

## Accumulation of Sellafield-derived radiocarbon ( $^{14}\text{C}$ ) in Irish Sea and West of Scotland intertidal shells and sediments



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### ABSTRACT

The nuclear energy industry produces radioactive waste at various stages of the fuel cycle. In the United Kingdom, spent fuel is reprocessed at the Sellafield facility in Cumbria on the North West coast of England. Waste generated at the site comprises a wide range of radionuclides including radiocarbon ( $^{14}\text{C}$ ) which is disposed of in various forms including highly soluble inorganic carbon within the low level liquid radioactive effluent, via pipelines into the Irish Sea. This  $^{14}\text{C}$  is rapidly incorporated into the dissolved inorganic carbon (DIC) reservoir and marine calcifying organisms, e.g. molluscs, readily utilise DIC for shell formation. This study investigated a number of sites located in Irish Sea and West of Scotland intertidal zones. Results indicate  $^{14}\text{C}$  enrichment above ambient background levels in shell material at least as far as Port Appin, 265 km north of Sellafield. Of the commonly found species (blue mussel (*Mytilus edulis*), common cockle (*Cerastoderma edule*) and common periwinkle (*Littorina littorea*)), mussels were found to be the most highly enriched in  $^{14}\text{C}$  due to the surface environment they inhabit and their feeding behaviour. Whole mussel shell activities appear to have been decreasing in response to reduced discharge activities since the early 2000s but in contrast, there is evidence of continuing enrichment of the carbonate sediment component due to in-situ shell erosion, as well as indications of particle transport of fine  $^{14}\text{C}$ -enriched material close to Sellafield.

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### 1. Introduction

The Sellafield nuclear fuel reprocessing plant (formerly known as Windscale), located in Cumbria on the North West coast of England (Fig. 1), is the primary source of anthropogenic radiocarbon ( $^{14}\text{C}$ ) discharges to the UK environment. The  $^{14}\text{C}$  waste that arises during fuel reprocessing is discharged under authorisation to the atmosphere and the Irish Sea (Fig. 2). Discharges of low-level liquid radioactive effluent, containing  $^{14}\text{C}$ , are via pipelines that extend 2.1 km offshore, while regulated discharges to the atmosphere are made from a wide range of facilities at the site, including the fuel storage ponds, reprocessing plants and waste treatment plants (RIFE, 2011). Reprocessing of radioactive waste has been ongoing since 1952, however, monitoring of  $^{14}\text{C}$  discharges only began in 1984 (BNFL, 1985). Subsequently, discharges for the earlier period to both the atmosphere and the NE Irish Sea were estimated by

measuring the  $^{14}\text{C}$  activity in annual rings from trees felled in close proximity to Sellafield (Gray et al., 1995; McNamara and McCartney, 1998; Isogai et al., 2002) and annually collected seaweed (Cook et al., 2004a), respectively. Between 1984 and 1993 Sellafield discharged, on average, 1.78 TBq year<sup>-1</sup> of  $^{14}\text{C}$  to the Irish Sea (BNFL, 1985–1989; MAFF, 1992–1994). However, an increase in the volume of waste reprocessed and, to a larger extent, a change in discharge policy in 1994 resulted in an increase in aquatic  $^{14}\text{C}$  discharges to 8.17 TBq for that year.  $^{14}\text{C}$  discharges peaked in 2003 and although discharged activities have since reduced, they have remained relatively high. On average, Sellafield has discharged 8.13 TBq year<sup>-1</sup> between 1994 and 2013 (MAFF, 1995; RIFE, 1996–2014). Its long half-life (5730 years), high environmental mobility and high bio-availability make Sellafield-derived  $^{14}\text{C}$  the largest contributor to the collective dose commitment to UK and European populations from the entire nuclear industry (BNFL, 2002). Also,  $^{14}\text{C}$  is estimated to be the largest contributor to the collective total dose that the global population receives from nuclear fuel processes (UNSCEAR, 2008). Therefore, it is very

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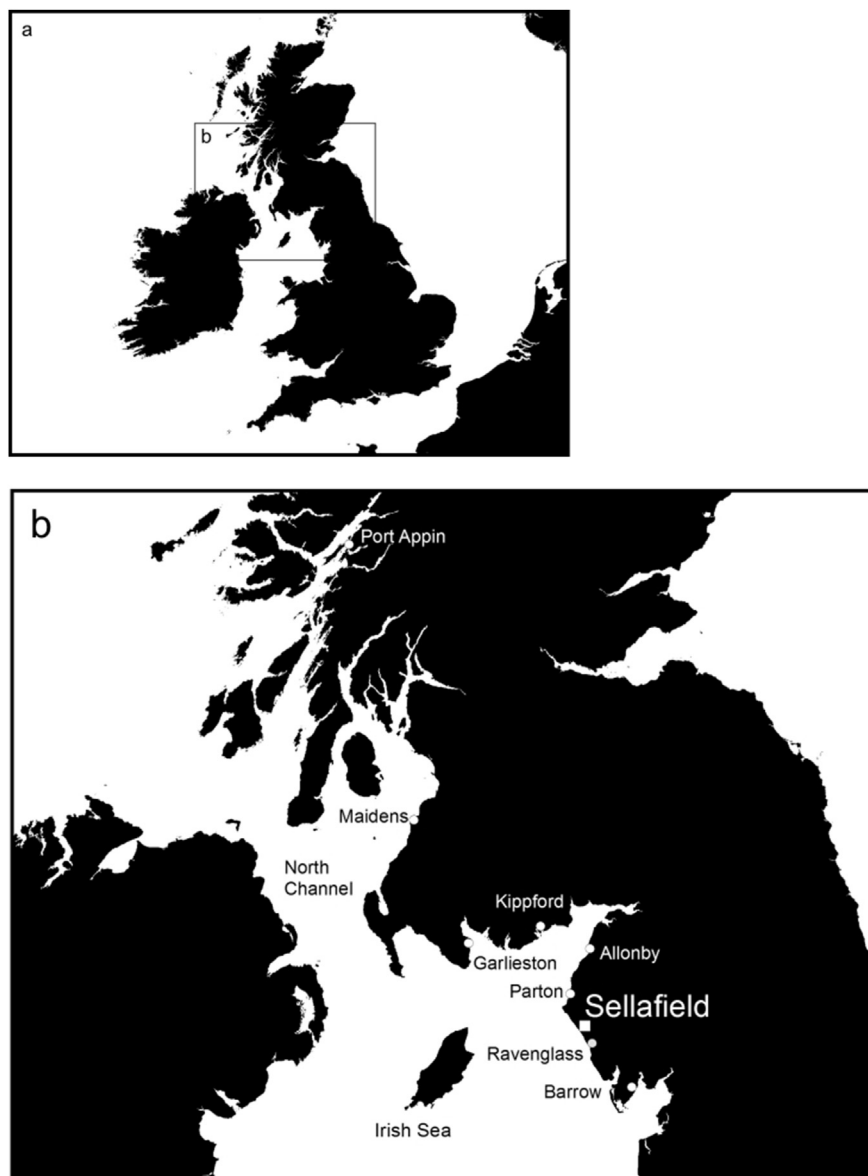


Fig. 1. UK map (a) with study area (b) showing Sellafeld and study sites.

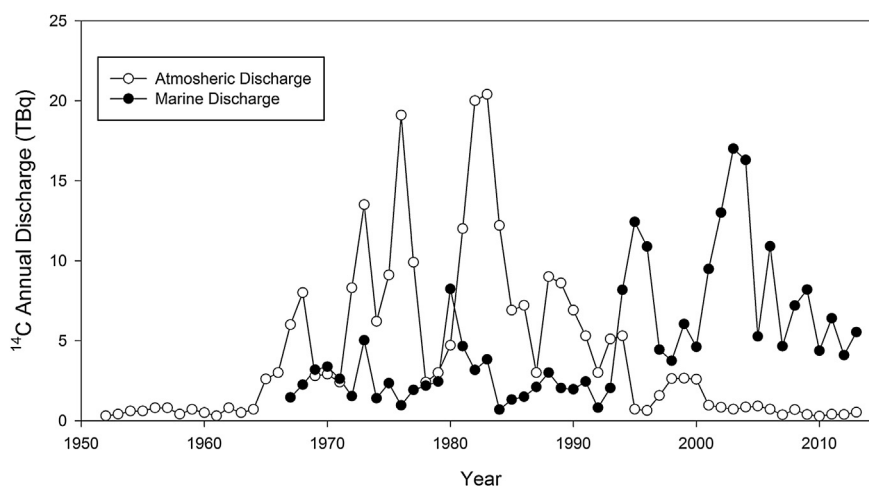
important to understand its distribution and long-term fate in the environment.

$^{14}\text{C}$  is discharged into the Irish Sea primarily as inorganic carbon and is incorporated into the dissolved inorganic carbon (DIC) component of seawater (Begg et al., 1992). Enhanced  $^{14}\text{C}$  activities in the DIC component of seawater have previously been detected at a range of sites around the British coastline (Cook et al., 1998). Marine mollusc species predominantly utilise DIC for shell formation (McConnaughey et al., 1997) and so have the potential to incorporate  $^{14}\text{C}$  during calcification. Analysis of shells and sedimentary inorganic carbon by Cook et al. (2004b) revealed enhanced activities in whole shell and, to a lesser extent, in coarse sediment (>500  $\mu\text{m}$ ) fractions at near-field sites to the north of Sellafeld, with a trend of decreasing activity with increasing distance from Sellafeld. Following this study, Muir et al. (2015) found shell and sediment  $^{14}\text{C}$  activities had increased at the same sites between 2001 and 2011. It was also confirmed that as  $^{14}\text{C}$ -enriched shells erode they contribute  $^{14}\text{C}$  to the sediment, gradually increasing the activity of progressively finer sediments within the intertidal zone

(Muir et al., 2015). These two studies were confined to an area where transport of Sellafeld-derived radionuclides is largely dominated by particle transport (MacKenzie et al., 1987), which has been suggested as a possible mechanism for redistributing fine material enriched in  $^{14}\text{C}$  (Muir et al., 2015).

Long-term dilution and dispersion of Sellafeld aquatic discharges are dictated by a net northerly movement of water through the North Channel and wind driven turbulent diffusion (Dunster, 1998). Water moving through the North Channel becomes a significant component of the Scottish Coastal Current (McKay et al., 1986; Hill and Simpson, 1988) and this, in turn, is a contributory source of water to the Fair Isle Current that flows round the northern Scottish coast and into the North Sea (Turrell and Henderson, 1990). Despite its high bioavailability, close to 100% of  $^{14}\text{C}$  discharged from Sellafeld is dispersed northwards through the North Channel (Wolstenholme et al., 1998; Gulliver et al., 2001) and is subsequently transported in solution around the Scottish coastline (Gulliver et al., 2004) where it has the potential to accumulate.

This study addresses both particle and solution transport of  $^{14}\text{C}$



**Fig. 2.** Sellafeld atmospheric and marine annual <sup>14</sup>C discharges (TBq). Data prior to 1995 for atmospheric discharges (Isogai et al., 2002) and prior to 1985 for marine discharges (Cook et al., 2004a) are estimated. The subsequent measured data were taken from BNFL (1985–1989), MAFF (1992–1995) and RIFE (1996–2014) reports.

by sampling a range of sites within the area dominated by particle transport and that dominated by solution transport, with particular attention being given to sites north of Sellafeld beyond the area dominated by particle transport. In addition, sites south of Sellafeld were sampled to investigate any southward transport of <sup>14</sup>C. A background value for the west coast UK marine environment was determined, allowing any enrichment in <sup>14</sup>C concentration to be identified. The work presented here is a component of a larger study investigating the fate of Sellafeld-derived <sup>14</sup>C in the marine environment including transport and uptake in intertidal sediments, offshore sediments and marine organisms.

## 2. Methodology

Samples were collected in late 2013/early 2014 from eight intertidal sites on the UK west coast as shown in Fig. 1. Six of these sites are located north of Sellafeld with two (Parton and Allonby) studied previously (Cook et al., 2004b; Muir et al., 2015). Parton and Allonby were chosen to gain an understanding of how the <sup>14</sup>C activity in shells/intertidal sediment was responding to changes in discharge over time. The other four northern sites (Kippford, Garieston, Maidens and Port Appin) are increasingly distant from Sellafeld and of these, Maidens and Port Appin are well beyond the area dominated by particle transport of Sellafeld-derived radionuclides (MacKenzie et al., 1987) and designated as far-field due to being located north of the North Channel. Two sites south of Sellafeld were also sampled (Ravenglass and Barrow).

Several kilograms of surface sediment, including shells, were collected randomly along the high water mark at each of the eight sites. Shell collection was non-species-specific and species were later identified in the laboratory. In addition, mussel shells from recently dead individuals (shells were still hinged) were sourced from Bunbeg on the west coast of Ireland, to provide a measure of contemporary marine inorganic <sup>14</sup>C background. This site is geographically close to a background sampling site used previously (Cook et al., 1998), and on the Atlantic coastline, thus virtually free of UK coastal influences.

The sediments were oven dried at 40 °C and sieved into four size fractions; >2 mm, 500 μm–2 mm, 63–500 μm and <63 μm. Shell fragments were picked from the >2 mm fraction and homogenised using a mortar and pestle. Common cockle (*Cerastoderma edule*), common periwinkle (*Littorina littorea*) and blue mussel (*Mytilus edulis*) shells were the most ubiquitous whole shells collected

across all sites and, where more than two of these shells were available, they were analysed for <sup>14</sup>C activity. Cockle shells were available from four, mussel shells from six, and winkle shells from seven sites. The shells were placed in a sonic bath for approximately 10 min to remove any adhering sediment and organic matter (i.e. extraneous algae) and then washed thoroughly with distilled water. They were subsequently crushed, homogenised and sub-sampled to provide a single composite sample for each species at each site.

Samples were hydrolysed within a vacuum system using excess 1 M hydrochloric acid (HCl) and the liberated CO<sub>2</sub> was cryogenically purified under vacuum using liquid N<sub>2</sub>. Sub-samples (3 mL) of CO<sub>2</sub> were converted to graphite according to the method of Slota et al. (1987) and measured on a NEC 250 kV single-stage accelerator mass spectrometry (SSAMS) (Naysmith et al., 2010). A further sub-sample of CO<sub>2</sub> was taken for δ<sup>13</sup>C measurement by isotope ratio mass spectrometry using a VG SIRA 11 (Ascough et al., 2012). Results were converted from AMS fraction modern values to specific activity in Becquerel's per kilogram of carbon (Bq kg<sup>-1</sup> C) using the regime described for enhanced <sup>14</sup>C activities in Mook and van der Plicht (1999). Uncertainties are less than 0.5% of the measured activity.

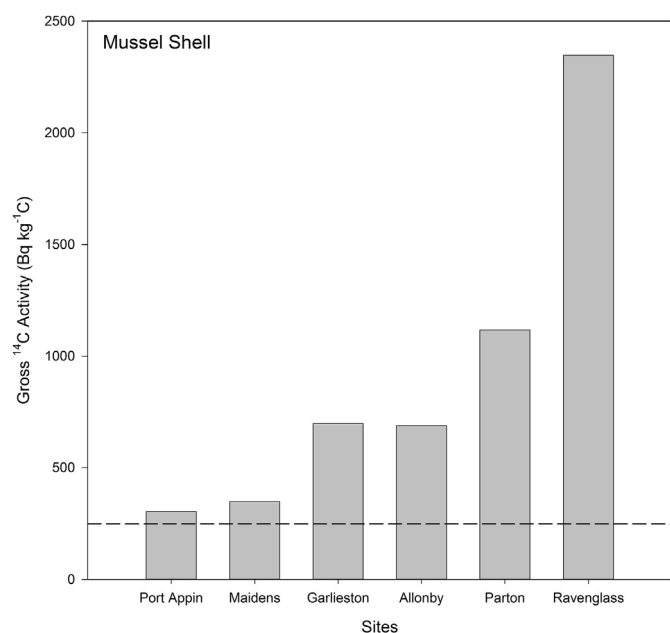
## 3. Results and discussion

### 3.1. <sup>14</sup>C Background activity

Analysis of a combined sample of 6 hinged mussel shells from the west coast of Ireland produced a <sup>14</sup>C activity of 249 ± 1 Bq kg<sup>-1</sup> C. This value is comparable to the background activity for 1995 published by Cook et al. (1998) of 247.6 ± 1.0 Bq kg<sup>-1</sup> C and indicates a steady-state <sup>14</sup>C activity for the marine environment in this area. Mussels predominantly utilise DIC directly from the water column to build their shells, although shell carbon can also be sourced metabolically from their diet (McConnaughey et al., 1997; Gillikin et al., 2006). Due to their selective filter feeding habit, mussels primarily consume phytoplankton, and as phytoplankton also derive carbon from DIC during photosynthesis (Lalli and Parsons, 1993), it follows that mussel shell <sup>14</sup>C activity will reflect the local <sup>14</sup>C concentration in the DIC. The west coast of Ireland is relatively free of UK anthropogenic inputs with water being predominantly Atlantic in origin. This value is therefore used as a background activity and a baseline against which to measure enriched <sup>14</sup>C in west coast UK marine samples.

### 3.2. Shell $^{14}\text{C}$

Results for whole shells are presented in Fig. 3 (mussel shells), Fig. 4 (winkle shells) and Fig. 5 (cockle shells), and in Table 1. The highest measured activities across all shell types were at Ravenglass (2350 Bq kg $^{-1}$  C for mussel shells) which, although located south of Sellafield, is the site closest to the reprocessing facility. Despite the net yearly northward flow, seasonal southward flow, due to prevailing winds, is known to occur in the Irish Sea (Davies et al., 2002; Dabrowski and Hartnett, 2008; Dabrowski et al., 2010), which would disperse discharged effluent south of Sellafield. Only winkle shells were available from the most southern site, Barrow, and were found to have a  $^{14}\text{C}$  activity less than background (234 Bq kg $^{-1}$  C), the only site where this was the case. The  $\delta^{13}\text{C}$  for this sample was  $-11.4\text{‰}$  which indicates that these organisms were not living in a truly marine environment and that there is a freshwater carbonate contribution to their shell formation; in comparison, the  $\delta^{13}\text{C}$  values for all other samples were between  $-0.5$  and  $+2.8\text{‰}$ , indicative of a marine environment (Keith et al., 1964). The Barrow samples were collected on the Duddon Estuary, fed largely by the River Duddon, which is likely to be the source of this terrestrial/freshwater  $\delta^{13}\text{C}$  signal and below-background  $^{14}\text{C}$  activity. This reduction in activity below ambient background could be due to a number of factors including dissolution of geological carbonate in the catchment or oxidation of old organic matter in the water column. As Barrow shell fragment activity (discussed in 3.3) is above background and produced a marine  $\delta^{13}\text{C}$  signal ( $+0.1$ ) it is probable that the whole winkle shells are not representative of the environment they were found in and have been washed downstream from a site closer to the river mouth. At other sites, whole shell activities generally reduce moving north from Sellafield but remain above background. All shell types found at the two far-field sites (Maidens and Port Appin) were enriched, indicating significant  $^{14}\text{C}$  enrichment of the DIC component of Scottish coastal water. A preliminary result of direct analysis of the DIC component of water in the Firth of Lorn (West Scotland) in spring 2014 (298 Bq kg $^{-1}$  C) confirms this enrichment.



**Fig. 3.** Gross  $^{14}\text{C}$  specific activities (Bq kg $^{-1}$  C) in mussel shells. The dashed line indicates the measured background activity of 249 Bq kg $^{-1}$  C measured in mussel shells from the West Coast of Ireland. Note that errors are minimal and would not be clearly observable on this scale, they can, however, be seen in Table 1.

Mussel shells typically had the highest activities at each site (average for all sites = 917 Bq kg $^{-1}$  C) followed by winkle (690 Bq kg $^{-1}$  C) and then cockle shells (495 Bq kg $^{-1}$  C). The disparities between species may be explained to some extent by their respective ecologies. Mussels are filter feeders predominantly feeding on phytoplankton which derive all their carbon from DIC. Winkles graze on algae and some intertidal algae such as sea lettuce (which is a known food source for winkles), can utilise atmospheric carbon when exposed to the atmosphere (Murthy et al., 1987). The influence of Sellafield on the atmospheric  $^{14}\text{C}$  activity only extends to around 10 km from the plant, thereafter, the activity is greatly diluted and the general atmospheric activity is relatively constant (McCartney et al., 1988). The  $^{14}\text{C}$  activity of terrestrial vegetation is a good proxy for atmospheric activity and the  $^{14}\text{C}$  activity of a Scottish barley mash (a bi-product of the whisky industry) from 2013, was 229 Bq kg $^{-1}$  C, significantly lower than the DIC  $^{14}\text{C}$  activity measured at sites remote from Sellafield, such as the Firth of Lorn (298 Bq kg $^{-1}$ ). The lower atmospheric  $^{14}\text{C}$  activity would result in a reduced algal activity relative to the DIC. As some of the carbon used in shell building by marine molluscs is metabolically derived, this will manifest itself in a reduced winkle shell  $^{14}\text{C}$  activity relative to mussel shells. Cockles have the lowest activity although the reason for this is less obvious. Like mussels, cockles are filter feeders and will be sourcing similar food-stuffs at the same sites. However, mussels and winkles inhabit surface environments whereas cockles bury themselves in the sediment. It would seem unlikely that cockles are sourcing less enriched DIC from sediment pore water in their immediate vicinity as they are only shallow burrowers (typically down to 5–10 cm maximum) and it is well established that the sediments are well mixed to significant depths primarily due to bioturbation (Kirby et al., 1983), hence, the pore water here is likely to be well mixed with water overlying the sediment. However, the  $^{14}\text{C}$  activity of the organic component of surface sediments can be significantly depleted. For example, Wolstenhome et al. (1998) demonstrated depletion in surface sediments of the NE Irish Sea while the particulate organic carbon (POC) and DIC fractions of the water column were enriched above the ambient background value. Therefore, if organic matter in the surface sediment contributes some carbon to shell formation, this could account for the lower activities.

### 3.3. Sediment $^{14}\text{C}$

Results for sediment fractions are presented in Fig. 6 and Table 1. Shell fragments were enriched above background at all sites, including Barrow. Large shell fragments are unlikely to have been transported from sites closer to Sellafield and suggest that whole shells in this area, and therefore DIC, were above background. Circulation models have suggested that seasonal southward flow of water will disperse dissolved radionuclides from Sellafield as far as Liverpool Bay (Dabrowski and Hartnett, 2008). The highest measured activity was again south of Sellafield at Ravenglass (627 Bq kg $^{-1}$  C in shell fragments). Overall,  $^{14}\text{C}$  activity generally decreases with distance from Sellafield. At far-field sites, enhanced activities were found in shell fragments at Maidens (334 Bq kg $^{-1}$  C) and Port Appin (273 Bq kg $^{-1}$  C) with the 500  $\mu\text{m}^{-2}$  mm fraction also enriched at the latter site (276 Bq kg $^{-1}$  C). As the higher-activity, whole shells are gradually broken down by in-situ erosion, the finer material that is produced will be incorporated into the sediment, gradually increasing its activity (Cook et al., 2004b). This is on the assumption that whole shells break down to coarse fragments and subsequently to finer and finer size fractions. If in-situ erosion of shells is the predominant source of  $^{14}\text{C}$  to sediment, it follows that currently, there should be a general reduction in activity with decreasing particle size as there will be a larger proportion of older

**Table 1**Gross  $^{14}\text{C}$  specific activities in intertidal shells and sediments ( $\text{Bq kg}^{-1}\text{C}$ ). The  $\delta^{13}\text{C}$  values are relative to VPDB (Craig, 1957).

Sample type	Sampling site							
	Port Appin	Maidens	Garlieston	Kippford	Allonby	Parton	Ravenglass	Barrow
	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)	$^{14}\text{C}$ ( $\text{Bq kg}^{-1}\text{C}$ ) ( $\delta^{13}\text{C}$ ‰)
<b>Whole Shells</b>								
Mussel Shells	304 ± 2 (0.5)	348 ± 2 (0.7)	698 ± 3 (2.2)	na	688 ± 3 (−0.4)	1120 ± 5 (−0.2)	2350 ± 11 (−0.5)	na
Cockle Shells	267 ± 1 (0.3)	na	418 ± 2 (2.8)	365 ± 2 (0.2)	na	na	929 ± 6 (−0.1)	na
Winkle Shells	275 ± 1 (0.7)	374 ± 2 (0.3)	333 ± 2 (0.4)	na	245 ± 2 (1.5)	1210 ± 5 (0.6)	2160 ± 9 (0.5)	234 ± 1 (−11.4)
<b>Sediment</b>								
Shell fragments (>2 mm)	273 ± 1 (1.0)	334 ± 2 (0.1)	302 ± 2 (0.7)	322 ± 2 (0.3)	527 ± 2 (−0.1)	444 ± 2 (2.0)	627 ± 3 (−2.5)	290 ± 1.0 (0.1)
Sediment 500 $\mu\text{m}^{-2}$ mm	276 ± 1 (0.9)	241 ± 1 (−0.7)	224 ± 1 (0.2)	427 ± 2 (0.1)	223 ± 1 (0.6)	152 ± 1 (1.8)	161 ± 1 (0.6)	22.0 ± 0.1 (0.2)
Sediment 63–500 $\mu\text{m}$	17.7 ± 0.1 (−1.7)	86.8 ± 0.3 (0.9)	92.9 ± 0.4 (−1.6)	283 ± 1 (−0.2)	139 ± 1 (1.6)	214 ± 1 (0.0)	194 ± 1 (−1.4)	14.0 ± 0.1 (0.1)
Sediment <63 $\mu\text{m}$	44.9 ± 0.2 (1.0)	87.8 ± 0.3 (−2.9)	63.7 ± 0.2 (0.2)	115 ± 1 (−0.4)	308 ± 2 (−0.3)	443 ± 2 (0.1)	174 ± 1 (−2.8)	31.2 ± 0.1 (−1.1)

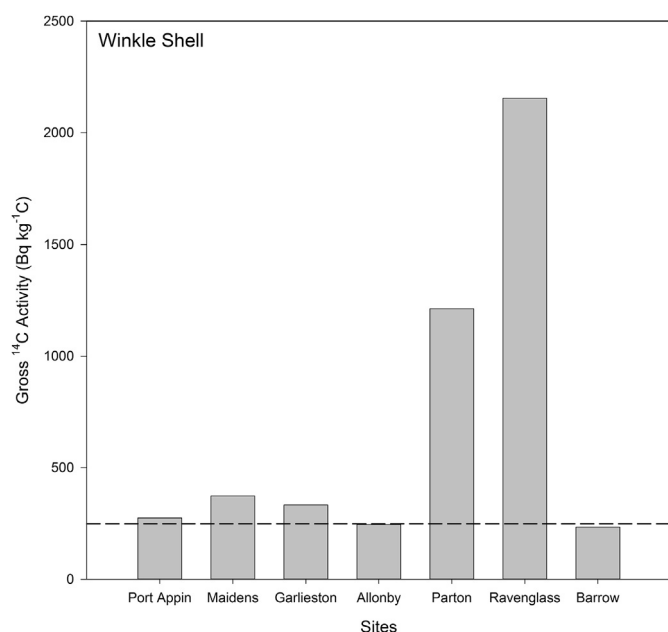
na – no species available.

(and therefore less enriched) material within the finer sediment fractions (Cook et al., 2004b). However, this is not the case for several sites and is particularly evident at Allonby and Parton. At these sites, shell fragments and the finest sediment (<63  $\mu\text{m}$ ) were found to be enriched above background but both intermediate sediment sizes (500  $\mu\text{m}^{-2}$  mm and 63–500  $\mu\text{m}$ ) had activities that were lower than the ambient background. Similar results were found in 2011 by Muir et al. (2015) at Parton and another site not investigated in the present study (Flimby). Two possible mechanisms for this enrichment of finer material were proposed: 1. greater northwards movement in the water column of the finest fraction compared to coarse material, or 2. rapid breakdown of the shell material at these sites. The second mechanism could also involve the gradual weathering of a shell surface, where fine material is eroded off rather than shell breakdown to intermediate

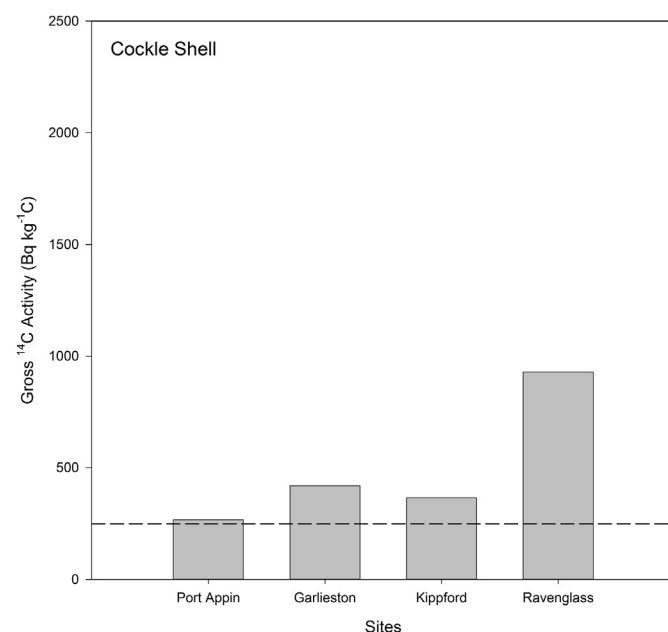
particle sizes. The inside surface of some mollusc shells including mussels and winkles, is made from strong aragonite layers called nacre. This could take longer to erode than other calcified layers which break down relatively quickly and contribute to sediment enrichment.

### 3.4. Intertidal $^{14}\text{C}$ activity 2001–2014

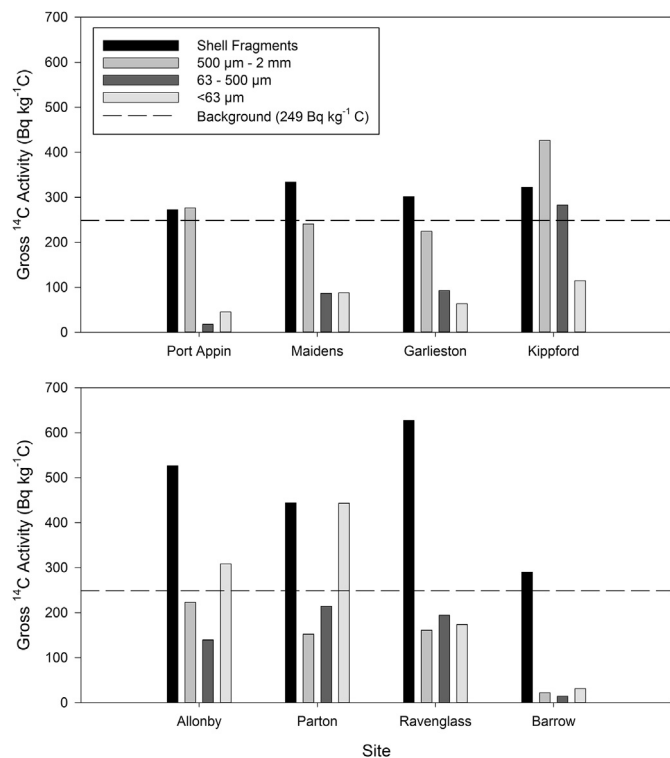
As noted in Section 3.3, two sites in the current study have been investigated previously; Parton and Allonby. These sites were first visited in 2001 (Cook et al., 2004b) and again in 2011 (Muir et al., 2015). The measured  $^{14}\text{C}$  activities at these sites in the current and previous studies are presented in Fig. 7. At Parton, both mussel shell and coarse sediment (>500  $\mu\text{m}$ ) activities increased between 2001 and 2011, before decreasing in 2014. The intermediate



**Fig. 4.** Gross  $^{14}\text{C}$  specific activities ( $\text{Bq kg}^{-1}\text{C}$ ) in winkle shells. The dashed line indicates the measured background activity of 249  $\text{Bq kg}^{-1}\text{C}$ .



**Fig. 5.** Gross  $^{14}\text{C}$  specific activities ( $\text{Bq kg}^{-1}\text{C}$ ) in cockle shells. The dashed line indicates measured background activity of 249  $\text{Bq kg}^{-1}\text{C}$ .

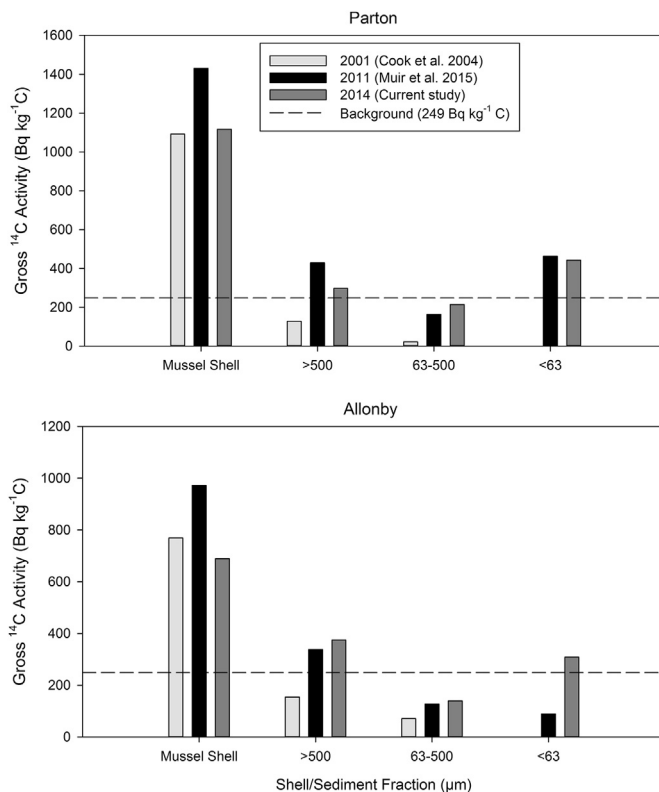


**Fig. 6.** Gross  $^{14}\text{C}$  specific activities ( $\text{Bq kg}^{-1} \text{C}$ ) in different size fractions of the carbonate component of Scottish (top) and English (bottom) west coast intertidal sediments.

sediment (63–500  $\mu\text{m}$ ) activity increased between each study whereas there is little change in fine sediment (<63  $\mu\text{m}$ ) activity. At Allonby, mussel shell activity again increases between 2001 and 2011 and decreases by 2014. All sediment fractions increased in activity towards 2014, most significantly in the finest fraction (<63  $\mu\text{m}$ ) between 2011 and 2014.

The shell lengths of mussel shells used in this study were typically 5–6 cm, meaning the mussels would have been about 5 years in age (Bayne and Worrall, 1980). If, for the three studies, the mean aquatic  $^{14}\text{C}$  discharged activity for the 5 years prior to sampling is compared to the whole mussel shell activities, it can be observed that mussel shell activity responds in accordance with discharge activity (Table 2). The activity of whole mussel shells at Parton increased from 1090  $\text{Bq kg}^{-1} \text{C}$  in 2001 to 1430  $\text{Bq kg}^{-1} \text{C}$  in 2011 in response to an increase in the 5 year average discharge from 5.93  $\text{TBq y}^{-1}$  to 7.06  $\text{TBq y}^{-1}$ . This was followed by a reduction in mussel shell activity in 2014 to 1120  $\text{Bq kg}^{-1} \text{C}$ , corresponding to a reduction in average discharge over the previous 5 years to 5.71  $\text{TBq}$ . A similar pattern in  $^{14}\text{C}$  activities is observed at Allonby.

The increasing activity in sediment fractions at Allonby (which is also apparent in the intermediate fraction at Parton) supports the hypothesis that as whole shells erode they will contribute enhanced  $^{14}\text{C}$  activities to the sediment. However, a considerable change is found in the finest sediment at Allonby, from  $^{14}\text{C}$ -depleted in 2011 (89  $\text{Bq kg}^{-1} \text{C}$ ) to significantly enriched in this study (308  $\text{Bq kg}^{-1} \text{C}$ ). It is unlikely that the difference between these two studies could be solely explained by erosional processes within the time interval of about 3 years. Although, it is possible that this difference could be the result of sampling location on site, a more likely explanation may be offered by particle transport processes. Fine, highly enriched particulate material from sites closer to Sellafield may be re-suspended (possibly during storm events), transported northwards with prevailing currents and re-



**Fig. 7.** Gross  $^{14}\text{C}$  specific activities ( $\text{Bq kg}^{-1} \text{C}$ ) in mussel shells and intertidal sediment fractions at Parton (top) and Allonby (bottom). The >500  $\mu\text{m}$  fraction for the current study is an average of shell fragments (>2 mm) and the 500  $\mu\text{m}^{-2}$  mm sediment fraction. No data is available for the <63  $\mu\text{m}$  sediment fraction from 2001.

deposited at Allonby. This would be consistent with northward currents and known northward movement of sediment within the Irish Sea (Mackenzie et al., 1987, 1994, 1998, 1999; McDonald et al., 1990; Cook et al., 1997). The selective particle transport of fine material over coarser material from more enriched areas may help explain the relatively high activities found in finer material at other sites including Parton. The pre-existing  $^{14}\text{C}$  enriched activity at Parton may be due to previous sedimentary deposition of enriched material. Subsequently, there was no observed  $^{14}\text{C}$  increase in the finest sediment fraction at Parton between 2011 and 2014 as the activity of any newly deposited material was similar.

#### 4. Conclusions

The results of this study suggest that the  $^{14}\text{C}$  activity in whole mussel shells at two previously-investigated sites on the NE Irish Sea coast, north of Sellafield, are varying in response to the average  $^{14}\text{C}$  discharge over the preceding 5 years. In contrast, there is a

**Table 2**

Mussel shell activities at Parton and Allonby over three studies and the corresponding average marine  $^{14}\text{C}$  discharge ( $\text{TBq}$ ) from Sellafield in the 5 years prior to shell collection in each study.

Year of shell collection (study)	Mussel shell Activity ( $\text{Bq kg}^{-1} \text{C}$ )		5 Year average Sellafield marine discharge previous to collection date ( $\text{TBq}$ )
	Parton	Allonby	
2001 (Cook et al., 2004b)	1090	769	5.93
2011 (Muir et al., 2015)	1430	972	7.06
2014 (present study)	1120	688	5.71

general increase in the  $^{14}\text{C}$  activity of the finer fractions of the inorganic intertidal material, confirming the previous hypothesis of an increased activity in fine material as whole shells/larger fragments formed during the nuclear era are broken down over time. Consequently, the  $^{14}\text{C}$  activity of the inorganic carbon component of intertidal and sub-tidal NE Irish Sea sediments will gradually increase. The  $^{14}\text{C}$  activity of shell fragments at all Scottish sites were also enriched relative to ambient background (with the 500  $\mu\text{m}$ –2 mm fraction close to ambient background), suggesting that a similar trend will be observed in time at these more remote sites. On average, the  $^{14}\text{C}$  activity in whole shells follows the trend of mussels > winkles > cockles which reflects their feeding habits and the ecological niche they occupy.

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### References

- Ascough, P.L., Church, M.J., Cook, G.T., Dunbar, E., Gestsdóttir, H., McGovern, T.H., Dugmore, A.J., Friðriksson, A., Edwards, K.J., 2012. Radiocarbon reservoir effects in human bone collagen from northern Iceland. *J. Archaeol. Sci.* 39, 2261–2271.
- Bayne, B., Worrall, C., 1980. Growth and production of mussels *Mytilus edulis* from two populations. *Mar. Ecol. Prog. Ser.* 3, 317–328.
- Begg, F.H., Cook, G.T., Baxter, M.S., Scott, E.M., McCartney, M., 1992. Anthropogenic radiocarbon in the eastern Irish Sea and Scottish coastal waters. *Radiocarbon* 34 (3), 704–716.
- BNFL, 1985–1989. Annual Report on Radioactive Discharges and Monitoring of the Environment. British Nuclear Fuels plc. Risley.
- BNFL, 2002. Discharges and Monitoring of the Environment in the UK—Annual Report 2001. British Nuclear Fuels plc. Risley.
- Cook, G.T., MacKenzie, A.B., McDonald, P., Jones, S.R., 1997. Remobilisation of Sellafield derived radionuclides and transport from the north-east Irish Sea. *J. Environ. Radioact.* 35, 227–241.
- Cook, G.T., MacKenzie, A.B., Naysmith, P., Anderson, R., 1998. Natural and anthropogenic  $^{14}\text{C}$  in the UK coastal marine environment. *J. Environ. Radioact.* 40, 89–111.
- Cook, G.T., Scott, E., Mackenzie, A.B., Naysmith, F., Isogai, K., Kershaw, P., Anderson, R., Naysmith, P., 2004a. Reconstructing the history of  $^{14}\text{C}$  discharges from Sellafield Part 2. Aquatic discharges. *J. Radioanal. Nucl. Chem.* 260, 239–247.
- Cook, G.T., Mackenzie, A.B., Muir, G.K.P., Mackie, G., Gulliver, P., 2004b. Sellafield-derived anthropogenic  $^{14}\text{C}$  in the marine intertidal environment of the NE Irish Sea. *Radiocarbon* 46, 877–883.
- Craig, H., 1957. Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. *Geochim. Cosmochim. Acta* 12, 133–149.
- Dabrowski, T., Hartnett, M., 2008. Modelling travel and residence times in the eastern Irish Sea. *Mar. Pollut. Bull.* 57, 41–46.
- Dabrowski, T., Hartnett, M., Olbert, A.I., 2010. Influence of seasonal circulation on flushing of the Irish Sea. *Mar. Pollut. Bull.* 60, 748–758.
- Davies, A.M., Hall, P., Howarth, M.J., Knight, P., 2002. Modelling and measuring the wind forced inflow to the Irish Sea through the North Channel. *Cont. Shelf Res.* 22, 749–777.
- Dunster, H.J., 1998. An historical perspective of radioactive effluents: discharges from Sellafield to the Irish Sea. *Radiat. Prot. Dosim.* 75, 15–21.
- Gillikin, D.P., Dehairs, F., Lorrain, A., Steenmans, D., Baeyens, W., André, L., 2006. Barium uptake into the shells of the common mussel (*Mytilus edulis*) and the potential for estuarine paleo-chemistry reconstruction. *Geochim. Cosmochim. Acta* 70 (2), 395–407.
- Gray, J., Jones, S., Smith, A., 1995. Discharges to the environment from the Sellafield site, 1951–1992. *J. Radiol. Prot.* 15, 99–131.
- Gulliver, P., Cook, G.T., MacKenzie, A.B., Naysmith, P., Anderson, R., 2001. Transport of Sellafield-derived  $^{14}\text{C}$  from the Irish Sea through the North Channel. *Radiocarbon* 43 (2B), 869–877.
- Gulliver, P., Cook, G.T., MacKenzie, A.B., Naysmith, P., Anderson, R., 2004. Sources of anthropogenic  $^{14}\text{C}$  to the North Sea. *Radiocarbon* 46, 869–875.
- Hill, A., Simpson, J., 1988. Low-frequency variability of the Scottish coastal current induced by along-shore pressure gradients. *Estuarine, Coast. Shelf Sci.* 27, 163–180.
- Isogai, K., Cook, G.T., Anderson, R., 2002. Reconstructing the history of  $^{14}\text{C}$  discharges from Sellafield: part 1—atmospheric discharges. *J. Environ. Radioact.* 59, 207–222.
- Keith, M.L., Anderson, G.M., Eichler, R., 1964. Carbon and oxygen isotopic composition of mollusk shells from marine and fresh-water environments. *Geochim. Cosmochim. Acta* 28, 1757–1786.
- Kirby, R., Parker, W.R., Pentreath, R.J., Lovett, M.B., 1983. Sedimentation Studies Relevant to Low-level Radioactive Effluent Dispersal in the Irish Sea. Part III. An Evaluation of Possible Mechanisms for the Incorporation of Radionuclides into Marine Sediments. Institute of Oceanographic Sciences, p. 66. Report, No. 178.
- Lalli, C.M., Parsons, T.R., 1993. In: *Biological Oceanography: an Introduction*. Pergamon Press, Oxford, pp. 52–79.
- MacKenzie, A.B., Cook, G.T., McDonald, P., 1999. Radionuclide distributions and particle size associations in Irish Sea surface sediments: implications for actinide dispersion. *J. Environ. Radioact.* 44, 273–296.
- MacKenzie, A.B., Cook, G.T., McDonald, P., Jones, S.R., 1998. The influence of mixing timescales and re-dissolution processes on the distribution of radionuclides in north east Irish Sea sediments. *J. Environ. Radioact.* 39, 35–53.
- MacKenzie, A.B., Scott, R.D., Allan, R.L., Ben Shaban, Y.A., Cook, G.T., Pulford, I.D., 1994. Sediment radionuclide profiles: implications for mechanisms of Sellafield waste dispersal in the Irish Sea. *J. Environ. Radioact.* 23, 39–69.
- MacKenzie, A.B., Scott, R.D., Williams, T.M., 1987. Mechanisms for northward dispersion of Sellafield waste. *Nature* 239, 42–45.
- MAFF, 1992–1995. Radioactivity in Surface and Coastal Water of the British Isles, 1990–1994. Aquatic Environment monitoring report No. 29, 34, 38, 42, 45. Ministry of Agriculture, Fisheries and Food, Lowestoft.
- McCartney, M., Baxter, M.S., Scott, E.M., 1988. Carbon-14 discharges from the nuclear fuel cycle: 2. Local effects. *J. Environ. Radioact.* 8, 157–171.
- McConnaughey, T.A., Burdett, J., Whelan, J.F., Paull, C.K., 1997. Carbon isotopes in biological carbonates: respiration and photosynthesis. *Geochim. Cosmochim. Acta* 61 (3), 611–622.
- McDonald, P., Cook, G.T., Baxter, M.S., Thomson, J.C., 1990. Radionuclide transfer from Sellafield to south-west Scotland. *J. Environ. Radioact.* 12, 285–298.
- McKay, W.A., Baxter, M.S., Ellett, D.J., Meldrum, D.T., 1986. Radiocaesium and circulation patterns west of Scotland. *J. Environ. Radioact.* 4, 205–232.
- McNamara, N., McCartney, M., 1998. A new estimate of atmospheric  $^{14}\text{C}$  discharges from Sellafield. *J. Environ. Radioact.* 41, 1–10.
- Mook, W., van der Plicht, J., 1999. Reporting  $^{14}\text{C}$  activities and concentrations. *Radiocarbon* 41, 227–239.
- Muir, G.K.P., Cook, G.T., Tripney, B.G., Mackenzie, A.B., Stewart, H., Tierney, K.M., 2015. Temporal trend in the transfer of Sellafield-derived  $^{14}\text{C}$  into different size fractions of the carbonate component of NE Irish Sea sediment. *Radiocarbon* 57 (3), 347–354.
- Murthy, M., Naresh, J., Faldu, P., Rao, Y., 1987. Photosynthesis of *Ulva lactuca* at different tidal levels during submergence and emergence. *Funct. Ecol.* 1, 387–390.
- Naysmith, P., Cook, G.T., Freeman, S.P.H.T., Scott, E.M., Anderson, R., Xu, S., Dunbar, E., Muir, G.K.P., Dougans, A., Wilcken, K., Schnabel, C., Russell, N., Ascough, P.L., Maden, C., 2010.  $^{14}\text{C}$  AMS measurements at SUERC: Improving QA data from the 5 MV Tandem AMS and 250 kV SSAMS. *Radiocarbon* 52, 263–271.
- RIFE, 1996–2014. Radioactivity in Food and the Environment. Annual reports 1–19.
- Slota Jr., P.J., Jull, T., Linick, T.W., Toolin, L.J., 1987. Preparation of small samples for  $^{14}\text{C}$  accelerator targets by catalytic reduction of CO. *Radiocarbon* 29 (2), 303–306.
- Turrell, W., Henderson, E., 1990. Transport events within the Fair Isle current during the Autumn Circulation Experiment (ACE). *Estuar. Coast. Shelf Sci.* 31, 25–44.
- United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR, 2008. Report to the General Assembly, Annex B: Exposure of the Public and Workers of Various Sources of Radiation, vol. 1, p. 247.
- Wolstenholme, A., Cook, G.T., Mackenzie, A.B., Naysmith, P., Meadows, P.S., McDonald, P., 1998. The behaviour of Sellafield-derived  $^{14}\text{C}$  in the Northeast Irish Sea. *Radiocarbon* 40, 447–458.