella communis* (Risso) obtained from various depths within the cores. The results demonstrated that the bulk carbonate ages were much greater than those of *T. communis* at equivalent depths with the latter being much more variable. In some cases, the *T. communis*

profiles produced logical progressions of increasing age with depth and the authors interpreted this observation as indicating that the larger *T. communis* shells were not susceptible to the same biological mixing processes as the finer bulk carbonate fraction of the sediment and, on the basis of the trend in age of the *T. communis* shells with depth, derived accumulation rates of 0.02 to 0.3 cm a⁻¹ for the three cores under study.

More recently, Cook *et al.* (1995) presented data for two cores, one of which was from a position close to the end of the Sellafield discharge pipeline and the other from *ca.* 20 km south of the discharge point. Both cores exhibited discontinuous increases in age of the bulk carbonate with depth. The age range of 4980–8980 BP (over a depth of 25 cm) for the core from the vicinity of the pipeline was significantly lower than any other ages reported for northeastern Irish Sea sediment. Cook *et al.* (1995) also demonstrated that the bulk organic carbon gave markedly younger ages than the bulk carbonate component of these cores. Significantly, the activity of the bulk organic carbon was enriched above ambient modern throughout the core from the pipeline area, providing unambiguous evidence of input of contaminant ^{14}C to the sediment system. This observation is consistent both with the work of Begg *et al.* (1992), who reported enhanced ^{14}C levels in seaweed and in the flesh and shells of winkles and mussels in the vicinity of Sellafield, and with a more recent study by Cook *et al.* (1997b), which verified the enrichment of ^{14}C in an extensive range of biota and in the DIC component of seawater in this area.

Developing a better understanding of the behavior of Sellafield-derived ^{14}C in the Irish Sea is therefore important with respect to: 1) quantifying the radiological implications of the discharge (in this context, fluxes of ^{14}C at the sediment-water interface and processes controlling ^{14}C distribution within the sediment column are key areas of uncertainty) and 2) developing quantitative models of sediment mixing and accumulation processes, with implications for the long-term fate of other contaminant radionuclides. As part of a study aimed to address these issues, we present data for a site close to the outlet of the Sellafield low level, liquid waste pipeline, including: 1) ^{14}C activities for the four biogeochemical fractions of the water column (DIC—dissolved inorganic carbon, PIC—particulate inorganic carbon, DOC—dissolved organic carbon, and POC—particulate organic carbon), 2) bulk carbonate and organic carbon ^{14}C age profiles for a 76 cm depth sediment core, and 3) activity profiles for Sellafield-derived ^{137}Cs and ^{241}Am in the core.

METHODS

Sediment Sampling and Pretreatment

We collected a 76 cm depth sediment core on 14 November 1995 from a position 5 km south of the discharge pipe outlet (54°17'N, 03°38'W), using a gravity corer (Pedersen *et al.* 1985) equipped with a 12.5 cm diameter core tube. We used this type of corer because it preserves the vertical integrity of the sediment and minimizes disturbance of the sediment/seawater interface. Following collection, we immediately sealed the core on-board ship and extruded and sectioned it on return to the quay. We divided the upper 20 cm into 1 cm depth increments and the remainder into 2 cm increments. We also discarded the outer 0.5 cm circumference to avoid contamination through smearing within the core tube and then dried the remainder at 60°C to constant weight. Finally, we ground the samples in a ball mill in preparation for analyses.

Seawater Sampling and Pretreatment

We collected volumes of 200–700 L during 1995–1996 on each sampling trip. We filtered the entire sample through GF/F glass fiber filter paper (nominal pore size 0.7 μm) and poisoned it with mer-

curic chloride. We stored the filter papers in a refrigerator until they were required for analysis of the POC and PIC. We required the bulk of the seawater for radiocaesium and plutonium analyses (not presented here) and removed subsamples for DIC and DOC analyses.

DIC Analysis

We opened the sample and transferred it to a 500-mL volume reaction vessel in a CO₂-free glovebox environment. We then connected the sealed reaction vessel to a purpose built vacuum line where we acidified the sample, purged it with nitrogen and trapped out the CO₂ using liquid N₂. On completion of the reaction, we transferred the CO₂ to a cold finger surrounded by liquid N₂ and pumped it under high vacuum for *ca.* 30 min to remove impurities. We then sealed the CO₂ in a Pyrex[®] tube in preparation for AMS analysis.

DOC Analysis

With small modifications, we used the method of Fry *et al.* (1996) and converted the purified CO₂ to graphite, in preparation for AMS analysis, according to the method of Jull *et al.* (1986), again with minor modifications.

PIC Analysis

We placed the filter papers containing the particulate material in a reaction vessel which was then evacuated. We slowly added 2M HCl to allow the hydrolysis reaction to proceed over a period of *ca.* 2 h. We collected, purified and stored the CO₂ as described above, in preparation for AMS analysis.

POC Analysis

We thoroughly washed the residue from the hydrolysis with distilled water, oven dried it and then placed it in a Pyrex[®] tube containing copper oxide as the oxidant. We then evacuated and sealed the tube and placed it in a furnace overnight at 500°C. We then isolated and purified the CO₂ in preparation for AMS analysis.

We sent all samples that were prepared for AMS analysis to the University of Arizona AMS Facility for ¹⁴C measurement.

Radiometric ¹⁴C Analyses

We combined the sediment samples to give 4 cm depth increments for ¹⁴C analysis. Initially, we reacted each sample with 2 M hydrochloric acid to hydrolyze the bulk carbonate to CO₂ and then converted it to benzene for ¹⁴C analysis according to the method of Begg (1992). We then washed the residual sample with distilled water and then dried and combusted it to produce CO₂ which we again converted to benzene for subsequent ¹⁴C analysis.

Gamma Spectroscopy

We pressed 20 g subsamples of sediment into 5 cm diameter pellets using a 20-ton press and sealed them with plastic film. We then counted the pellets on a Canberra Industries N-type HPGe gamma photon detector with a carbon-epoxy thin window. Typical sample counting times were 24 h. We determined detection efficiencies for the Sellafield-derived, gamma-emitting radionuclides present in the samples (¹³⁷Cs and ²⁴¹Am) by counting samples of a similar density which we had spiked with known activities of each.

RESULTS

We present results for ^{14}C activities in the DIC, DOC, PIC and POC components of seawater in Table 1 and Figures 2 and 3. We present ^{14}C activities and apparent ages for the bulk inorganic and bulk organic carbon components of the sediment core in Table 2 and Figure 5, and ^{137}Cs and ^{241}Am activities for the core in Figure 4. Throughout the text, we have used the term “apparent age” for our data as it is likely that many of the samples have been contaminated with Sellafield-derived ^{14}C .

TABLE 1. ^{14}C activities (“absolute” percent modern (pMC) $\pm 1\sigma$) in the PIC, POC, DIC and DOC components of seawater at the Sellafield pipeline sampling site, 1995–1996. Values in parenthesis are apparent ages (BP $\pm 1\sigma$) for depleted samples.

Date	PIC	POC	DIC	DOC
February 1995	63.1 \pm 0.8 (3660 \pm 90)	36.3 \pm 0.5 (8090 \pm 100)	104.7 \pm 1.2	95.4 \pm 0.5 (330 \pm 45)
July 1995	120.4 \pm 1.4	176.2 \pm 1.2	462.3 \pm 3.1	46.8 \pm 2.2 (6060 \pm 380)
November 1995	61.2 \pm 0.5 (3900 \pm 65)	197.4 \pm 1.0	647.5 \pm 4.1	33.5 \pm 0.4 (8750 \pm 90)
March 1996	60.8 \pm 0.5 (3960 \pm 65)	208.8 \pm 0.8	397.9 \pm 1.6	58.0 \pm 0.4 (4330 \pm 55)
June 1996	76.2 \pm 0.5 (2140 \pm 50)	268.6 \pm 1.5	515.7 \pm 2.0	80.3 \pm 0.5 (1720 \pm 50)
November 1996	87.7 \pm 0.6 (1010 \pm 55)	269.6 \pm 1.1	706.0 \pm 3.7	263.2 \pm 1.1

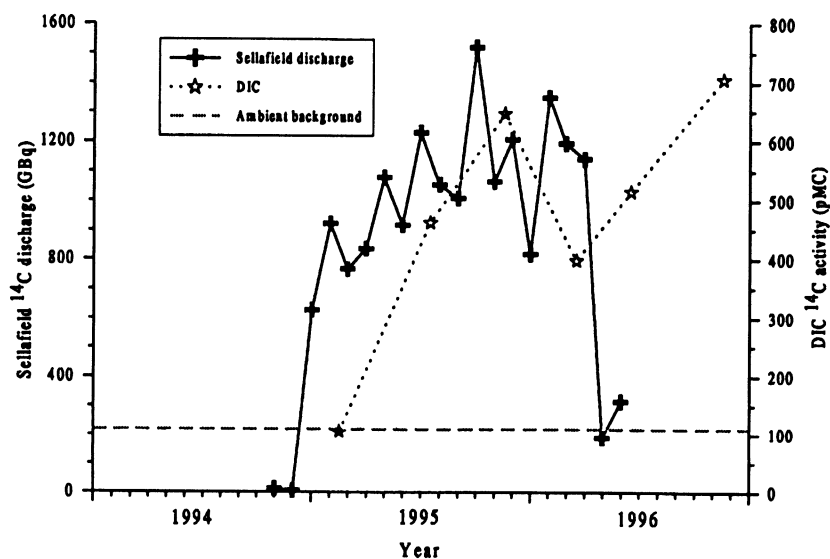


Fig. 2. Monthly Sellafield ^{14}C discharges (GBq) for October 1994–May 1996 and ^{14}C activities (pMC) in DIC (1995–96)

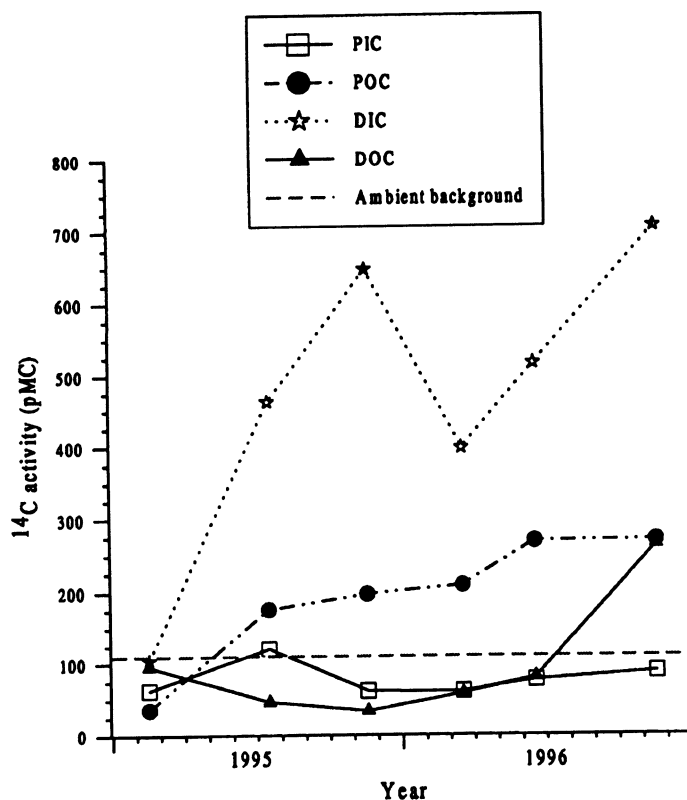


Fig. 3. ¹⁴C activities (pMC) in biogeochemical fractions of seawater from the Sellafeld sampling site

TABLE 2. ¹⁴C activities ("absolute" percent modern (pMC) $\pm 1\sigma$) for the bulk inorganic and bulk organic carbon components of the core collected from 5 km south of Sellafeld. Values in parenthesis are apparent ages (BP $\pm 1\sigma$).

Depth (cm)	Inorganic carbon	Organic carbon
0-4	21.1 \pm 0.4 (12,460 \pm 160)	81.8 \pm 1.3 (1570 \pm 130)
16-20	19.2 \pm 0.5 (13,210 \pm 210)	69.1 \pm 0.6 (2940 \pm 70)
36-40	19.6 \pm 0.5 (13,040 \pm 190)	57.1 \pm 1.1 (4470 \pm 150)
56-60	20.4 \pm 0.9 (12,720 \pm 340)	59.7 \pm 0.6 (4100 \pm 80)
72-76	22.2 \pm 0.7 (12,040 \pm 260)	57.9 \pm 1.1 (4350 \pm 150)

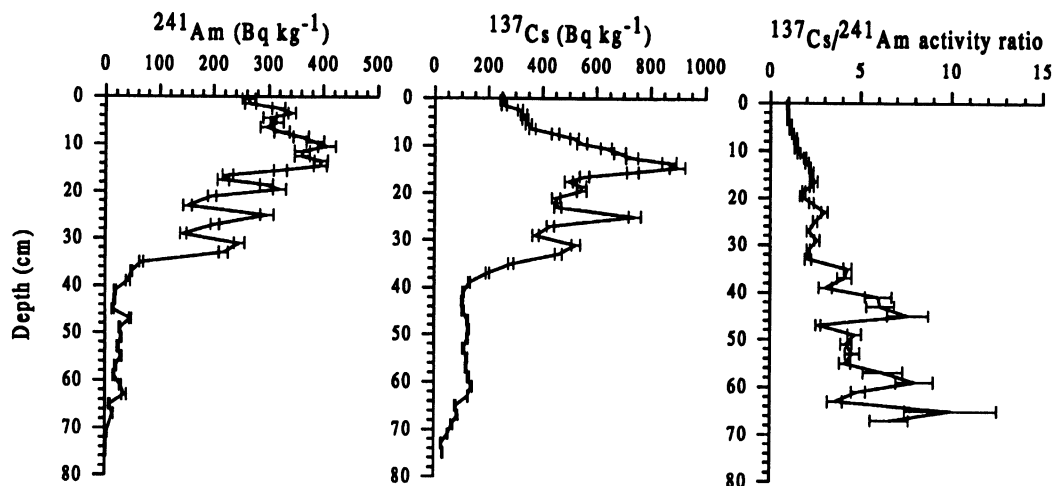


Fig. 4. ^{241}Am and ^{137}Cs specific activities (Bq kg $^{-1}$) and $^{137}\text{Cs}/^{241}\text{Am}$ activity ratios in the sediment core from the Sellafield sampling site

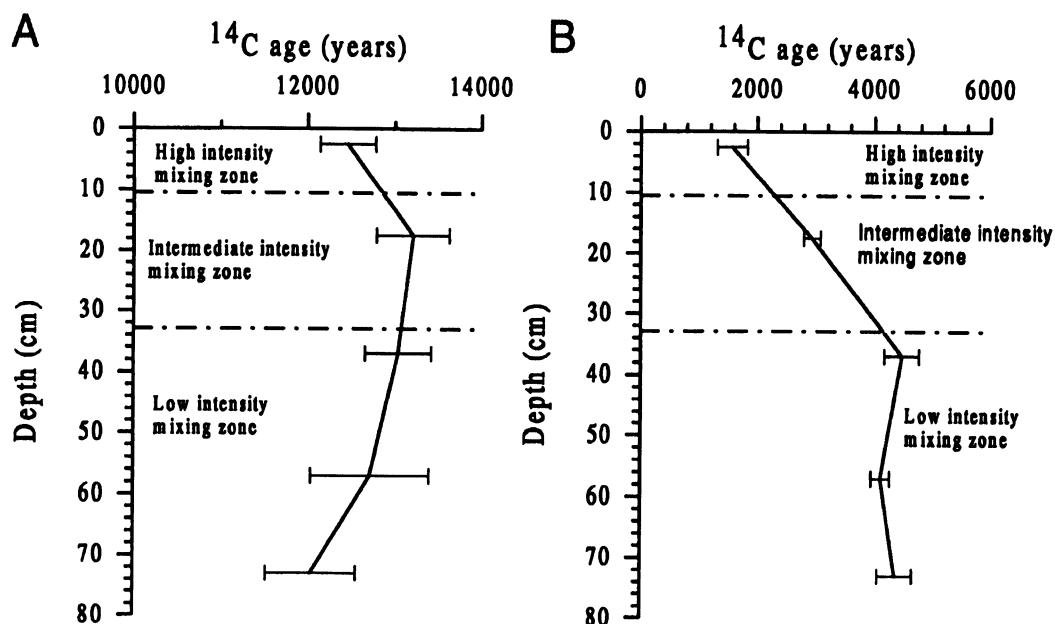


Fig. 5. ^{14}C "apparent age" profiles for (A) bulk inorganic carbon and (B) bulk organic carbon in the sediment core from the Sellafield sampling site, together with mixing zones

DISCUSSION

Discharges of ^{14}C from Sellafield varied markedly during the course of this study and the activities of the DIC samples exhibited clear variations in response to these changes, as shown in Figure 2. Thus, the DIC activity increased from 104.7 pMC in February 1995, a value which is close to the ambient background level of 109.7 pMC (Cook *et al.* 1997b), to 706.0 pMC in November 1996,

with a subsidiary minimum of 397.9 pMC in March 1996 in response to decreased discharges in October, November and December 1995. The poorer temporal resolution of the empirical data (quarterly sampling) relative to the discharge data (monthly reporting) makes detailed comparison of the two data sets difficult, but they appear to indicate a lag time of several months before the influence of variations in the discharge are apparent in the DIC activities, suggesting a buffering of the impact as a consequence of the effluent being mixed in the surrounding body of seawater.

The PIC ^{14}C activities were all much lower than the corresponding DIC values and were less obviously influenced by the Sellafield discharge, with only the July 1995 sample exhibiting a ^{14}C enrichment (120.4 pMC), as shown in Figure 3. The remaining five PIC samples had depleted ^{14}C activities in the range 60.8 to 87.7 pMC, corresponding to apparent ages of 3960 and 1010 BP, respectively. The $\delta^{13}\text{C}$ values for these samples were in the range -2.0‰ to $+1.5\text{‰}$, indicating a marine origin for this material and the most probable source is from resuspension of the underlying sediment. However, the apparent ages of the PIC samples are all substantially younger than those for the surface layers of the underlying sediment, for which reported ages have been in the range 10,810 to 13,030 BP, with the exception of one sample from the immediate vicinity of the pipeline which had an age of 4980 BP (Kershaw 1986; Kershaw, Swift and Denoon 1988; Cook *et al.* 1995), indicating that the PIC consists of a mixture of old, resuspended carbonate along with younger material. Recently produced carbonate will have incorporated some Sellafield-derived ^{14}C , as evidenced by the work of Begg *et al.* (1992) who reported ^{14}C activities of 574.1 pMC and 486.7 pMC for mussel and winkle shells, respectively, from this area in 1988–1989 and the present observation of an enhanced activity (120.4 pMC) in the July 1995 PIC sample.

The ^{14}C activities of the POC samples exhibited a pronounced variation in response to the changing discharge levels (Fig. 3), with an increase from a value of 36.3 pMC in February 1995 (corresponding to an apparent age of 8090 BP) to a maximum of 296.6 pMC in November 1996. Although a similar trend was observed, the variations in POC activities were more muted than those for DIC and a systematic disequilibrium was observed between the two, with POC activities in the range 0.30 to 0.52 of the corresponding DIC values. These results therefore show that the particulate organic matter (POM) consists of a mix of older material, with depleted ^{14}C activities, and recently produced POM that is enriched as a consequence of incorporation of Sellafield-derived ^{14}C .

Over the period February 1995 to June 1996, the DOC ^{14}C activities showed no clear evidence of the influence of the Sellafield discharge, with depleted activities in the range 33.5 to 95.4 pMC, corresponding to apparent ages in the range 8750 to 330 BP. However, the November 1996 value of 263.2 pMC provided definite evidence of the incorporation of Sellafield-derived ^{14}C in the DOC, with a value close to equilibrium with the corresponding PIC sample. Notably, a period of *ca.* 1 yr elapsed between the onset of enrichment in the DIC and POC components and the corresponding enrichment in the DOC in response to the increased discharges of ^{14}C . This indicates either a slower rate of transfer of contaminant ^{14}C into the DOC system or a relatively greater degree of buffering of the impact of such input to this system.

The implication of the observed enhancements in ^{14}C activities in the biogeochemical fractions of seawater and in biota (Begg *et al.* 1992; Cook *et al.* 1997b) is that deposition of inorganic or organic detrital biogenic material will result in a flux of Sellafield-derived ^{14}C to the sediment. This is of considerable importance both with respect to evaluating the dose implications of the ^{14}C discharges and to interpreting observed ^{14}C age profiles in the sediment. A significant aspect of this situation is that the ^{14}C transferred to the sediment will be structurally incorporated in detrital carbonate and organic material which will undergo varying diagenetic reactions in the sediment. Such reactions

may result in redissolution of some of the contaminant ^{14}C , but the geochemical conditions and the thermodynamic controls on these reactions will be different from those governing the initial uptake of ^{14}C in these materials. Consequently, the overall behavior of ^{14}C in this system will not be controlled by a simple reversible equilibrium reaction and, as such, will not be amenable to modeling by a K_d (distribution coefficient) approach, as is often employed in such cases.

In view of the intensity of mixing and the low accumulation rate, mixing processes will exert a dominant control on the distribution of detrital biogenic material in the sediment and the effects of mixing can be inferred from the distribution of Sellafield waste radionuclides in the sediment. As shown in Figure 4, both ^{241}Am and ^{137}Cs were detectable to the base of the core at 76 cm, indicating transfer to this depth by mixing on a time scale of 43 yr or less. Moreover, both profiles show a sharp decrease in activity below 33 cm, indicating a marked decline in the efficiency of mixing below this level. ^{241}Am had generally high activities from 33 cm to the surface, with irregular variations in the range 144 to 406 Bq kg $^{-1}$. ^{137}Cs also showed high activities in the range 375 to 897 Bq kg $^{-1}$ over the depth range 33 to 15 cm, with trends similar to those of ^{241}Am , suggesting that they represent variations in the mineralogical composition of the sediment. Above 15 cm, ^{137}Cs activities decreased towards the surface, consistent with efficient redissolution from this section of the sediment. The $^{137}\text{Cs}/^{241}\text{Am}$ profile provides further evidence of this, with small variations of the activity ratio, in the range 0.95 to 1.42, from the surface to a depth of 10 cm. The low and relatively constant values for the ratio in this zone are consistent with a high intensity of mixing, resulting in rapid equilibration of the sediment with the overlying water and efficient redissolution of the radiocaesium (MacKenzie *et al.* 1998). From 10 to 33 cm, slightly higher $^{137}\text{Cs}/^{241}\text{Am}$ activity ratios were observed but the relatively small range of values from 1.56 to 3.01, is indicative of a high degree of mixing of the sediment and very efficient redissolution of the radiocaesium originally incorporated in this material. Below 33 cm, the $^{137}\text{Cs}/^{241}\text{Am}$ activity ratio exhibited much greater variability, revealing less efficient mixing and with values as high as 8.0, suggesting a low efficiency for redissolution of radiocaesium from sediment at this depth. Taken together, the ^{137}Cs and ^{241}Am data suggest that the sediment column for this core can be divided into a zone of highly intense mixing from the surface to *ca.* 10 cm depth, a zone of intermediate intensity mixing from *ca.* 10–33 cm depth and a zone of low intensity mixing below 33 cm.

The bulk carbonate and bulk organic ^{14}C age profiles for the core are shown in Figure 5, along with the mixing zones derived from the ^{137}Cs and ^{241}Am data. The bulk carbonate results show limited variations in the range 12,040 to 13,210 BP, which are clearly too old to represent an average age for input of carbonate material produced during the Holocene and reveal the presence of glacial or pre-glacial carbonate in the sediment. The 0–4 cm sample, from the high-intensity mixing zone, exhibits a slightly younger apparent age than the 16–20 cm and 36–40 cm samples, but this cannot be unambiguously interpreted as evidence of addition of contaminant ^{14}C to the surface sediment, since the 0–4 cm sample age is indistinguishable from that of the deepest sample in the core at 72–76 cm. Thus, despite the evidence of enrichment of ^{14}C activities in the DIC and PIC components of seawater and in contemporary shell material from the Irish Sea, there is no discernable influence of input of such material in this core and, indeed, in the majority of the other cores studied from this area. The implication of this is either that the prevailing water circulation patterns and sedimentary processes result in negligible transfer of recently produced carbonate into this deposit, with preferential deposition of such material in other areas, or that the buffering capacity of the old carbonate in the sediment is sufficient to render the effects of any input negligible. It is, therefore, apparent that bulk carbonate analysis of the sediment represents an insensitive means of investigating the behavior of ^{14}C in this system. However, the observation of the age discrepancy between the ages of the bulk carbonate and discrete shells of *T. communis* by Kershaw, Swift and Denoon (1988) suggests that

analysis of the ^{14}C activity in different size fractions of the sediment may provide useful information.

In contrast to the bulk carbonate, the bulk organic carbon ages exhibited a significant variation with depth as shown in Figure 5. In the low-intensity mixing section of the core below 33 cm, the apparent bulk organic ages were effectively constant with a mean age of 4307 ± 154 BP, which is consistent with an average age for organic carbon produced at a relatively constant rate throughout the Holocene. Progressively younger ages were observed for the samples from the intermediate and high intensity mixing zones, consistent with an input of younger material at the surface, followed by penetration into the sediment by mixing. The fact that Sellafield waste ^{137}Cs and ^{241}Am have been mixed to the bottom of the core in a period of 43 yr or less implies that, if the input of younger organic carbon represented a long-term steady state condition, then the system should have been effectively homogenized with respect to the age of the organic carbon. The observed profile thus implies a recent perturbation of the system, consistent with the introduction of contaminant ^{14}C from Sellafield and possibly from weapons testing fallout.

CONCLUSION

The above discussion leads to the following conclusions:

- The discharge of low-level liquid radioactive waste from Sellafield has resulted in enhanced levels of ^{14}C in the DIC and POC components of seawater in the northeast Irish Sea, with temporal trends in the activities of these components that can be related to varying levels of discharge. Smaller but discernable enrichments of the PIC and POC components of seawater also occur as a result of the discharge.
- The distribution of ^{137}Cs and ^{241}Am reveals that the sediment at the study site can be classified into three zones of decreasing intensity of mixing as a function of increasing depth.
- The apparent bulk carbonate ages for the core, in the range 12,040 to 13,210 BP, revealed the presence of glacial or preglacial carbonate throughout the sediment and provided no evidence of the input of contaminant ^{14}C to this system. Since contemporary DIC, PIC and shell material have been shown to exhibit enhanced ^{14}C activities, this implies either that such materials are preferentially deposited elsewhere, with negligible input to the sediment studied, or that the quantity of old carbonate in the sediment is large enough to render any such input insignificant. The study indicates that analysis of bulk sediment carbonate is an insensitive method for investigating the behavior of ^{14}C or attempting to establish sediment accumulation characteristics in this system.
- The bulk organic carbon analyses provided evidence of a recent perturbation of a well-mixed system, with an average apparent age of *ca.* 4300 BP, by addition of younger organic matter to the surface sediment. The age profile of the bulk organic matter was consistent with the input of contaminant ^{14}C from Sellafield (and possibly weapons testing fallout) followed by penetration into the sediment by mixing, with the intensity of mixing decreasing with depth.

ACKNOWLEDGMENTS

This study was funded by Westlakes Research Institute (Contract Ref PCN0001/ W400/ 373). We gratefully acknowledge the assistance given to us by Ernie Bennett and the crew of the British Nuclear Fuels plc boat, the Seascan, during sampling cruises. We also acknowledge the technical expertise of Robert Anderson and Alison Stewart.

REFERENCES

- Begg, F. H. (ms.) 1992 Anthropogenic ^{14}C in the natural (aquatic) environment. Ph.D Dissertation, University of Glasgow.
- Begg, F. H., Cook, G. T., Baxter, M. S., Scott, E. M. and McCartney, M. 1992 Anthropogenic radiocarbon in the eastern Irish Sea and Scottish coastal waters. In Long, A. and Kra, R. S., eds., Proceedings of the 14th International ^{14}C Conference. *Radiocarbon*, 34(3): 707–716.
- BNFL 1977–1994 *Annual Reports on Radioactive Discharges and Monitoring of the Environment*. Risley, UK, British Nuclear Fuels Limited.
- Cook, G. T., Begg, F. H., Naysmith, P., Scott, E. M. and McCartney, M. 1995 Anthropogenic ^{14}C marine geochemistry in the vicinity of a nuclear fuel reprocessing plant. In Cook, G. T., Harkness, D. D., Miller, B. F. and Scott, E. M., eds., Proceedings of the 15th International ^{14}C Conference. *Radiocarbon* 37(2): 459–467.
- Cook, G. T., MacKenzie, A. B., McDonald, P. and Jones, S. R. 1997a Remobilisation of Sellafield derived radionuclides and transport from the north-east Irish Sea. *Journal of Environmental Radioactivity* 37: 227–241.
- Cook, G. T., MacKenzie, A. B., Naysmith, P. and Anderson, R. 1997b Natural and anthropogenic ^{14}C in the UK coastal marine environment. *Journal of Environmental Radioactivity*, in press.
- Cronan, D. S. 1969 Recent sedimentation in the central north-east Irish Sea. *Institute of Geological Sciences Report No. 69/8*: 10 p.
- Fry, B., Peltzer, E. T., Hopkinson, Jr., C. S., Nolin, A. and Redmond, L. 1996 Analysis of marine DOC using a dry combustion method. *Marine Chemistry* 54: 191–201.
- Gray, J., Jones, S. R. and Smith, A. D. 1995 Discharges to the environment from the Sellafield Site, 1951–1992. *Journal of Radiological Protection* 15(2): 99–131.
- Hunt, G. J. and Kershaw, P. J. 1990 Remobilisation of artificial radionuclides from the sediment of the Irish Sea. *Journal of Radiological Protection* 10: 147–151.
- Jones, D. J., Roberts, P. D. and Miller, J. M. 1988 The distribution of gamma-emitting radionuclides in near surface subtidal sediments near the Sellafield plant. *Estuarine, Coastal and Shelf Science* 27: 143–161.
- Jull, A. J. T., Donahue, D. J., Hatheway, A. L., Linick, T. W. and Toolin, L. J. 1986 Production of graphite targets by deposition from CO/H_2 for precision accelerator ^{14}C measurements. *Radiocarbon* 28(1): 191–197.
- Kershaw, P. J. 1986 Radiocarbon dating of Irish Sea sediments. *Estuarine, Coastal and Shelf Science* 23: 295–303.
- Kershaw, P. J., Swift, D. J., Pentreath, R. J. and Lovett, M. B. 1983 Plutonium redistribution by biological activity in Irish Sea sediments. *Nature* 306: 774–775.
- Kershaw, P. J., Swift, D. J., Pentreath, R. J. and Lovett, M. B. 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., Swift, D. J. and Denoon, D. C. 1988 Evidence of recent sedimentation in the Eastern Irish Sea. *Marine Geology* 85: 1–14.
- Kershaw, P. J., Gurbutt, P. A., Young, A. K. and Allington, D. J. 1988 Scavenging and bioturbation in the Irish Sea from measurements of $^{234}\text{Th}/^{238}\text{U}$ and $^{210}\text{Pb}/^{226}\text{Ra}$ disequilibria. In Guary, J. C., Guegueniat, P. and Pentreath, R. J., eds., *Radionuclides: A Tool for Oceanography*. London, Elsevier Applied Science: 131–142.
- Kirby, R., Parker, W. R., Pentreath, R. J. and Lovett, M. B. 1983 Sediment studies relevant to low level radioactive effluent dispersal in the Irish Sea. Part 3: An evaluation of possible mechanisms for the incorporation of radionuclides into marine sediments. *IOS Report No. 178*. Godalming, UK, Institute of Oceanographic Sciences.
- MAFF 1996 Radioactivity in food and the environment, 1995. *Ministry of Agriculture, Fisheries and Food RIFE-1*, London, UK.
- MacKenzie, A. B., Scott, R. D., Allan, R. L., Ben Shaban, Y. A., Cook, G. T. and Pulford, I. D. 1994 Sediment radionuclide profiles: implications for mechanisms of Sellafield waste dispersal in the Irish Sea. *Journal of Environmental Radioactivity* 23: 39–69.
- MacKenzie, A. B., Cook, G. T., McDonald, P. and Jones, S. R. 1998 The influence of mixing timescales and redissolution processes on the distribution of radionuclides in the north-east Irish Sea. *Journal of Environmental Radioactivity* 39: 35–53.
- McCartney, M., Kershaw, P. J., Woodhead, D. S. and Denoon, D. C. 1994 Artificial radionuclides in the surface sediments of the Irish Sea, 1968–1988. *Science of the Total Environment* 141: 103–138.
- Miller, J. M., Thomas, B. W., Roberts, P. D. and Creamer, S. C. 1982 Measurement of marine radionuclide distribution using a towed sea-bed spectrometer. *Marine Pollution Bulletin* 13: 315–319.
- Pantin, H. M. 1977 Quaternary sediments of the northern Irish Sea. In Kidson, C. and Tooley, M. J., eds., *The Quaternary History of the Irish Sea*. Liverpool, Seel House Press: 27–54.
- _____. 1978 Quaternary sediments from the north-east Irish Sea: Isle of Man to Cumbria. *Bulletin of the Geological Survey of Great Britain*, No. 64: 43 p.
- Pedersen, T. S., Sholkovitz, E. R. and Malcolm, S. J. 1985 A lightweight gravity corer for undisturbed sampling of soft sediments. *Canadian Journal of Earth Science* 22: 133–135.
- Pentreath, R. J., Lovett, M. B., Jefferies, D. F., Woodhead, D. S., Talbot, J. W. and Mitchell, N. T. 1984 Impact on public radiation exposure of transuranium nuclides discharged in liquid wastes from fuel element reprocessing at Sellafield, United Kingdom. In *Radioactive Waste Management. Vol. 5*. IAEA, Vienna.

Smith, T. J., Parker, W. R. and Kirby, R. 1980 Sedimentation studies relevant to low-level radioactive effluent dispersal in the Irish Sea. Part 1: Radionuclides in marine sediments. *IOS Report No. 110*. Godalming, UK, Institute of Oceanographic Sciences: 87 p.

Williams, S. J., Kirby, R., Smith, T. J. and Parker, W. R.

1981 Sediment studies relevant to low level radioactive effluent dispersal in the Irish Sea. Part 2: Seabed morphology, sediments and shallow sub-bottom stratigraphy of the eastern Irish Sea. *IOS Report No. 120*. Godalming, UK, Institute of Oceanographic Sciences.