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Sellafield-derived ^{14}C and ^{129}I in the UK West Coast Intertidal Environment

Helen Rose Kinch

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COLLEGE OF SCIENCE & ENGINEERING

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Abstract

The Sellafield nuclear fuel reprocessing plant, situated on the west coast of the UK, releases both liquid and airborne discharges of radionuclides to the environment. Liquid discharges from Sellafield have been shown to travel up the west coast of the UK and out of the Irish Sea. The focus of this study was to investigate two long-lived radionuclides, ^{14}C and ^{129}I. ^{14}C has a half-life of 5,730 years and is incorporated into the marine carbon cycle where it is readily bioavailable and thus becomes part of the entire food chain. It has a large impact on human populations as, in a global context, the collective dose from ^{14}C, integrated over 10,000 years, comprises about 25% of the collective dose from the complete nuclear fuel cycle. ^{129}I is of radiological importance as it is highly mobile and has a half-life of 15.7 million years. 95% of global anthropogenic ^{129}I is discharged from Sellafield and AREVA NC (La Hague). Recent studies have been undertaken to understand ^{14}C uptake by biota in the Irish Sea and west coast of Scotland but focussed on offshore samples while this study focussed on the intertidal environment.

The principle aims of this research were to improve our understanding of the distribution and geochemical behaviour of long-lived Sellafield-derived radionuclides, ^{14}C and ^{129}I, mainly in the organic carbon reservoir of a range of intertidal sites situated between the Irish Sea and the Firth of Lorne, NW Scotland. Specifically, this research has compared the ^{14}C in seaweeds collected from low tide and high tide areas of the intertidal environment, measured the ^{14}C in a range of intertidal biota and measured the ^{129}I in seawater.

The main findings of this research were that both ^{14}C and ^{129}I show approximately exponential decreases in activity in the intertidal environment of the west coast of the UK with increasing distance from the Sellafield site. The halving distance for the dispersion of ^{14}C was found to be between 68 km and 89 km while the halving distance for ^{129}I was 64 km. In addition, there is a higher ^{14}C activity in seaweed inhabiting the area of the intertidal environment near the low water mark when compared with seaweed inhabiting the area at the high water mark. It was also found that when seaweed samples from this study were compared to samples collected from 1988/1989, the ^{14}C activities had decreased, despite the fact that the aqueous discharges are now higher, although a large difference in ^{14}C activities was also observed in seaweed samples collected from the same site at different points in time throughout this study. All samples measured were found to have ^{14}C activities above the UK background value (249 ± 1 Bq kg^{-1} C) and that the organic fraction of biota had predominantly higher ^{14}C activities than the inorganic fraction.

When comparing the ^{14}C activity in biota collected from different sites; at Parton, the site closest to Sellafield, a pattern of decreasing activity was found in the biota as follows; seaweed > starfish > mussels > whelks > crabs > winkles ≈ limpets > sea anemones, whereas at Garlieston, the mid-range site, mussels had the highest activity and all other biota sampled were of similar ^{14}C activities while at Port Appin, the site furthest from Sellafield, there was no discernible difference between ^{14}C activities in biota. Finally, there appeared to be a relationship between diet and ^{14}C activity in biota, with biota with a similar diet having similar ^{14}C activities and similar ^{14}C activities between organisms and their food source.

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Chapter 1 – Introduction

1.1 Sellafield discharges through time

The Sellafield nuclear fuel reprocessing site, which is the largest nuclear complex in the UK, is situated in Cumbria on the Northwest coast of England (Figure 1-1) and releases liquid and airborne discharges of radionuclides to the environment. The Sellafield site (previously known as Windscale and Calder Works) was a nuclear facility for the military until the 1950s when ownership was transferred to the United Kingdom Atomic Energy Authority (UKAEA), after which it was developed into a facility for nuclear energy production and the reprocessing of nuclear waste (Jackson et al., 2000). Originally built to produce weapons grade plutonium, for which nuclear reactors were required, it later became the site of a prototype Advanced Gas Cooled Reactor. Calder Hall at Sellafield was the world's first commercial nuclear power station, and although its primary function was the production of weapons grade plutonium, it also provided power to the national grid. Irradiated fuel requires reprocessing to separate out the plutonium, and after plutonium production was no longer required, it was still necessary to reprocess waste accrued during the normal operation and maintenance of the reactors. Sellafield began planning to commercially reprocess waste in the 1970s and now contains "the largest inventory of untreated nuclear waste in the world" (https://www.gov.uk/government/organisations/sellafield-ltd/about#what-we-do).

Sellafield has a commercial reprocessing capacity of 2100 tonnes of irradiated fuel per year (World Nuclear Association, http://www.world-nuclear.org/information-library/country-profiles/countries-t-z/united-kingdom.aspx) and processes fuel from both the domestic and international markets. The highest risk waste dealt with at Sellafield is historic waste, fuel and sludge that has been held in storage ponds and silos and is now being reprocessed as on-site decommissioning occurs.

Figure 1-1: Map of the UK showing the Sellafield nuclear fuel reprocessing site (yellow star), La Hague nuclear fuel reprocessing site (purple star) and Bundoran, Donegal (green star) where the background samples were collected.

Since 1952, discharges of low level liquid waste have been released into the Irish Sea via two 2.5 km pipelines. Improvements to the reprocessing facilities, such as the building of the Site Ion Exchange Effluent Plant (SIXEP) in 1985 and the Enhanced Actinide Removal Plant (EARP) in 1995, are responsible for the decrease in some of the radionuclides dispersed into the Irish Sea (Gray et al., 1995). The SIXEP removes mainly ^{137}Cs and ^{90}Sr from storage pond water belonging to the old Magnox de-canning plants and the Fuel Handling Plant (FHP), by passing it through sand filters and clinoptilolite ion exchange columns (Gray et al., 1995). Plutonium and other actinide waste is reduced by the EARP through a two-stage process involving ferric hydroxide floc production followed by removal of the precipitate by ultrafiltration (Hildred et al., 2000). High level liquid waste is stored before being processed in the Waste Vitrification Plant where it is incorporated into a glass-like material. Medium level liquid waste is sent to the Medium Active Evaporator or Salt Evaporator before being stored, to allow time for radioactive decay, before being processed at the EARP. The Segregated Effluent Treatment Plant (SETP), which was built in 1994, also helps decrease radionuclides released to the Irish Sea, and it is at this location that the process liquors are stored and pH adjusted before release (Sellafield Ltd, 2016).

Figure 1-2 and Figure 1-3 show the discharge histories of ^{134}Cs, ^{137}Cs, Pu α, ^{241}Pu and ^{241}Am from the period that discharges began up until 2016. It can be seen from the graph that annual discharges peaked for most radionuclides during the 1970s until the early 1980s; this is not the case for ^{14}C as can be seen in Figure 1-4 below. Discharges increased as historic waste began to be reprocessed, causing an overall increase in releases to the environment due to the larger volume of material being reprocessed (McMahon et al., 2005). Studies such as MacKenzie et al. (1987) and more recently, Gulliver et al. (2001) have shown that liquid effluent released from the Sellafield pipelines disperses mainly in a northwards direction beyond the Irish Sea due to the direction of ocean currents and can be observed as far away as Norway and Sweden as is shown in Figure 1-5 (Gomez-Guzman et al., 2014). More recently, marine models have been implemented to study the transport and dispersion of ^{129}I and ^{99}Tc from Sellafield to the Arctic Ocean (Villa et al., 2015, Simonsen et al., 2017).

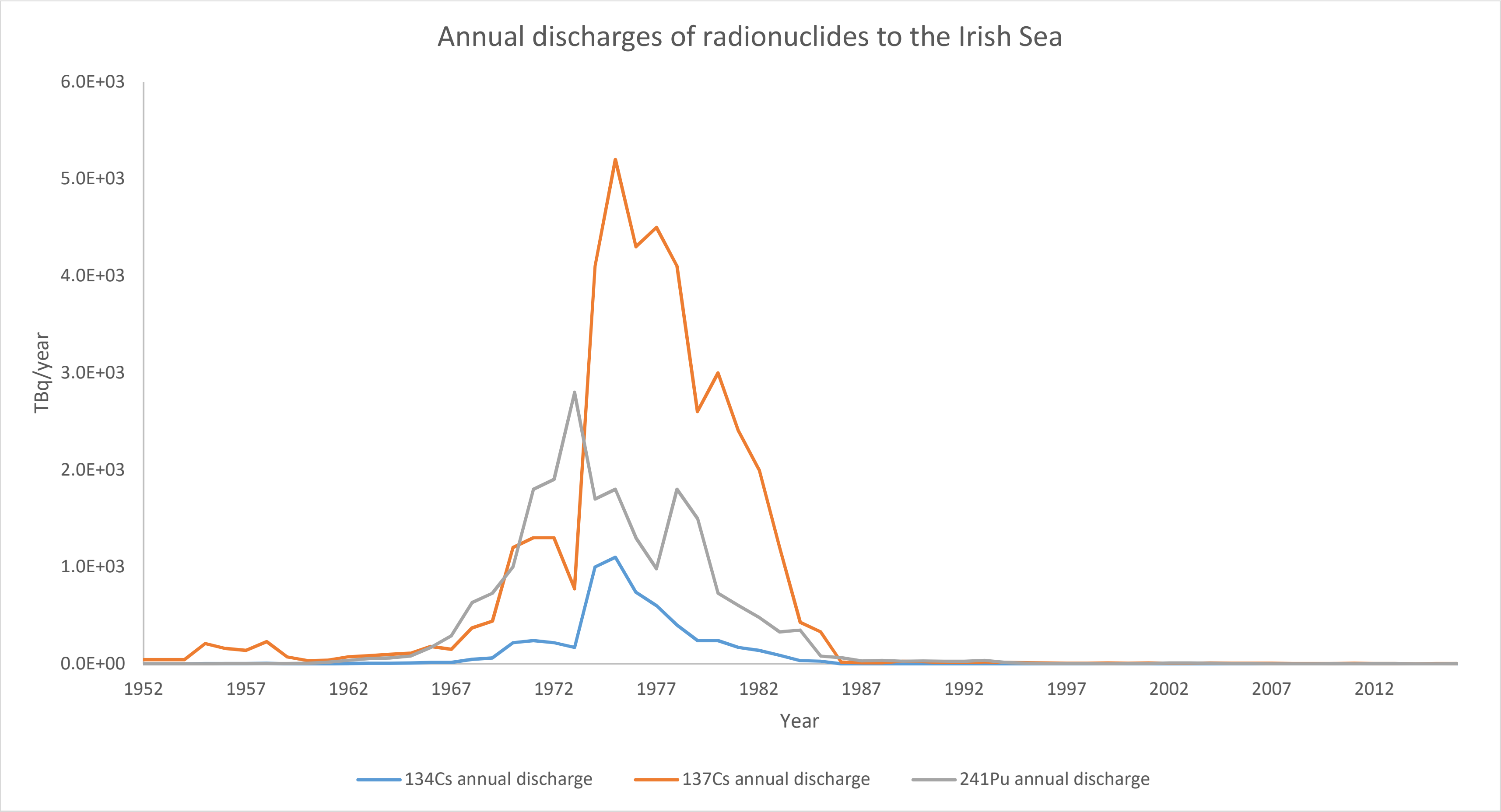
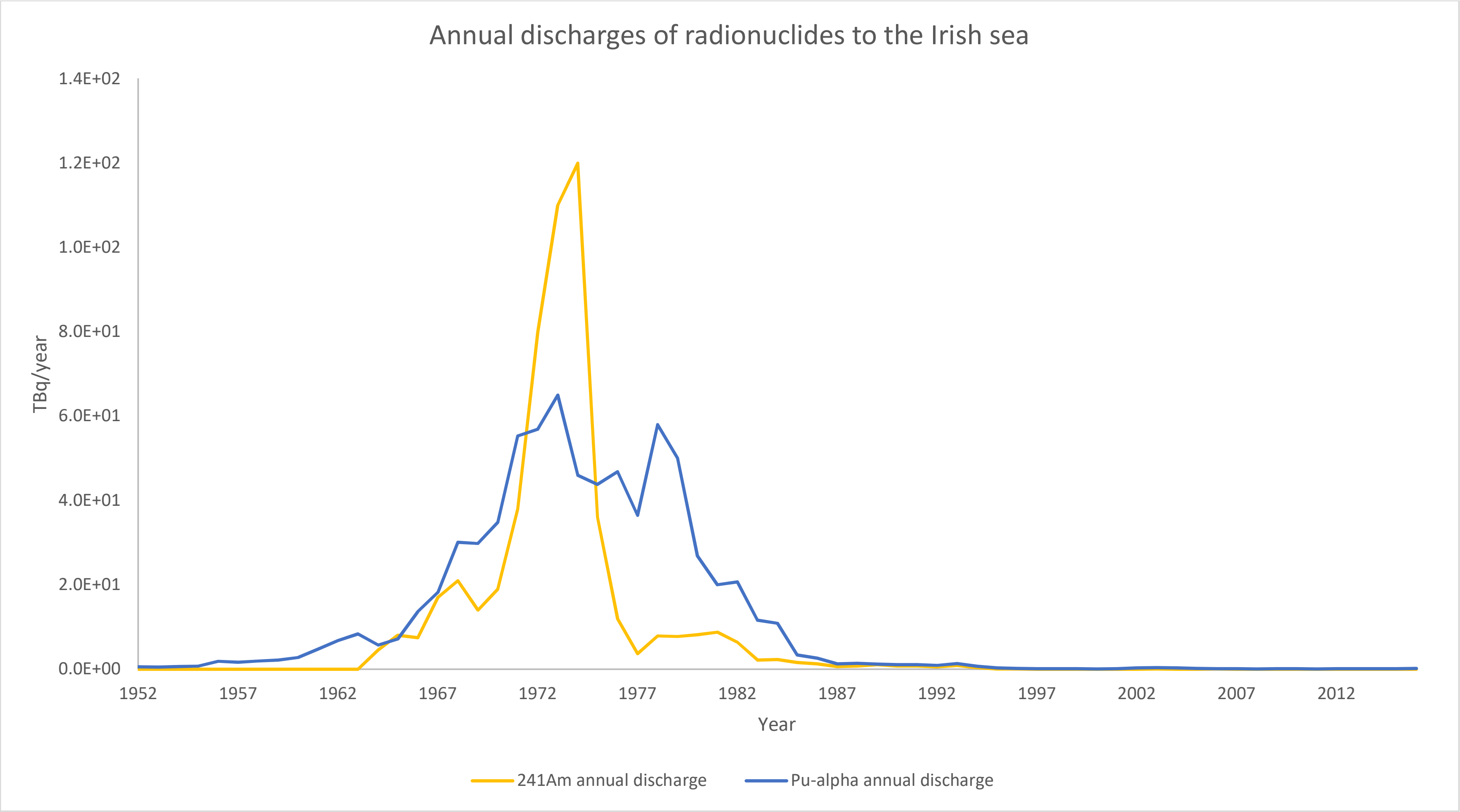


Figure 1-2: Annual discharges of ^{134}Cs, ^{137}Cs and ^{241}Pu to the Irish Sea from Sellafield between 1952 and 2016.



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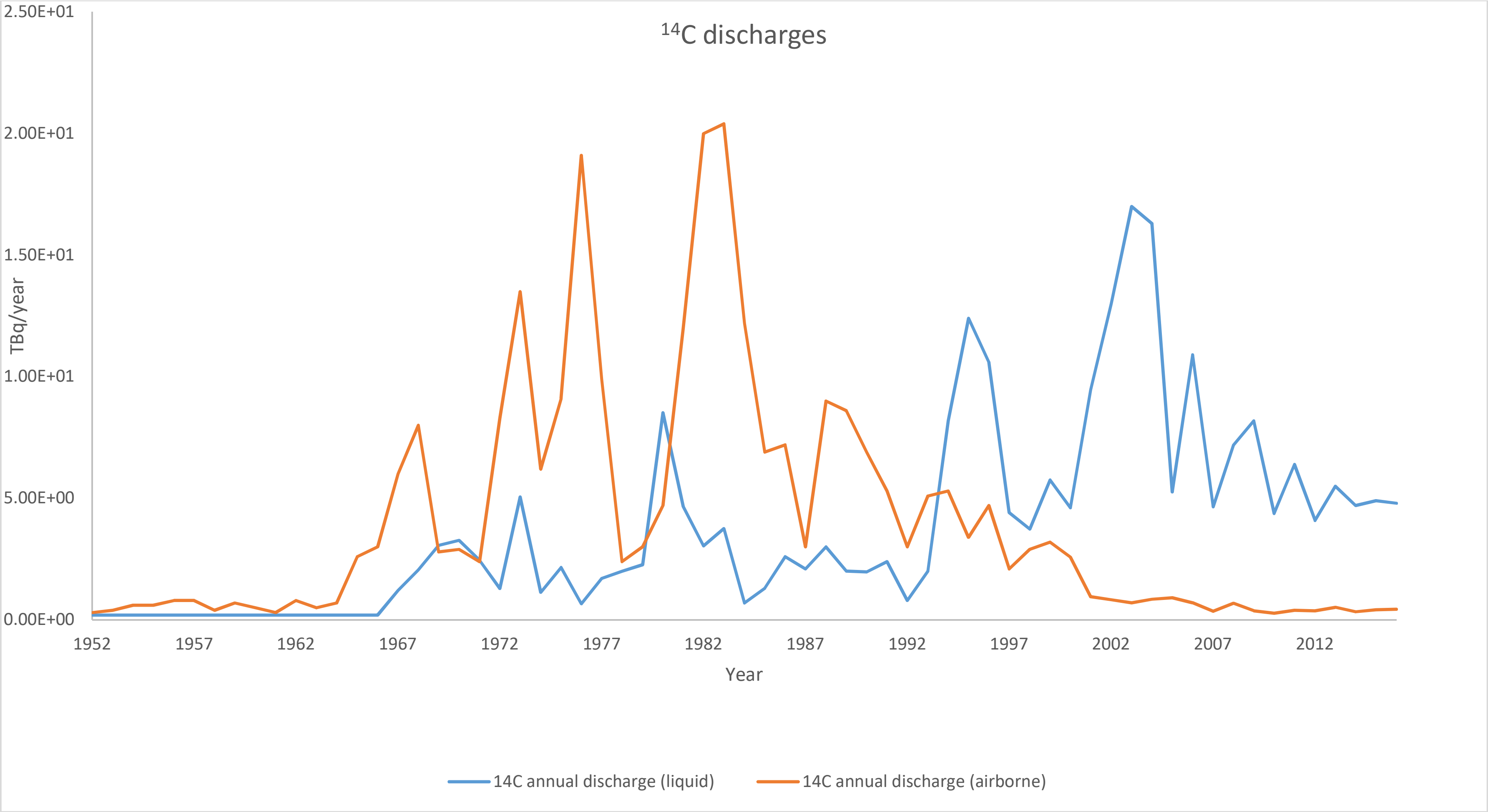

Figure 1-4: Airborne and liquid ^{14}C discharges from Sellafield between 1952 and 2016 (discharges between 1952 and 1985 are estimated (Muir et al., 2017)).

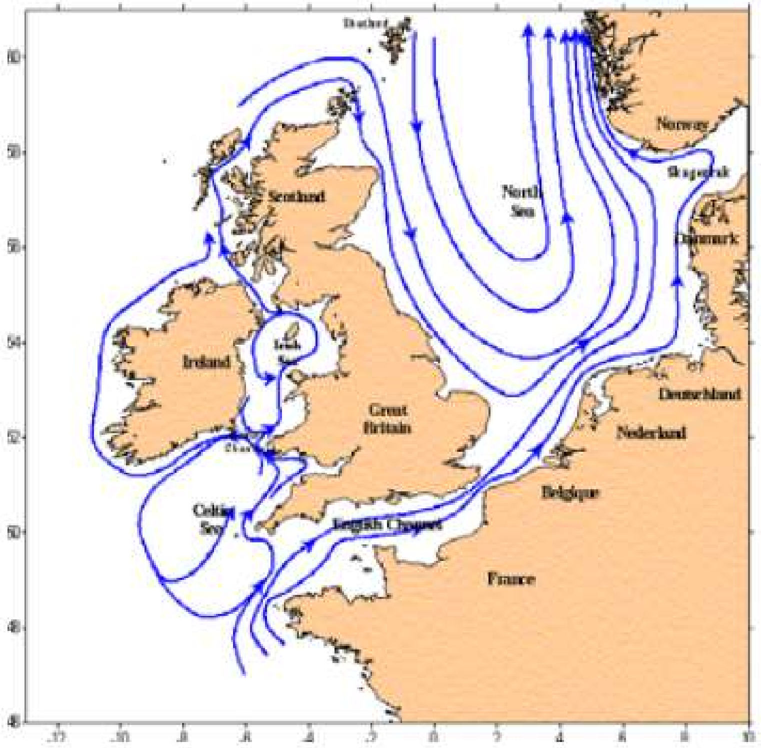

Figure 1-5: Map showing water circulation patterns around the UK (McMahon et al., 2005).

The intertidal sediment of the Irish Sea retains Sellafield discharges differently depending on both the chemistry of the radionuclides involved and the geochemistry of the sediment (MacKenzie et al., 1987, Hunt et al., 2013). Soluble radionuclides such as ^{90}Sr, ^{99}Tc and ^{137}Cs move in a north west direction, distributed by major currents in the Irish Sea and are dispersed to the north east coast of Ireland within a year, while less soluble particle-reactive radionuclides such as Pu and Am are largely bound to the fine sediments (McMahon et al., 2005). Although ^{137}Cs is highly soluble, some is retained in the sediment environment, while studies of Irish Sea sub-tidal sediments have also shown high concentrations of ^{99}Tc present in sediments. Currently, a major source of dissolved radionuclides in the Irish Sea is derived from the remobilisation of historic Sellafield discharges that were previously bound within the sediment and are now being released. In some cases, this is effectively doubling the effect of direct discharges (Hunt et al., 2013) and therefore, the legacy of Sellafield will have an impact on the environment long after discharge ceases.

MacKenzie et al. (1987,1999) and Muir et al. (2015b) identified areas around the Solway Firth in the Irish Sea where particle transport is dominant and thus higher concentrations of radionuclides from Sellafield can be found, compared to areas further north where solution transport becomes the dominant process.

The monitoring of liquid effluent releases from Sellafield has not always been as detailed as current standards require. In the past, few radionuclides were measured individually as it was not always possible within the scope of the techniques available at the time. More commonly, measurements would be taken for total alpha and total beta releases. To better our understanding of historic Sellafield discharges, models and environmental measurements have been utilised to improve the discharge records. Sediment cores, seaweeds and tree rings have all been used to assess radionuclide discharges to the environment (Gray et al., 1995, Fréchou and Calmet, 2003, Gomez-Guzman et al., 2014, Isogai et al., 2002, Cook et al., 2004b).

1.2 A summary of ^{14}C in the environment

^{14}C is a naturally occurring radionuclide with a half-life of 5,730 years. It is produced naturally in the upper atmosphere at a near constant rate by the absorption of neutrons by nitrogen. Neutrons are a product of cosmic ray interactions in the earth's atmosphere which, when absorbed by nitrogen, produce ^{14}C and a proton, ^{14}N (n,p)^{14}C. The ^{14}C is then oxidised to CO then CO_2. Under natural conditions, ^{14}C is in equilibrium in the atmosphere, with a natural level of F^{14}C = 1.0, but from 1890 until the early 1950s, the concentration was measurably diluted by the burning of fossil fuels, known as the Suess Effect, which releases ^{14}C-free CO_2 (Suess, 1955). By the mid-1950s, the effect on atmospheric ^{14}C was reversed by anthropogenic inputs of ^{14}C to the atmosphere from nuclear weapons testing, which resulted in levels of ^{14}C in the atmosphere that exceeded the concentration found before the burning of fossil fuels. Indeed, by 1963, the atmospheric activity was approximately double the pre-1890 activity. This can be seen in Figure 1-6 which shows the peak in ^{14}C, known as the 'bomb pulse', and how ^{14}C levels are returning to natural levels following the test ban treaty in 1963.

The concentration of ^{14}C in the atmosphere has also been increased by the contribution of releases of ^{14}C from the nuclear fuel cycle. Since the 1950s, nuclear weapons testing has been estimated to have released approximately 213 PBq of ^{14}C while nuclear facilities worldwide have released approximately 2.8 PBq of ^{14}C (UNSCEAR, 2000). Since the ban on above ground nuclear weapons testing in 1963, the nuclear fuel cycle has been the major source of anthropogenic ^{14}C, which is produced in the fuel, reactor coolant and core structural materials within nuclear reactors (Yim and Caron, 2006).

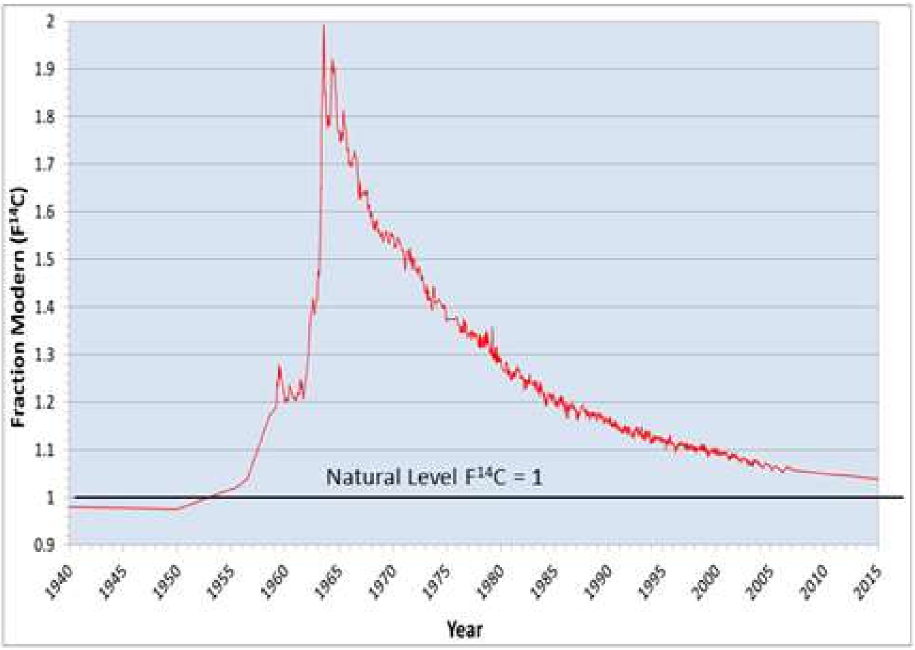

Figure 1-6: $F^{14}C$ values determined from atmospheric CO_2 and tree ring analysis (1940-2015), Northern Hemisphere Curve (NH1)(Hua et al., 2013).

Although the levels of ^{14}C discharged to the Irish Sea from Sellafield are much lower than those of other radionuclides (Figure 1-2, Figure 1-3), ^{14}C has an important impact on human populations. It has both a long half-life, is highly mobile in the natural environment and it is the largest contributor to collective doses in European and world populations (BNFL 2002).

^{14}C has been discharged by Sellafield both to the atmosphere and to the Irish Sea since 1952. But prior to 1978, atmospheric discharges were not recorded, and between 1978 and 1983 discharges were only measured from one of two comparable sources. Discharges prior to 1978 have only been estimated and discharges since 1978 have been re-evaluated using ^{14}C analysis of tree rings from a site close to Sellafield (Isogai et al., 2002). As the comparable natural ^{14}C value for each tree ring can be determined from measurements on trees remote from Sellafield, it is possible to measure the enhanced ^{14}C from Sellafield in each tree ring, which relates to the atmospheric concentration in the area (Gray et al., 1995, Isogai et al., 2002). Similar estimations have been made for aquatic discharges using annually collected seaweed in the place of tree rings (Cook et al., 2004b).

Gaseous discharges of ^{14}C have followed a broadly similar pattern to the radionuclides in Figure 1-2 and Figure 1-3, with discharges peaking in the 1970s and reducing to low levels in the 1990s. This is not the case for aquatic discharges which remained relatively constant until 1994, after which they increased, peaking in 2003 (Figure 1-4). This is in part due to a change in discharge policy which resulted in discharges previously released to atmosphere being redirected as liquid discharges, by the introduction of a gas scrubber, which reduces emissions, and also due to an increase in reprocessing (Cook et al., 2004a).

A study by Begg et al. (1992) looked at trends in ^{14}C uptake by biota along the west coast of the UK and found that the feeding behaviour and type of organism affected the uptake of ^{14}C from the environment. Samples from Begg, et al. (1992) were collected in 1988 and 1989 before the change in the ^{14}C disposal route. Immediately, this raises the question of how the change in disposal route has affected the activity of ^{14}C in biota at these sites. It would also be of benefit to update the data from that of the study by Begg, et al. (1992) to investigate if the same trends observed at the time of that study still hold true today.

1.3 A summary of ^{129}I in the environment

Iodine has 37 isotopes, including ^{127}I which is the only stable isotope and ^{129}I which has the longest half-life at 15.7 million years. More than 70% of the mobile iodine in the environment is found in the world's oceans. 90% of ^{129}I in the oceans is anthropogenic and 95% of the anthropogenic ^{129}I can be traced back to two European nuclear fuel reprocessing facilities, La Hague in France and Sellafield in the UK (He et al., 2013). ^{129}I is strongly conservative, meaning that it does not react with particles in its environment and therefore remains dissolved in seawater for a long time (Vivo-Vilches et al., 2018) and has also been shown to decrease in concentration rapidly with depth in the Pacific Ocean, with the highest concentrations being found in the surface (Kusuno et al., 2015).

Less than 10% of ^{129}I is naturally occurring, formed by cosmic ray interactions with xenon in the atmosphere and by the spontaneous fission of natural uranium isotopes (He et al., 2013). The anthropogenic sources of ^{129}I include atmospheric releases from nuclear weapons testing, fallout from nuclear reactor accidents and as a product of uranium and plutonium fission during nuclear power production. Most ^{129}I generated in nuclear power production is held in the spent fuel and only a small portion is released during fuel reprocessing (Hou et al., 2009).

^{129}I can be used as an environmental tracer to study water mass transport (Villa et al., 2015, Vivo-Vilches et al., 2018) and can be used to predict the source of radioactive contamination (Ezerinskis et al., 2016).

^{129}I is released from Sellafield as both liquid discharge into the Irish Sea and as atmospheric discharge but as can be seen from Figure 1-7, the discharges of liquid effluent have exceeded atmospheric releases since the mid-1960s and unlike other radionuclides (Figure 1-2 and Figure 1-3), the discharges have increased since the 1990s, with peak discharges in 2002. After a period of decreasing discharges, they are now beginning to increase again.

In a study by Fréchou and Calmet (2003), which analysed the environment around La Hague, after analysing 16 different species of seaweed it was recommended that *Fucus serratus* should be used for monitoring ^{129}I. *Fucus vesiculosus* has also been used as a bio-indicator in the study of ^{129}I in the marine environment (Gomez-Guzman et al., 2014) as *Fucus sp.* hyper-accumulate iodine.

Both ^{129}I activity and ^{129}I/^{127}I ratios are often measured as the ratio determines if the input of ^{129}I is anthropogenic in nature - pre-nuclear ratios have been estimated at between 10^{-12} to 10^{-10} (Fréchou and Calmet, 2003). Other studies have also published results as ^{129}I/^{127}I ratios (López-Gutiérrez et al., 2004, Atarashi-Andoh et al., 2007, Schnabel et al., 2007) but it is not possible to measure ^{127}I by AMS at this point in time as an ^{127}I carrier is added to the sample before it is measured.

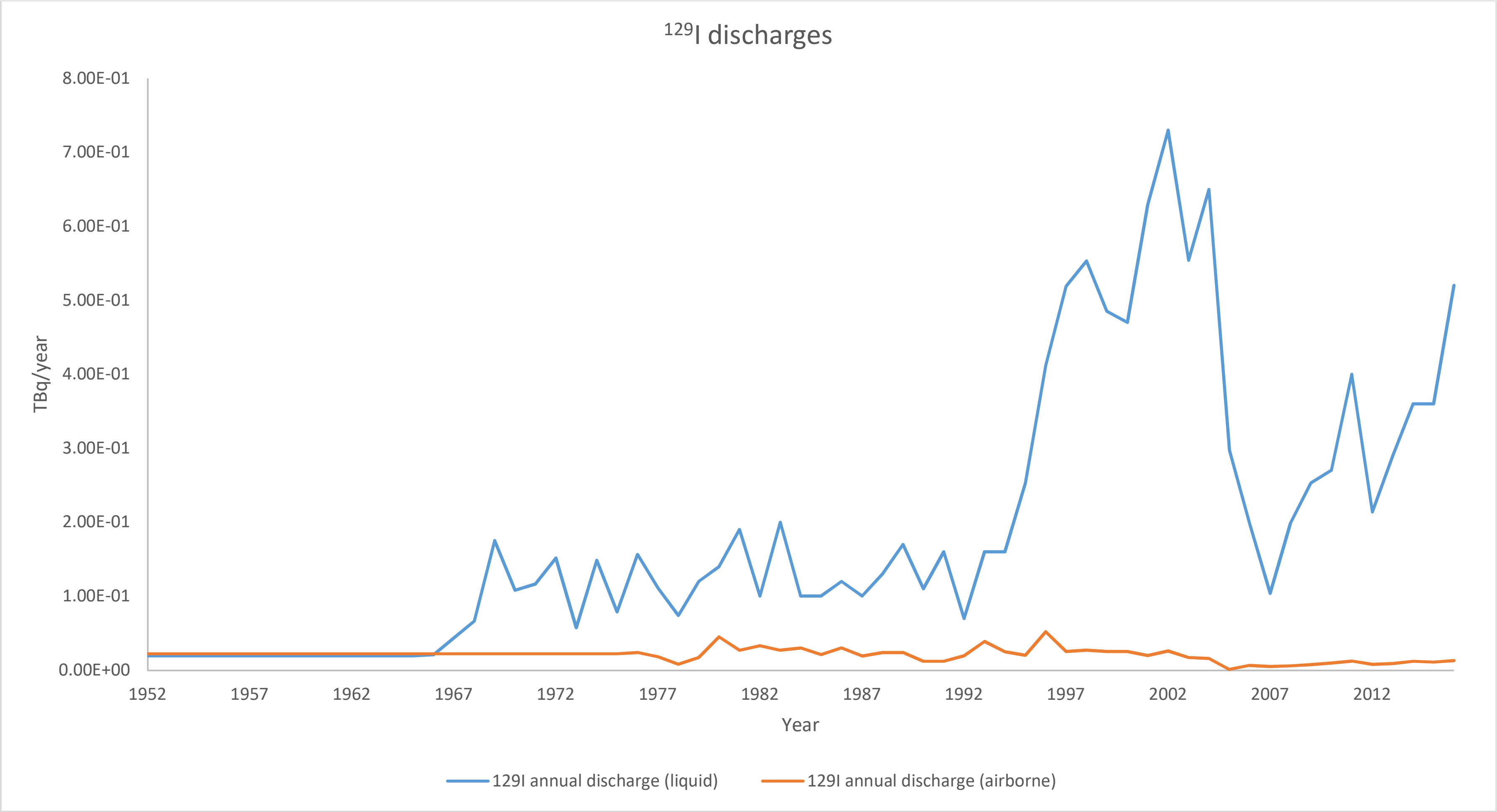

Figure 1-7: Airborne and liquid ^{129}I discharges from Sellafield between 1952 and 2016 (López-Gutiérrez et al., 2004) and Sellafield Ltd. Annual reports.

1.4 The intertidal environment

Several studies have looked at a variety of biota with different feeding habits, including species such as mussels (*Mytilus edulis*) which are filter feeders, winkles (*Littorina littorea*) and limpets (*Patella vulgate*) which are graze on algae, and seaweed (*Fucus sp.*) which is a primary producer (Begg et al., 1992, Cook et al., 1998, Cook et al., 2004a) to determine how these habits influence ^{14}C activities. These include studies of ^{14}C in the North Sea (Gulliver et al., 2004), the English Channel (Fievet et al., 2006), and the Irish Sea and West Coast of Scotland (Tierney et al., 2016).

Muir et al. (2015a) looked at enrichment of ^{14}C in biota and sediment at sites in the Hartlepool area on the east coast of the UK and measured ^{14}C in both biota flesh and shell material. They found that mussel/seaweed activity ratios measured at the site did not match the ratios of the enrichment in ^{14}C expected from Sellafield discharges which may imply the ^{14}C discharge at this site is organic as appose to the inorganic discharge from Sellafield. Although they were unable to determine the source of the enriched ^{14}C, the study is still a valuable contribution to the literature as it shows a relationship between different biota and ^{14}C enhancement. It was found that mussels had a higher ^{14}C activity than winkles, and these in turn had a higher activity than seaweed. This agrees with previous studies (Begg et al., 1992, Cook et al., 2004a) and will be compared to the current study being undertaken. In the Muir et al. paper, biota tissue was found to have a lower ^{14}C activity than the biota shell.

A second study by Muir et al. (2015b) contributed to the understanding of the long-term fate of ^{14}C-enriched biota shells from sites on the west coast of the UK. By measuring the ^{14}C activity in different size fractions of sediments, from whole shell and shell fragments through to <63 µm sized grains, we can better understand how the natural breakdown of enriched shells in the environment adds to the ^{14}C enhancement of sediment. It was found that all whole shell measured had enhanced ^{14}C activities while this was not the case for all smaller size fractions, which has implications for the distribution, transport and long-term fate of Sellafield ^{14}C discharges as particle size can influence transportation rates of sediments.

Tierney et al. (2016) measured ^{14}C in intertidal shells and sediments along the west coast of Scotland. While understanding the incorporation of ^{14}C into the inorganic fraction of biota is important, it leaves questions about the organic fraction of biota which the current study plans to address. Such as, what is the ^{14}C activity in these bioavailable food sources which can play a key role in the intertidal ecosystem? As the study by Muir et al. (2015b) showed, the inorganic fraction is important for future sediment activity but the organic fraction is the fraction accessible to organisms in higher trophic levels and so is more relevant to the understanding of ^{14}C cycling in the food web.

Although there have been several studies which have measured ^{129}I in seaweed (Fréchou and Calmet, 2003, Gomez-Guzman et al., 2014) and at least one that looked at fish (Kusuno et al., 2015) there has been much less research undertaken in understanding ^{129}I concentrations in marine biota and the transport of ^{129}I through the intertidal environment.

In conclusion, while there has been significant research of ^{14}C levels in the UK coastal environment there are still gaps in our knowledge that require further investigation, particularly in relation to bioavailability in the intertidal ecosystem. In comparison, ^{129}I is much less understood and further studies would be of benefit to the current research.

1.5 Aims and objectives

To address the need to better understand the long-term fate of nuclear waste. It is critical that it is known where it is in our environment and its potential long term fate.

Objectives

- To investigate suitable method to extract ^{129}I from biota and seawater samples
- To compare the ^{14}C and ^{129}I in seaweed collected from low tide and high tide areas of the intertidal environment
- To measure the ^{14}C in a range of intertidal biota
- To measure the ^{129}I in seawater and a range of intertidal biota
- To identify sites for independent in-depth study of biota
- To quantify ^{14}C in different carbon fractions of the biota

Aims

- To understand the fate of ^{14}C in the intertidal environment
- To understand the fate of ^{129}I in the intertidal environment
- To compare the behaviours of ^{14}C and ^{129}I

Chapter 2 – Methods

2.1 Sample sites

In the initial study, eleven sites were chosen on the west coast of the UK to undertake measurements on organisms from a range of intertidal environments at varying distances from the Sellafield reprocessing plant. These sites include those that MacKenzie et al. (1987) proposed were dominated by particle transport and sites dominated by solution transport, which have been investigated in previous studies (Begg et al., 1992, Cook et al., 1998, Gulliver et al., 2001, Cook et al., 2004a, Muir et al., 2015b).

The sites are shown in Figure 2-1 with Sellafield denoted by a star.

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Figure 2-1: Map of sampling sites on west coast of UK with Sellafield denoted with a star.

Duplicate samples of seawater were collected into pre-cleaned Pyrex bottles at each site. At the same time as water sampling samples of seaweed were collected from each site at approximately the high water and the low water regions of the intertidal area. Sampling was undertaken during the spring tide phase in the tidal cycle when there is the greatest difference between low and high water. Seawater samples were stored in cool, dark conditions in a refrigerator (~5°C) and filtered within 4 days of sampling while seaweed samples were frozen (-20°C) until they were processed.

During each sampling trip, a survey of biota at each site was carried out to select the most suitable sites for an in-depth ^{14}C study of biota.

On the 13th of February 2015, samples were collected from Ravenglass, Nethertown, Parton, Maryport and Allonby. At the Ravenglass site, it was only possible to collect high water seaweed as the tide was too far out and there was a possible danger associated with walking to the low tide mark. At Allonby, there was no seaweed present above the low water section of the site.

On the 27th of February 2015, samples were collected from Rockcliffe, Maidens, Garlieston and Killantringan Bay. Seawater samples were collected at each site and seaweed was collected from both the high water and low water areas.

On the 27th of March 2015, samples were collected from Dunstaffnage and Port Appin. Seawater samples were collected at each site and seaweed was collected from both the high water and low water areas.

Samples of seaweed were also collected on the 4th of June 2015 from Bundoran on the west coast of Ireland (Figure 1-1) to provide a background measurement. The intertidal environment of the west coast of Ireland should not have any influences from Sellafield as demonstrated previously (Cook et al., 1998).

Three sites were also selected for further study: Port Appin, Garlieston and Parton. A range of biota and seaweeds were collected from these sites (Table 2-1) to provide a better understanding of ^{14}C and ^{129}I transport through the food web. A photograph of the sampling site at Parton is shown in figure 2-2 which illustrates a range of biota found in close proximity to one another.

Site		Parton	Garlieston	Port Appin
Biota collected	Cockles			X
	Crab	X	X	X
	Limpet	X	X	X
	Mussel	X	X	
	Sea anemone	X	X	
	Starfish	X		
	Whelk	X		
	Winkle	X	X	X

Table 2-1: Summary information of biota sampled from Port Appin, Garlieston and Parton.

All samples were frozen on the same day they were collected to both preserve the samples and kill the organisms humanely.

Figure 2-2: Photograph taken from Parton showing typical intertidal environment containing limpets, sea anemones, winkles and seaweed.

2.2 Sample preparation

2.2.1 Seawater

Seawater samples were filtered through a NALGENE® Disposable Filter Unit (pore size 0.45 µm) which had previously been rinsed with deionised water three times. 250 ml of each seawater sample was filtered into sterile polystyrene bottles then sealed and 250 ml of unfiltered seawater was retained as a back-up sample until after the extraction of iodine. Both fractions of the seawater samples were stored in cool (approx. 5°C), dark conditions in a refrigerator.

2.2.2 Seaweed

Seaweed samples were defrosted, having been stored in a freezer (-20°C), and rinsed several times in tap water until no sediment or other contaminants remained, before two final rinses in deionised water (13.9 $M\Omega \cdot cm^{-1}$). The samples were then weighed and placed in a drying oven at 40°C for several days until the weight no longer decreased. The dry weight was recorded, and the sample was homogenised to a fine powder in a blender. The powdered samples were stored in vials until required.

2.2.3 Biota

For some of the samples it was possible to separate the organisms in to large and small subgroups where sufficient numbers had been collected. The determination of what was considered to be large varied from species to species: for cockles, an individual with an approximate length of 4 cm or greater; for limpets, an individual with an approximate length of 4.5 cm or greater; for mussels, an individual with an approximate length of 5 cm or greater and for winkles, an individual with an approximate length of 2cm or greater. Samples were defrosted and then rinsed in deionised water. For some species, such as limpets, it was necessary to separate the flesh of the organism from the shell. Bulk samples were prepared by combining multiple organisms which was necessary to produce a representative sample. Larger specimens were cut into small pieces while most were left whole. This was to reduce the time necessary to dry samples in the case of the larger specimens and aid the subsequent homogenisation process. The samples were then placed in clean vials, weighed and frozen (-20°C). Once frozen, the samples were placed in a freeze drier for up to a week until all moisture had been removed. The dried samples were then reweighed and homogenised in a blender to a fine powder. All samples were stored in cool (approx. 5°C), dark conditions in a refrigerator.

The shell material was sonicated for 30 minutes in deionised water to remove surface contaminants and then dried overnight at 40°C before being crushed using a pestle and mortar and weighed. The same individuals had their inorganic component homogenised as had their organic components homogenised previously, in order to provide totally equivalent samples.

2.3 Solvent extraction procedure for the separation of Iodine from seawater for ^{129}I measurement

The method employed was based on Xu et al. (2015)

2.3.1 Preparation of solutions

a. Woodward iodine (2 mg/ml): Weigh 0.4 g Woodward I_2 crystals. Add 4 ml of 0.4 M NaOH and 0.01 M $K_2S_2O_5$. Transfer to a 200 ml volumetric flask and make up to the mark with deionized water.

b. 3 M HNO_3: Add 50 ml of concentrated HNO_3 to a 200 ml bottle then slowly add 150 ml deionised water.

c. 1 M $NaNO_2$: Add 3.5 g of $NaNO_2$ to a beaker and add a small amount of water to dissolve it. Transfer to a 50 ml volumetric flask and make up to the mark with deionized water.

d. 1 M $K_2S_2O_5$: Add 11.1 g of $K_2S_2O_5$ to a beaker, add water to dissolve it. Transfer to a 50 ml volumetric flask and make up to the mark with deionised water.

e. 0.05 M $K_2S_2O_5$: Add 2.5 ml of 1.0 M $K_2S_2O_5$ solution to a 50 ml volumetric flask and make up to the mark with deionised water.

f. 0.5 M $AgNO_3$: Add 4.25 g of $AgNO_3$ to a beaker and add water to dissolve it. Transfer to a 50 ml volumetric flask and make up to the mark with deionised water.

2.3.2 Solvent extraction

a. Take 100 ml of filtered seawater for the separation of iodine.

b. To the sample, add 1.0 ml of about 2 mg/ml Woodward iodine, 1 ml of 1 M $K_2S_2O_5$ solution, and between 2-10 ml of 3 M HNO_3 to the above solution, until the pH is less than 2.

c. Transfer the solution to a suitable separating funnel (250 ml for 100 ml seawater samples), add 40 ml of $CHCl_3$ to the funnel, then add about 2.5 ml of 1 M $NaNO_2$ to the funnel. Invert the funnel several times to extract iodine (as I_2) to the $CHCl_3$ phase (pink colour), collect the $CHCl_3$ phase (lower phase) to a beaker. Repeat this step by adding 20-50 ml more $CHCl_3$ to the remaining water sample in the funnel and invert the separating funnel several times to extract. Combine the $CHCl_3$ phases and if the water phase is still pink in colour, one more repeat of the extraction is needed.

d. Transfer the $CHCl_3$ phase (pink) to a small separating funnel (100 ml), wash the beaker with 30 ml water and add this wash water to the $CHCl_3$ phase in the funnel. Add 0.2 ml of 0.05 M $K_2S_2O_5$ solution. Shake the funnel to back extract the iodine into the water phase (no colour in both phases). Run off the $CHCl_3$ phase (lower phase) to a waste bottle.

e. Add 15 ml of $CHCl_3$ and 0.5 ml of 3 M HNO_3 to the funnel, and then add 0.05-0.1 ml of 1 M $NaNO_2$ solution. Shake the funnel to extract iodine to $CHCl_3$ phase (pink colour), collect the $CHCl_3$ (lower phase) in a beaker. Add another 15 ml of $CHCl_3$ to the funnel, repeat the extraction. Combine the two $CHCl_3$ phases in the collection beaker.

f. Run off the water phase in the funnel to waste and wash the funnel. Transfer the $CHCl_3$ phase to the funnel. Add 4 ml of water then 0.2 ml of 0.05 M $K_2S_2O_5$ solution to the $CHCl_3$ phase in the funnel. Shake to back extract iodine to water phase. Collect the $CHCl_3$ phase in a beaker, leaving the $K_2S_2O_5$ solution in the funnel and put the $CHCl_3$ in a waste bottle.

g. Transfer the water phase to a 15 ml centrifuge tube. Wash the separating funnel with 1 ml water twice and add these washings to the centrifuge tube.

2.3.3 AgI precipitation

a. Add 1 ml of 3 M HNO_3 to the centrifuge tube (pH less than 2). If any colour appears, add 1-2 drops 0.05 M $K_2S_2O_5$, mix the solution using a plastic disposable pipette.

b. Add 1 ml of 0.5 M $AgNO_3$, bubble using the same pipette for aggregating the precipitate.

c. Centrifuge the precipitate at 2500-3000 rpm for 3 min.

d. Discard the supernatant using a pipette.

e. Add 2-3 ml 3 M HNO_3 to wash the precipitation that is broken up by gently bubbling using the pipette, add another 7-8 ml of 3 M HNO_3, bubble, and centrifuge again.

f. Wash the precipitate twice using deionised water until the pH is 7, using pH paper to measure the pH.

g. Transfer the precipitate to a 1.5 ml vial using a small amount of water and centrifuge it.

h. Take the supernatant (water phase) off again with a Pasteur pipette and leave the solid residue to dry at 70°C for 3 hours.

i. Weigh the precipitate.

2.4 ^{14}C and δ^{13}C analysis of seaweed and biota (organic)

The method employed was based on Dunbar et al. (2016)

a. Between 15 mg and 20 mg of dried, homogenised seaweed or biota were weighed into a pre-combusted quartz combustion tube containing 0.5g copper oxide and a small piece of silver foil, which was then sealed under vacuum and combusted overnight at 850°C. This converts the sample to CO_2.

b. The CO_2 was then cryogenically purified on a vacuum line; the quartz combustion tube was cracked under vacuum, releasing the gas which then passed through an ethanol/solid CO_2 slush trap (-80°C) (to trap water), followed by a liquid nitrogen trap (-196°C) which freezes down the CO_2.

c. The CO_2 was then expanded and measured in a calibrated finger and 3 ml was collected for graphitisation. A smaller volume of CO_2 (1 ml) was taken for δ^{13}C analysis and the remaining CO_2 was archived.

d. The sample of CO_2 collected for δ^{13}C analysis was measured on a VG SIRA 11 isotope ratio mass spectrometer. CO_2 from samples are compared to a working standard reference gas of a known isotopic composition produced from international reference materials NBS19 and IAEA-CO-1.

e. The 3 ml aliquot of CO_2 was graphitised using zinc/iron reduction under vacuum (Slota et al., 1987). 70 mg of zinc were heated at 450°C to convert the CO_2 to CO, then the CO was converted to C with 3 mg of iron at 550°C overnight.

f. The graphite was then pressed into an Al cathode and the ^{14}C measured on the AMS.

2.5 ^{14}C and $\delta^{13}C$ analysis of biota (inorganic)

The method employed is based on a modification of Dunbar et al. (2016)

a. 0.1g of shell material was weighed into a hydrolysis unit and attached to the vacuum line and pumped.

b. The hydrolysis unit was then isolated from the vacuum system and an excess of 1 M HCl was added to the shell material.

c. Once all the shell material had been dissolved, the CO_2 was cryogenically purified following steps b. to f. above (2.4 - ^{14}C and $\delta^{13}C$ analysis of seaweed and biota (organic)).

2.6 Alkali fusion for ^{129}I analysis in biota

Method (Gomez-Guzman et al., 2014)

a. 0.5 g of solid material was mixed with 5 mg of ^{127}I carrier solution (Woodward iodine with ratio $^{129}I/^{127}I \approx 7 \times 10^{-14}$) and 6 ml of a 30% KOH and 3% KNO_3 solution, in a crucible.

b. The crucible was placed in an oven at 90 °C and the solution evaporated to dryness.

c. The crucible was then covered and transferred to a preheated muffle furnace at 550 °C for 60 minutes.

d. The crucible was cooled to room temperature and the fused solid dissolved in deionized water.

e. The sample was treated to the same method (2.3 - Solvent extraction procedure for the separation of Iodine from seawater) as seawater samples without the addition of Woodward iodine in step b. as this had already been added.

2.7 AMS Measurement

2.7.1 ^{14}C

The graphite samples produced from the combustion of the seaweed and other biota, and from the hydrolysis of shell were measured on a NEC 5 MV accelerator mass spectrometer (Figure 2-3). The cathodes containing the pressed samples were loaded onto a 134 position carousel.

Each carousel of ^{14}C samples run on the AMS contains 130 samples arranged in 13 groups of 10. Within each group are 7 unknown-age samples and 3 quality assurance standards. The standards in a typical group are an oxalic acid II (NIST primary standard: SRM-4990C), a humic acid secondary standard (Table 2-2), and either a bulk barley mash standard (Table 2-2) or a background standard (Table 2-3). The humic acid, barley mash and background standards have been measured in international intercomparison exercises which generated consensus values and acted as a quality assurance exercise for laboratories. The laboratory standards and backgrounds have been part of the Third International Radiocarbon Intercomparison (TIRI), the Fifth International Radiocarbon Intercomparison (VIRI) and the Sixth International Radiocarbon Intercomparison (SIRI) (see Tables 2-2 and 2-3). The results from standards in batches containing samples from this study can be seen in Table 2-4. For a more detailed description of batch preparation see Dunbar et al. (2016).

The results obtained from the radiocarbon laboratory are received as fraction modern corrected for background, from which absolute activity in Bq g^{-1} C can be calculated. The results are de-normalized using the $^{13}\delta$, then the absolute activity in the year 1950 is calculated followed by the results being corrected to the year of sampling (Mook and van der Plicht, 1999).

		Consensus value ($F^{14}C$ ± 1σ or ^{14}C years BP ±1σ)	SUERC mean value ($F^{14}C$ ± 1σ or ^{14}C years BP ±1σ)
Barley Mash	TIRI sample A (2003)	1.1635 ± 0.0041	1.1653 ± 0.0056
Humic Acid	SIRI sample N (2015)	3370 ± 4 years BP	3367 ± 30 years BP

Table 2-2: Known age secondary standards – Consensus values vs.
SUERC radiocarbon laboratory batch values (2016).

		SUERC mean $F^{14}C$ value (± 1σ) 2016
Icelandic doublespar (carbonate)	TIRI sample F (2003)	0.0014 ± 0.0006
Heidelberg wood (Organic, non-bone)	VIRI sample K (2009)	0.0012 ± 0.0005
Mammoth bone	Latton Quarry LQH12 (MIS 7)	0.0034 ± 0.0013

Table 2-3: SUERC radiocarbon laboratory batch background values (2016).

Batch ID	Humic Acid (^{14}C years BP ± 1σ)	Barley Mash ($F^{14}C$ ± 1σ)	Background ($F^{14}C$ ± 1σ)
AMSEK2015 BatchEleven	3355 ± 26	1.1639 ± 0.0033	0.0008 ± 0.0002
AMSEK2015 BatchFourteen	3362 ± 26	1.1645 ± 0.0041	0.0012 ± 0.0003
AMSEK2015 BatchTwentysix	3380 ± 30	1.1669 ± 0.0095	0.0014 ± 0.0003
AMSEK2015 BatchThirtyeight	3367 ± 28	1.1677 ± 0.0033	0.0009 ± 0.0001
AMSEK2016 BatchThree	3351 ± 30	1.1662 ± 0.0031	0.0009 ± 0.0004
AMSEK2016 BatchFive	3370 ± 30	1.1566 ± 0.0125	0.0012 ± 0.0005
AMSEK2016 BatchTwelve	3359 ± 29	1.1715 ± 0.0064	0.0009 ± 0.0003
AMSEK2017 BatchOne	3346 ± 33	1.1698 ± 0.0047	0.0011 ± 0.0004

Table 2-4: Values for standards from batches containing samples from this study.

2.7.2 ^{129}I

The AgI samples produced from the extraction of iodine from seawater were measured on the NEC 5 MV accelerator mass spectrometer (Figure 2-3). Before the AgI was pressed into an Al cathode it was mixed with Ag powder at a ratio of 2:1 Ag:AgI. A relatively low current was used for the ion source due to the low melting point of AgI and samples were measured in sequence from low to high ^{129}I/^{127}I ratios to avoid any possible memory effects in the ion source. For the seawater samples the samples were measured starting with those from sites furthest from Sellafield and for the samples that had undergone alkali fusion the published values were used to determine the order they should be measured in. For a more detailed description of ^{129}I measurement on AMS see Xu et al. (2015).

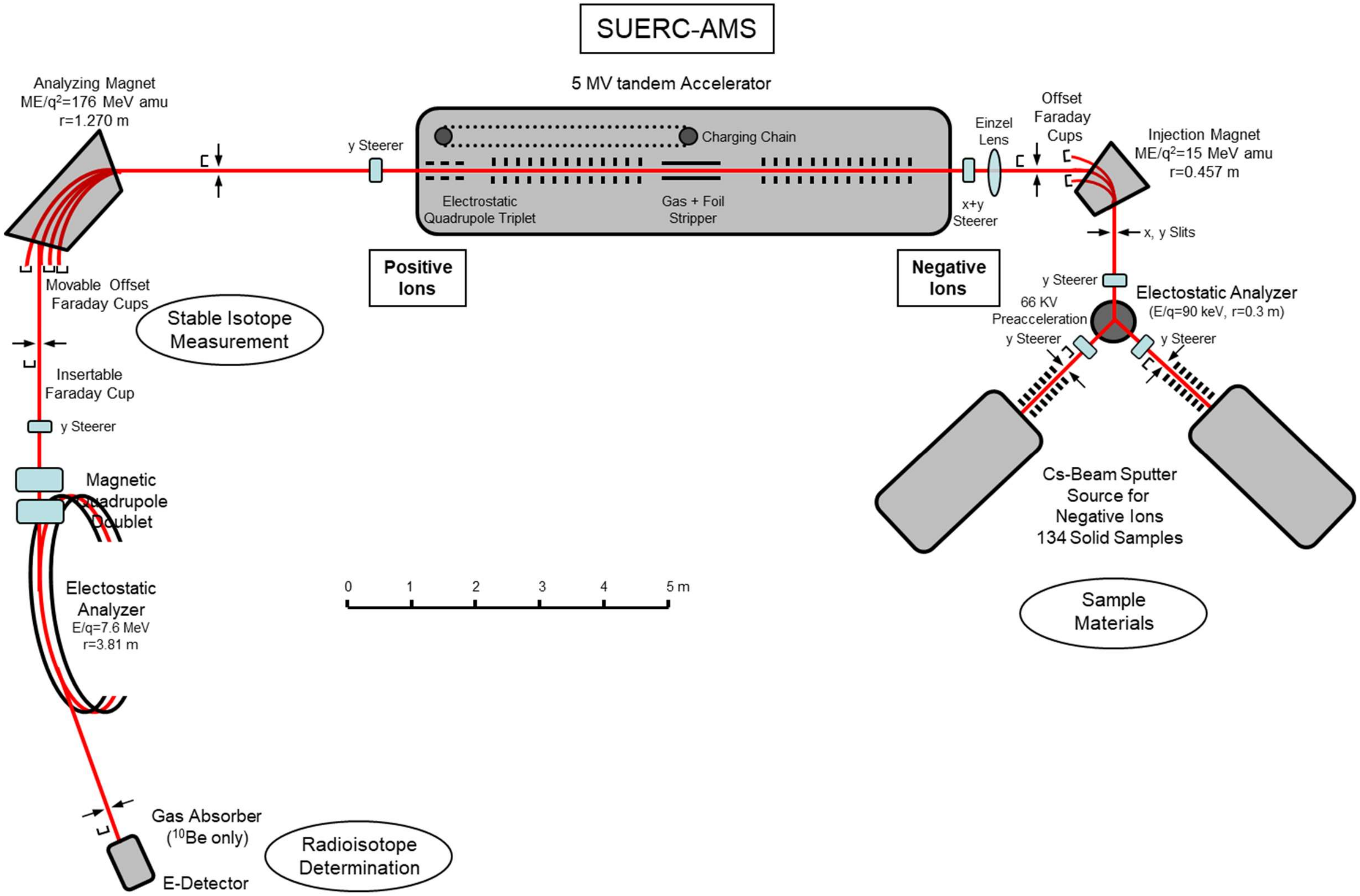

Figure 2-3: Diagram of the SUERC 5MV AMS.

Chapter 3 – Results

3.1 ^{14}C in Seaweed

Sample ID	**Site number**	**Site**	**Species**	**Specific activity (Bq kg^{-1} C ± 1σ)***
SUERC-59372	Site 0	Ravenglass	Bladderwrack (*Fucus sp.*)	470 ± 2
SUERC-59376	Site 1	Nethertown	Bladderwrack (*Fucus sp.*)	387 ± 2
SUERC-59378	Site 2	Parton	Bladderwrack (*Fucus sp.*)	339 ± 2
SUERC-59380	Site 3	Maryport	Bladderwrack (*Fucus sp.*)	315 ± 2
SUERC-59386	Site 5	Rockcliffe	Bladderwrack (*Fucus sp.*)	264 ± 1
SUERC-59390	Site 7	Garlieston	Bladderwrack (*Fucus sp.*)	255 ± 1
SUERC-59392	Site 8	Killantringan Bay	Bladderwrack (*Fucus sp.*)	243 ± 1
SUERC-59388	Site 6	Maidens	Bladderwrack (*Fucus sp.*)	248 ± 1
SUERC-60053	Site 9	Dunstaffnage	Bladderwrack (*Fucus sp.*)	237 ± 1
SUERC-60055	Site 10	Port Appin	Bladderwrack (*Fucus sp.*)	239 ± 1
SUERC-62386	*Site 11*	*Bundoran, Donegal †*	*Bladderwrack (Fucus sp.)*	*233 ± 1*

Table 3-1: Gross ^{14}C specific activities in seaweed samples collected from the high water mark of the intertidal environment, all sites (February 2015).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

† 'Background' site

The ^{14}C specific activity ranged from 470 Bq kg^{-1} C to 233 Bq kg^{-1} with a mean of 294 Bq kg^{-1} for the seaweed collected from the high-water mark.

Sample ID	**Site number**	**Site**	**Species**	**Specific activity (Bq kg^{-1} C ± 1σ)***
SUERC-59377	Site 1	Nethertown	Bladderwrack (*Fucus sp.*)	468 ± 2
SUERC-59379	Site 2	Parton	Bladderwrack (*Fucus sp.*)	388 ± 2
SUERC-59381	Site 3	Maryport	Bladderwrack (*Fucus sp.*)	303 ± 1
SUERC-59382	Site 4	Allonby	Bladderwrack (*Fucus sp.*)	277 ± 1
SUERC-59387	Site 5	Rockcliffe	Bladderwrack (*Fucus sp.*)	295 ± 1
SUERC-59391	Site 7	Garlieston	Bladderwrack (*Fucus sp.*)	314 ± 2
SUERC-59396	Site 8	Killantringan Bay	Bladderwrack (*Fucus sp.*)	261 ± 1
SUERC-59389	Site 6	Maidens	Bladderwrack (*Fucus sp.*)	253 ± 1
SUERC-60054	Site 9	Dunstaffnage	Bladderwrack (*Fucus sp.*)	244 ± 1
SUERC-60056	Site 10	Port Appin	Bladderwrack (*Fucus sp.*)	246 ± 1
SUERC-62387	*Site 11*	*Bundoran, Donegal †*	*Bladderwrack (Fucus sp.)*	*235 ± 1*

Table 3-2: Gross ^{14}C specific activities in seaweed samples collected from the low water mark of the intertidal environment, all sites (February 2015).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

† 'Background' site

It was not possible to collect a sample from the low tide area of the Ravenglass site as the tide as the intertidal area was treacherous.

At the Allonby site there was no live seaweed at the high water area on the beach.

The ^{14}C specific activity ranged from 468 Bq kg^{-1} C to 235 Bq kg^{-1} with a mean of 299 Bq kg^{-1} for the seaweed collected from the low water mark.

3.2 ^{14}C in Biota

3.2.1 Site 2 – Parton

Sample ID	Distance from water at low tide (m)	Species sampled	No. of organisms in each sample	Specific activity (Bq kg^{-1} C ± 1σ)*
SUERC-65298	20	Carrageen Moss (*Chondrus crispus*)	n/a	1237 ± 5
SUERC-65291	0	Carrageen Moss (*Chondrus crispus*)	n/a	1258 ± 5
SUERC-65320	20	Crab (*Carcinus maenas*)	4	979 ± 5
SUERC-65293	5	Kelp (*Laminaria digitate*)	n/a	1195 ± 5
SUERC-65299	15	Limpet (*Patella vulgata*) (Large)	8	874 ± 4
SUERC-65300	15	Limpet (*Patella vulgata*) (Large)	8	923 ± 4
SUERC-65309	25	Limpet (*Patella vulgata*) (Large)	5	860 ± 4
SUERC-65301	15	Limpet (*Patella vulgata*) (Small)	7	933 ± 4
SUERC-65310	25	Limpet (*Patella vulgata*) (Small)	7	722 ± 3
SUERC-65317	25	Mussel (*Mytilus edulis*)	9	975 ± 5
SUERC-65318	25	Mussel (*Mytilus edulis*)	9	1039 ± 5
SUERC-65307	15	Mussel (*Mytilus edulis*) (Large)	12	1028 ± 5
SUERC-65308	15	Mussel (*Mytilus edulis*) (Small)	17	1120 ± 5
SUERC-65302	15	Sea anemone (*Actinia equine*)	10	787 ± 4
SUERC-65311	25	Sea anemone (*Actinia equine*)	8	864 ± 4
SUERC-65292	5	Serrated Wrack (*Fucus serratus*)	n/a	1197 ± 5
SUERC-65321	20	Starfish (*Asterias rubens*)	2	1076 ± 4
SUERC-65297	15	Straggly Bush Weed (*Rhodomela confervoides*)	n/a	1262 ± 6
SUERC-65319	25	Whelk (*Nucella lapillus*)	11	1021 ± 5
SUERC-65303	15	Winkle (*Littorina littorea*)	10	974 ± 4
SUERC-65312	25	Winkle (*Littorina littorea*)	10	784 ± 4
SUERC-65313	25	Winkle (*Littorina littorea*)	10	844 ± 4

Table 3-3: Gross ^{14}C specific activities in the organic fraction of biota collected from Parton (August 2015) (large limpets ≥ 4.5 cm in diameter, large mussels ≥ 5 cm in length).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

Bulk sampling was required to get a representative sample. In some cases, due to the large volume of samples collected, samples were divided into two groups, resulting in two measurements. The limpets had a mean ^{14}C specific activity of 897 Bq kg^{-1}, the mussels had a mean ^{14}C specific activity of 1040 Bq kg^{-1} C, the sea anemones had a mean ^{14}C specific activity of 825 Bq kg^{-1} C and the winkles had a mean ^{14}C specific activity of 867 Bq kg^{-1} C.

Sample ID	**Distance from water at low tide (m)**	**Species sampled**	**No. of organisms in each sample**	**Specific activity (Bq kg^{-1} C ± 1σ)***
SUERC-66933	25	Mussel (*Mytilus edulis*)	9	1002 ± 4
SUERC-66934	25	Mussel (*Mytilus edulis*)	9	927 ± 3
SUERC-66929	15	Mussel (*Mytilus edulis*) (Large)	12	893 ± 3
SUERC-66930	15	Mussel (*Mytilus edulis*) (Small)	17	853 ± 3
SUERC-66935	25	Whelk (*Nucella lapillus*)	11	766 ± 3
SUERC-66928	15	Winkle (*Littorina littorea*)	10	900 ± 3
SUERC-66931	25	Winkle (*Littorina littorea*)	10	786 ± 3
SUERC-66932	25	Winkle (*Littorina littorea*)	10	837 ± 3

Table 3-4: Gross ^{14}C specific activities in the inorganic fraction of biota collected from Parton (August 2015) (large mussels ≥ 5 cm in length).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

Samples that had previously been measured for organic ^{14}C had the inorganic ^{14}C fraction measured. When the samples were prepared initially, the inorganic material was kept with the corresponding organic material so that the inorganic and organic activities are directly comparable. The mussels had a mean ^{14}C specific activity of 919 Bq kg^{-1} C and the winkles had a mean ^{14}C specific activity of 841 Bq kg^{-1} C.

Sample ID	**Distance from water at low tide (m)**	**Species sampled**	**No. of organisms in each sample**	**Specific activity (Bq kg^{-1} C ± 1σ)***
SUERC-71038	10	Limpet (*Patella vulgata*)	1	1054 ± 5
SUERC-71039	10	Limpet (*Patella vulgata*)	1	894 ± 4
SUERC-71040	10	Limpet (*Patella vulgata*)	1	908 ± 4
SUERC-71044	10	Limpet (*Patella vulgata*)	1	895 ± 4
SUERC-71045	10	Limpet (*Patella vulgata*)	1	889 ± 4
SUERC-71046	10	Limpet (*Patella vulgata*)	1	816 ± 4
SUERC-71047	10	Limpet (*Patella vulgata*)	1	882 ± 4
SUERC-71048	10	Limpet (*Patella vulgata*)	1	811 ± 3
SUERC-71037	5	Sea Lettuce (*Ulva compressa*)	n/a	949 ± 4
SUERC-71036	5	Serrated Wrack (*Fucus serratus*)	n/a	672 ± 3

Table 3-5: Gross specific activities of ^{14}C in the organic fraction of seaweed and individual limpets collected from Parton (September 2016).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

Eight limpets of similar size were collected in close proximity to one another to study variability between individual organisms. Two seaweed samples were collected to provide a comparison to conditions when biota were previously sampled at Parton. The ^{14}C specific activity in the limpets ranged from 1054 Bq kg^{-1} C to 811 Bq kg^{-1}. They had a mean specific activity of ^{14}C of 894 Bq kg^{-1} and a standard deviation of 70 Bq kg^{-1} C (approx. 8%).

3.2.2 Site 7 – Garlieston

Sample ID	Distance from water at low tide (m)	Species sampled	No. of organisms in each sample	Specific activity (Bq kg^{-1} C ± 1σ)*
SUERC-65689	200	Crab (*Carcinus maenas*)	4	358 ± 2
SUERC-65690	300	Limpet (*Patella vulgata*)	4	293 ± 2
SUERC-65700	500	Limpet (*Patella vulgata*)	3	314 ± 2
SUERC-65680	200	Limpet (Large) (*Patella vulgata*)	5	391 ± 2
SUERC-65681	200	Limpet (Small) (*Patella vulgata*)	6	349 ± 2
SUERC-65682	200	Mussel (*Mytilus edulis*)	6	489 ± 3
SUERC-65691	300	Mussel (*Mytilus edulis*)	11	426 ± 2
SUERC-65688	200	Sea anemone (*Actinia equine*)	7	409 ± 2
SUERC-65692	300	Sea anemone (*Actinia equine*)	5	325 ± 2
SUERC-65678	200	Sea lettuce (*Ulva Sp.*)	n/a	311 ± 2
SUERC-65686	200	Winkle (*Littorina littorea*)	11	384 ± 2
SUERC-65687	200	Winkle (*Littorina littorea*)	11	388 ± 2
SUERC-65696	300	Winkle (Large) (*Littorina littorea*)	22	363 ± 2
SUERC-65697	300	Winkle (Large) (*Littorina littorea*)	22	358 ± 2
SUERC-65698	300	Winkle (Small) (*Littorina littorea*)	24	355 ± 2
SUERC-65699	300	Winkle (Small) (*Littorina littorea*)	24	389 ± 2
SUERC-65677	15	Wrack (*Fucus sp.*)	n/a	363 ± 2
SUERC-65679	500	Wrack (*Fucus sp.*)	n/a	322 ± 2

Table 3-6: Gross specific ^{14}C activities in the organic fraction of biota collected from Garlieston (November 2015) (large limpets ≥ 4.5 cm in diameter, large winkles ≥ 2 cm in length).

* Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

In some cases, due to the large volume of samples collected, samples were divided into two groups resulting in two measurements. The limpets had a mean ^{14}C specific activity of 337 Bq kg^{-1}, the mussels had a mean ^{14}C specific activity of 457 Bq kg^{-1}, the sea anemones had a mean ^{14}C specific activity of 367 Bq kg^{-1} and the winkles had a mean ^{14}C specific activity of 373 Bq kg^{-1} C.

3.2.3 Site 10 – Port Appin

Sample ID	**Distance from water at low tide (m)**	**Species sampled**	**No. of organisms in each sample**	**Specific activity (Bq kg^{-1} C ± 1σ)***
SUERC-64666	10	Cockles (*Cardium edule*) (Large)	6	255 ± 1
SUERC-64667	10	Cockles (*Cardium edule*) (Small)	8	253 ± 1
SUERC-64665	10	Crab (*Carcinus maenas*)	4	247 ± 1
SUERC-64668	20	Crab *(Carcinus maenas*)	12	250 ± 1
SUERC-64670	20	Limpet (*Patella vulgata*)	7	259 ± 2
SUERC-64674	40	Limpet (*Patella vulgata*)	5	255 ± 2
SUERC-64675	40	Limpet (*Patella vulgata*)	5	255 ± 2
SUERC-64669	20	Winkle (*Littorina littorea*)	11	256 ± 1
SUERC-64676	40	Winkle (*Littorina littorea*) (Large)	11	257 ± 1
SUERC-64677	40	Winkle (*Littorina littorea*) (Small)	9	250 ± 1
SUERC-64660	10	Wrack (*Fucus sp.*)	n/a	247± 1
SUERC-64664	40	Wrack (*Fucus sp.*)	n/a	246 ± 1

Table 3-7: Gross ^{14}C specific activities in the organic fraction of biota collected from Port Appin (September 2015) (large cockles ≥ 4 cm in length, large winkles ≥ 2 cm in length).

*Activities include background ^{14}C derived from natural production and atmospheric nuclear weapons testing in the 1950s and early 1960s.

In some cases, due to the large volume of samples collected, samples were divided into two groups resulting in two measurements. The overall ^{14}C specific activity ranged from 259 Bq kg^{-1} C to 246 Bq kg^{-1}. The cockles had a mean ^{14}C specific activity of 254 Bq kg^{-1}, the crabs had a mean ^{14}C specific activity of 249 Bq kg^{-1}, the limpets had a mean ^{14}C specific activity of 256 Bq kg^{-1} and the winkles had a mean ^{14}C specific activity of 254 Bq kg^{-1} C.

3.3 ^{129}I in Seawater

Sample ID	Site number	Site	^{129}I concentration (Atoms kg^{-1} ± 1σ)
i902	Site 1	Nethertown	$2.75E^{+12} \pm 7.97E^{+8}$
i903	Site 1	Nethertown	$3.78E^{+12} \pm 6.22E^{+8}$
i900	Site 2	Parton	$2.69E^{+11} \pm 0.99E^{+8}$
i901	Site 2	Parton	$2.63E^{+11} \pm 0.60E^{+8}$
i898	Site 3	Maryport	$3.05E^{+11} \pm 0.96E^{+8}$
i899	Site 3	Maryport	$4.19E^{+11} \pm 0.80E^{+8}$
i896	Site 4	Allonby	$3.42E^{+11} \pm 1.00E^{+8}$
i897	Site 4	Allonby	$3.44E^{+11} \pm 0.39E^{+8}$
i894	Site 5	Rockcliffe	$2.89E^{+11} \pm 0.78E^{+8}$
i895	Site 5	Rockcliffe	$2.91E^{+11} \pm 1.00E^{+8}$
i890	Site 7	Garlieston	$1.74E^{+11} \pm 0.48E^{+8}$
i891	Site 7	Garlieston	$2.12E^{+11} \pm 0.57E^{+8}$
i888	Site 8	Killantringan Bay	$5.82E^{+10} \pm 0.14E^{+8}$
i889	Site 8	Killantringan Bay	$5.17E^{+10} \pm 0.12E^{+8}$
i886	Site 6	Maidens	$8.27E^{+10} \pm 0.29E^{+8}$
i887	Site 6	Maidens	$8.70E^{+10} \pm 0.18E^{+8}$
i884	Site 9	Dunstaffnage	$1.75E^{+10} \pm 0.05^{+8}$
i885	Site 9	Dunstaffnage	$1.93E^{+10} \pm 0.07^{+8}$
i882	Site 10	Port Appin	$2.01E^{+10} \pm 0.05E^{+8}$
i883	Site 10	Port Appin	$2.02E^{+10} \pm 0.07E^{+8}$

Table 3-8: ^{129}I concentrations in seawater collected in duplicate from the intertidal environment at all sites except Ravenglass (February 2015).

It was not possible to collect a water sample from site 0 – Ravenglass as the tide was too far out and sampling could have proven hazardous. At each of the other sites, two samples of seawater were collected from the same point to provide duplicate analyses. ^{129}I concentration ranged from $3.78E^{+12}$ atoms kg^{-1} to $1.75E^{+10}$ atoms kg^{-1}.

3.4 Alkali Fusion

Sample ID	**sample**	**sample type**	**^{129}I concentration, x 10^8 (Atoms g^{-1} ± 1σ)**	
			measured value	**published value**
i919	ZIL2	soil	7.01 ± 0.29	2.01 ± 0.05
i920	ZIL2	soil	7.37 ± 0.33	2.01 ± 0.05
i921	ZIL2	soil	5.76 ± 0.27	2.01 ± 0.05
i924	ZIL2	soil	8.14 ± 0.36	2.01 ± 0.05
i925	ZIL2	soil	8.67 ± 0.37	2.01 ± 0.05
i926	ZIL2	soil	6.32 ± 0.28	2.01 ± 0.05
i927	ZIL2	soil	6.45 ± 0.30	2.01 ± 0.05
i940	ZIL2	soil	7.24 ± 0.16	2.01 ± 0.05
i941	IAEA-375	soil	12.4 ± 0.26	12.10 ± 0.51
i944	SIL	Soil	52.3 ± 0.72	34.16 ± 0.56
i945	SIL	Soil	53.4 ± 0.73	34.16 ± 0.56
i946	IAEA-446	*Fucus sp.*	967 ± 11.41	714
				929

Table 3-9: ^{129}I concentration in a range of IAEA standards and Lithuanian soils (Ezerinskis et al., 2016).

A selection of soil samples in which the concentration of ^{129}I had previously been measured (Ezerinskis et al., 2016) were used as internal standards during method development. It is not possible to determine if the published values above are from a single measurement of each soil or from replicate measurements on a single sample. For soil sample ZIL2, a range of ^{129}I concentrations were measured from 5.76E^{+08} atoms g^{-1} to 8.67E^{+08} atoms g^{-1}, with a mean value of 7.12E^{+08} atoms g^{-1} and a standard deviation of 9.0E^{+07} atoms g^{-1}. The average measured values of ZIL2 were more than three times the published value and when other samples were measured, the concentration was always greater than the expected value. IAEA-446 has two published ^{129}I values as the measurement of ^{129}I has not been carried out sufficiently on either IAEA standard for there to be a consensus value (Pham et al., 2016).

Chapter 4 – Discussion

This chapter will discuss the results in relation to the aims of this study which are understanding the fate of ^{14}C and ^{129}I in the intertidal environment. This will be achieved by comparing ^{14}C in seaweeds at all sites, comparing the ^{14}C in a range of biota at three of the aforementioned sites and comparing the ^{129}I in seawater from all sites.

4.1 ^{14}C in Seaweed

There is a general trend of exponentially decreasing ^{14}C activity as the distance from Sellafield increases (Figure 4-1). Distances from Sellafield were measured approximately along the coast rather than 'as the crow flies' to give a more accurate value for distance travelled by liquid discharges. Garlieston, which is approximately 70 km from Sellafield, has a slightly higher activity for seaweed collected from the low water mark than would be expected from the general trend, but this may be due to its position in Wigtown Bay and the direction that the sea currents transport the liquid discharges from Sellafield. The high water seaweed at the Garlieston site shows a ^{14}C activity with a more expected fit to the general trend, and the difference between the high water and low water ^{14}C activity in seaweed is unusually large for this site. This could be due to the topography of the site as the beach is relatively flat at the low water mark but by the high water mark there are large rocks and a far more uneven surface which leads to water pooling in this area of the beach which would include rainwater as well as seawater, thus diluting the ^{14}C concentration. Another cause for the difference between high water and low water seaweed could be a stream that flows through Garlieston; this source of freshwater could dilute the sea water around the high water sample but would have less of an effect on the low water seaweed.

Samples show ^{14}C activity close to background levels by around 100 kilometres from the Sellafield site, although every sample in the set shows some degree of ^{14}C enhancement above background. The ^{14}C activities in seaweed above background represent only a small fraction of the ^{14}C released from Sellafield as Gulliver et al. (2001) have shown that close to 100% of the ^{14}C discharged from Sellafield leaves the Irish Sea via the process of 'dilute and disperse'. The background value for seaweed was approximately 235 ± 1 Bq kg^{-1}, calculated from samples collected from Donegal on the west coast of Ireland, which had been shown in a previous study (Cook et al., 1998) to be relatively free of Sellafield discharges and other UK coastal influences, as the water around the coast is Atlantic in nature. A higher background value of 249 ± 1 Bq kg^{-1} has been observed when measuring mussel shell from the west coast of Ireland (Tierney et al., 2016) suggesting that background values vary slightly depending on species measured.

Another observable trend in the seaweed data is the higher ^{14}C activity observed in the vast majority of low water seaweed when compared to the high water seaweed collected from the same site (Figure 4-2). This trend was also observed at Parton in a study by Cook et al. (2004a). The difference is clearest between samples collected from sites closest to Sellafield which have the higher ^{14}C activities, although the trend is still present at sites further from Sellafield but is less noticeable. This higher activity in seaweed from the low tide area of the intertidal environment is most likely due to the seaweed in this area spending longer periods of time submerged in the seawater compared to the seaweed collected further up the beach. *Fucus* is able to photosynthesise both in the water and when exposed on the shoreline. While it is submerged, the *Fucus* uptakes dissolved inorganic carbon (DIC) which is the form in which most ^{14}C from Sellafield aqueous discharges are found (Keogh et al., 2011). While exposed, the *Fucus* can uptake CO_2 directly from the atmosphere, and a study by McCartney et al. (1988) has shown that the majority of atmospheric ^{14}C discharged from Sellafield has dispersed by 10 km, therefore the atmospheric CO_2 has a diluting effect on the ^{14}C activity in the seaweeds exposed to less seawater. The dilution effect is less noticeable at sites further from Sellafield as the atmospheric ^{14}C and seawater ^{14}C values become more similar to one another due to the decrease in ^{14}C in seawater as distance from Sellafield increases.

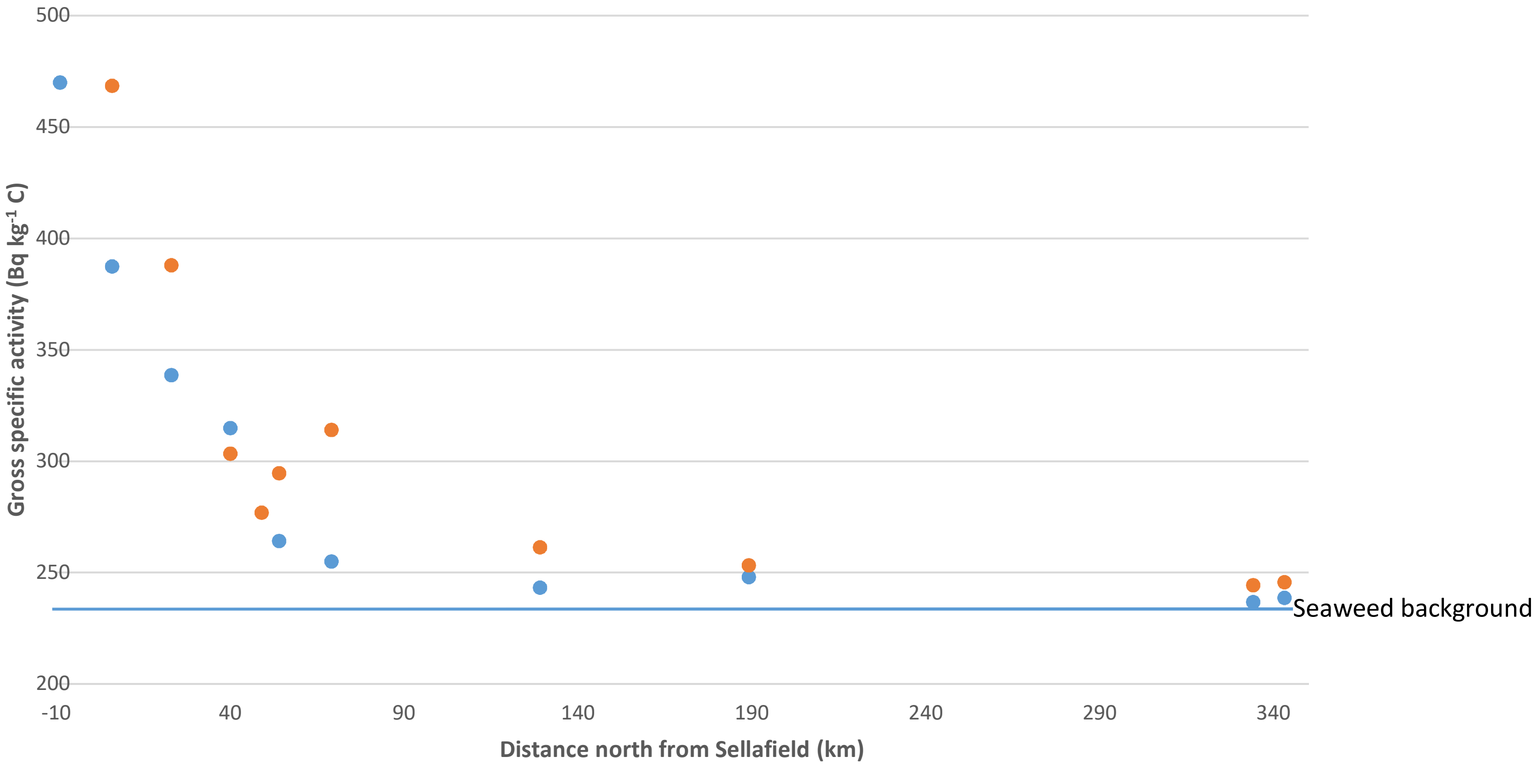

Figure 4-1: Gross specific activity of ^{14}C in seaweed collected at high and low water mark from 11 sites on the west coast of the UK, showing distance from Sellafield, error bars present but not visible due to small value (blue – high water mark, orange – low water).

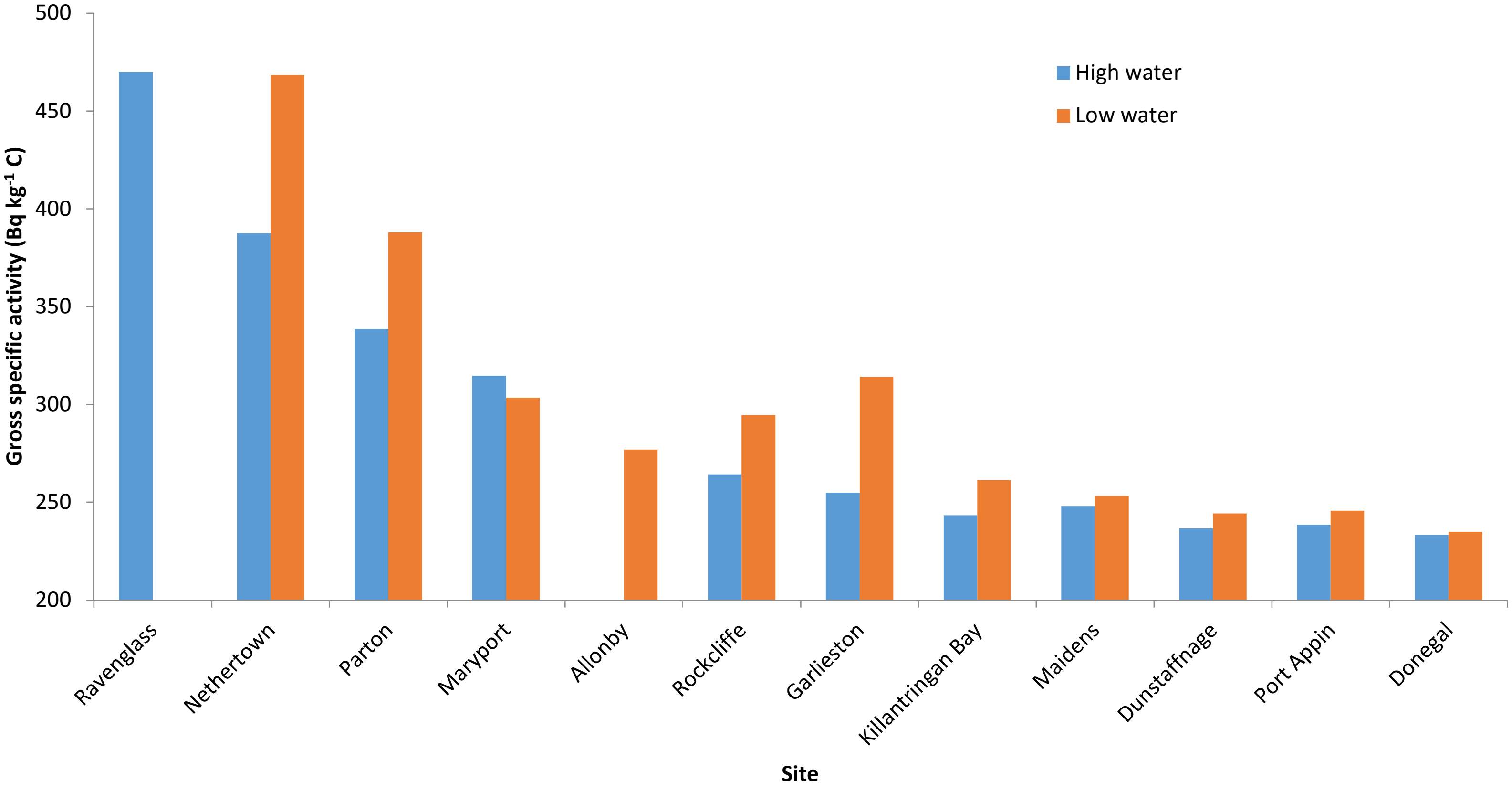

Figure 4-2: Gross specific activity of ^{14}C in seaweed from low water and high water collected from 12 sites on the west coast of the UK, error bars present but not visible due to small value.

As stated previously, close to 100% of the ^{14}C discharged from Sellafield is dispersed beyond the Irish Sea (Gulliver et al., 2001) therefore, the ^{14}C found in biota above ambient background level only accounts for a small fraction of the ^{14}C released from Sellafield. By using the ^{14}C activity in seaweed as a proxy for the ^{14}C activity in seawater it is possible to calculate the halving distance for the dilute and disperse mechanism. To calculate the halving distance, the natural log of the net specific activity (*i.e.* with natural background and nuclear weapons ^{14}C subtracted) of ^{14}C is plotted against the distance from Sellafield to determine the gradient of the line. For the seaweed collected from the high water mark (Figure 4-3) the halving distance for the general dispersion of ^{14}C from Sellafield can be calculated as follows:

$$\frac{ln2}{-0.0102} = \text{-68 km}$$

Equation 1 - halving distance for the general dispersion of ^{14}C from Sellafield (high water).

Whereas if the Ravenglass measurment is excluded from the high water seaweeds (Figure 4-4), as it is the only site south of Sellafield in this study, the halving distance for the northernly dispersion of ^{14}C from Sellafield can be calculated as follows:

$$\frac{ln2}{-0.0094} = \text{-77 km}$$

Equation 2 - halving distance for the northward dispersion of ^{14}C from Sellafield (high water).

From the net specific ^{14}C activity in seaweed collected from the low water mark (Figure 4-5) the halving distance of northward dispersion of ^{14}C from Sellafield is calculated as:

$$\frac{ln}{-0.0078} = \text{-89 km}$$

Equation 3 - halving distance of northward dispersion of ^{14}C from Sellafield (low water).

Finally, the natural log of the average of low and high water seaweed net specific activity of ^{14}C against distance from Sellafield (Figure 4-6) gives the halving distance of the general dispersion of Sellafield ^{14}C as:

$$\frac{ln}{-0.009} = -77 \text{ km}$$

Equation 4 - halving distance of the general dispersion of ^{14}C from Sellafield (average).

From Equations 1, 2, 3 and 4, the halving distance for the ^{14}C activity from Sellafield along the west coast of the UK due to dilution and dispersion is in the range of approximately 68 to 89 km with the value of 77 km, based on all data, most likely providing the best estimate.

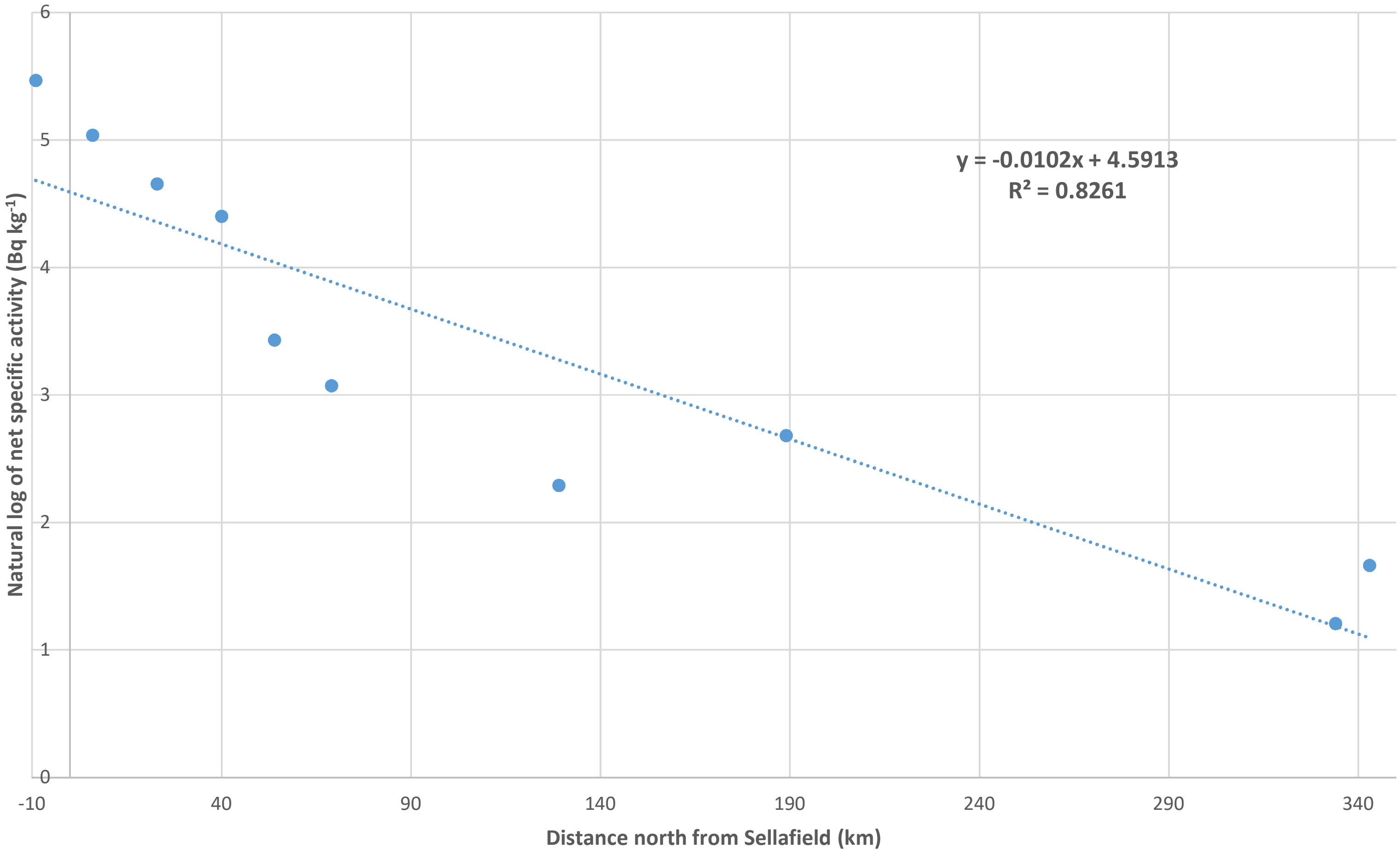

Figure 4-3: Natural log of net specific activity of ^{14}C in high water seaweeds against distance from Sellafield, including best fit equation of the line.

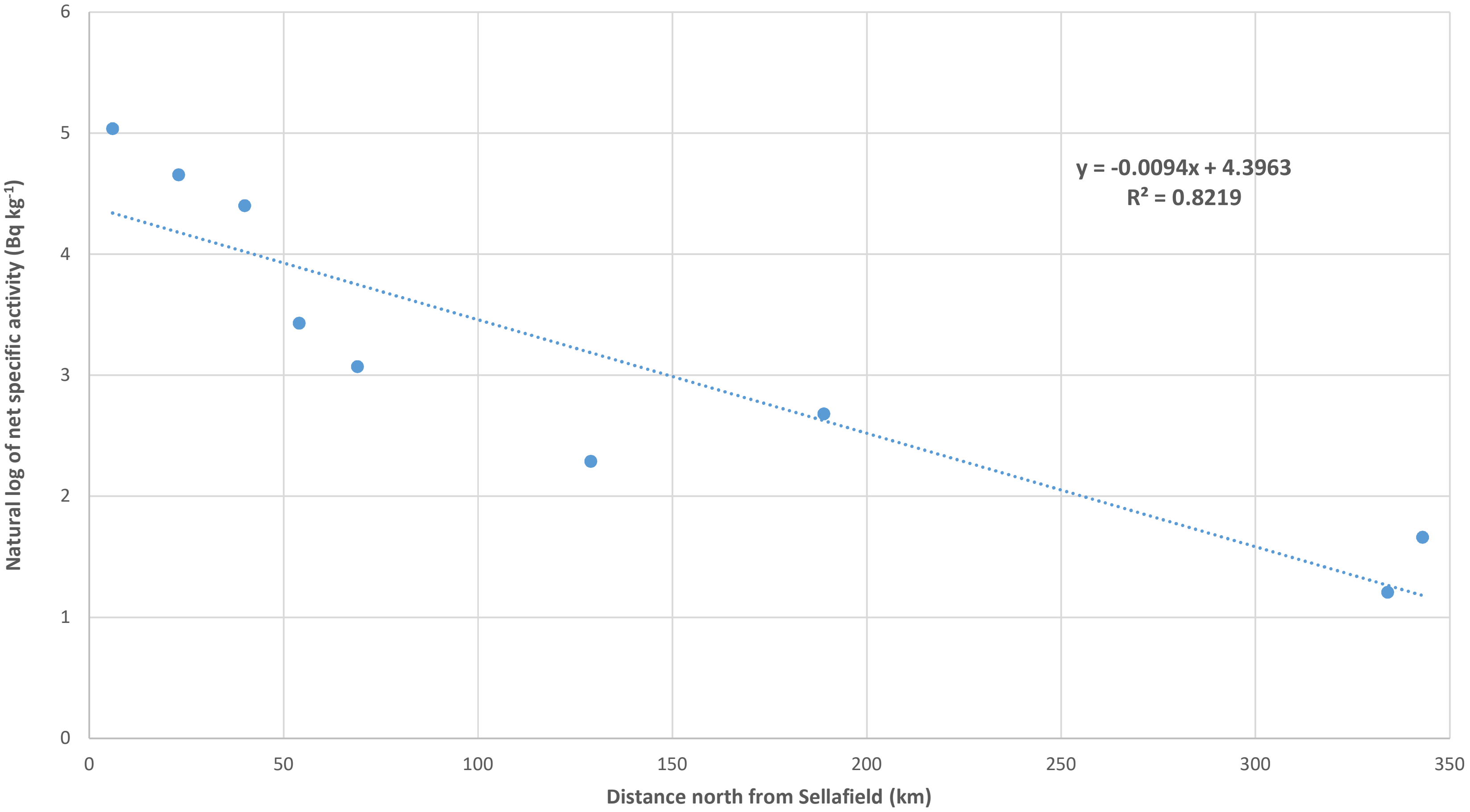

Figure 4-4: Natural log of net specific activity of ^{14}C in high water seaweeds north of Sellafield against distance from Sellafield, including best fit equation of the line.

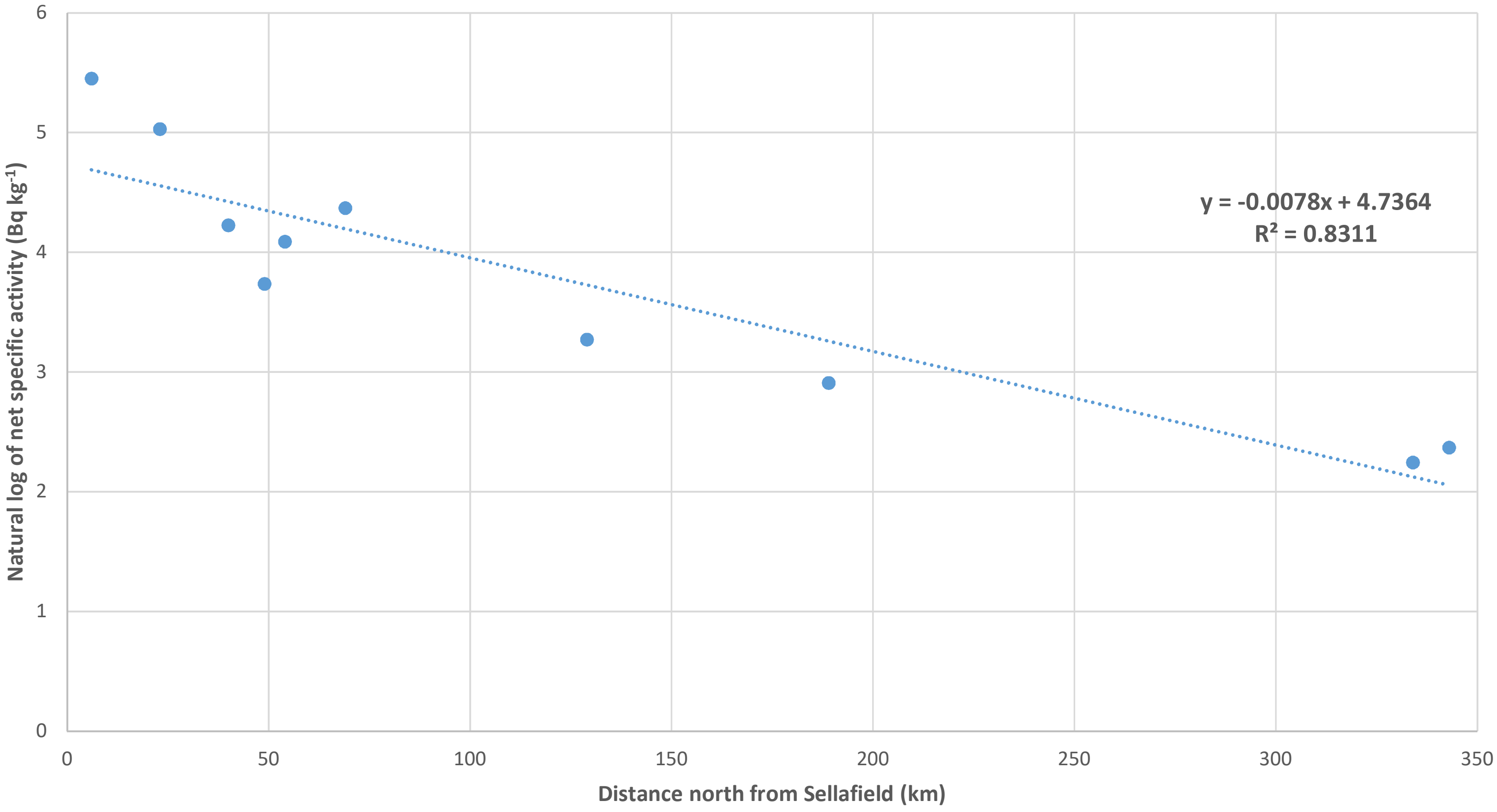

Figure 4-5: Natural log of net specific activity of ^{14}C in low water seaweeds against distance from Sellafield, including best fit equation of the line.

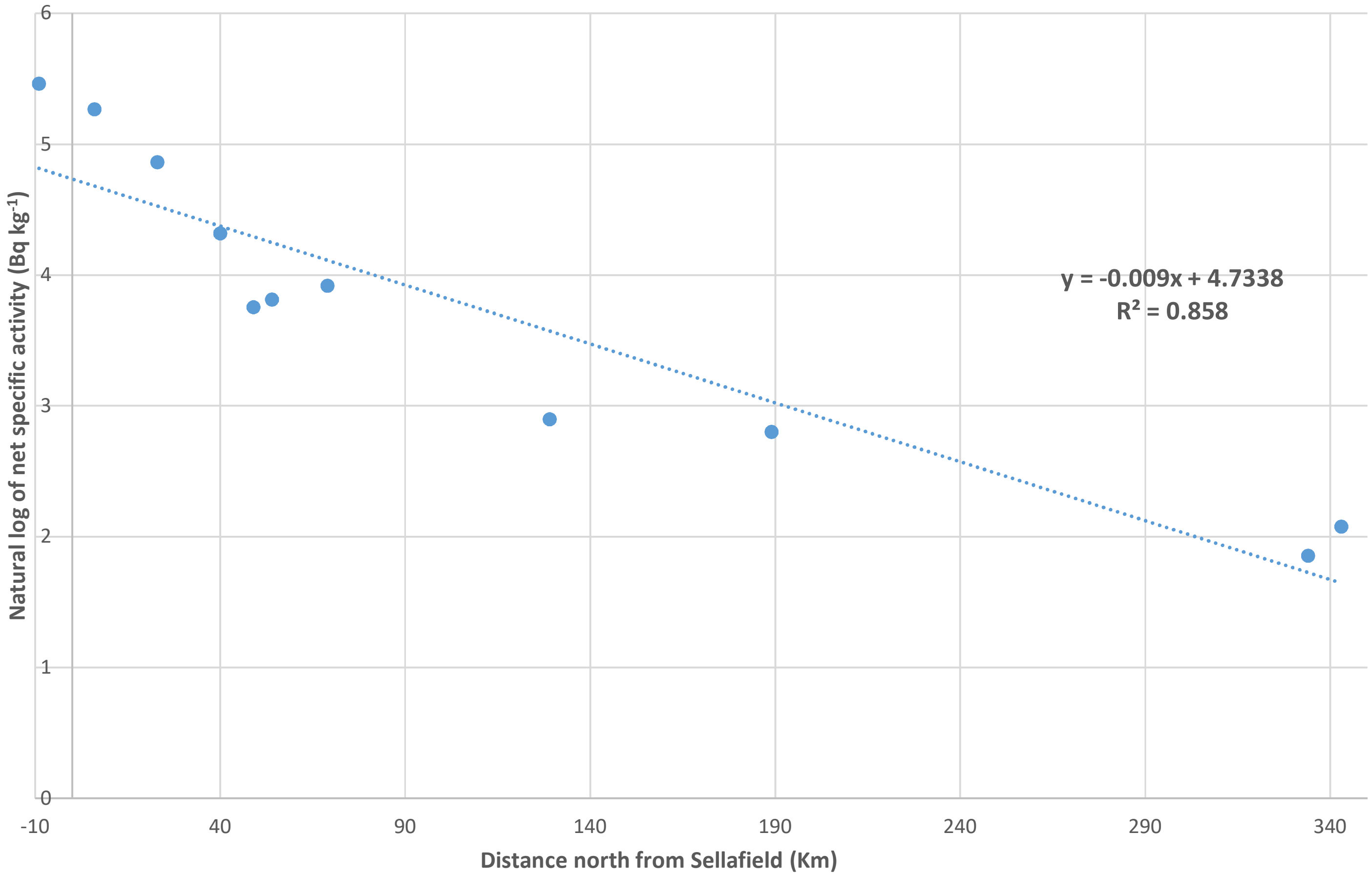

Figure 4-6: Natural log of average net specific activity of ^{14}C in high water and low water seaweeds against distance from Sellafield, including best fit equation of the line (includes sites with only one value).

Comparing the measurements of specific activity between *Fucus* collected in 2015 against *Fucus* collected in 1988/1989 (Begg et al., 1992) at four sites, we can see that the seaweeds from 1988/1989 have higher ^{14}C activities than the seaweeds from the present study (Figure 4-7). It was not possible to determine where in relation to the low water mark the seaweed from the Begg et al. (1992) study had been collected, therefore the results were compared to the average of the low water and high water results from this study, with the exception of Ravenglass where this was not possible.

The difference in ^{14}C activity in seaweed between the two sets of data (Figure 4-7) decreases as the sites increase in distance from the Sellafield site to the point that there is a barely perceivable difference between Rockcliffe samples. It should be noted that it was not possible to collect seaweed from the low tide area at Ravenglass for this study, therefore the difference in ^{14}C activities may be larger than would be otherwise expected between the two sets of data at this site. Liquid discharges of ^{14}C from Sellafield to the Irish Sea are greater now than they were in the 1980s (Figure 4-8), but atmospheric ^{14}C discharges have decreased significantly since the 1980s. Overall, the combined discharges of ^{14}C from Sellafield (both liquid and airborne) are lower now than in the 1980s; for example, the overall release of ^{14}C from Sellafield was 12 TBq in 1988 vs. 5 TBq in 2014.

This could explain the reduction in ^{14}C activity observed in the recent samples, as seaweed is able to utilise carbon from both atmospheric CO_2 and DIC in seawater. However, the study by McCartney et al. (1988) shows that the majority of atmospheric ^{14}C discharged from Sellafield has dispersed by 10 km from the site, so this would only account for the samples from Nethertown and to a lesser degree Ravenglass.

Another possibility is a change in discharge trend over an annual period; if the majority of aquatic discharges occurred during the winter months when photosynthesis will be minimal, this would have a significant influence on the ^{14}C levels and could account for the lower seaweed values in recent samples, despite the higher aquatic discharges. Figures 4-9 and 4-10 show monthly ^{14}C liquid discharges from Sellafield over a three-year period in the early 1990s and early 2010s respectively, however, there does not appear to be a clear difference in discharge patterns between summer and winter. It would appear from Figure 4-9 that there are lower discharges of ^{14}C in the early part of the year in the early 1990s but for the 2010s it varies between years with 2011 having more liquid ^{14}C discharges in the summer and 2012 having more in the winter (Figure 4-10).

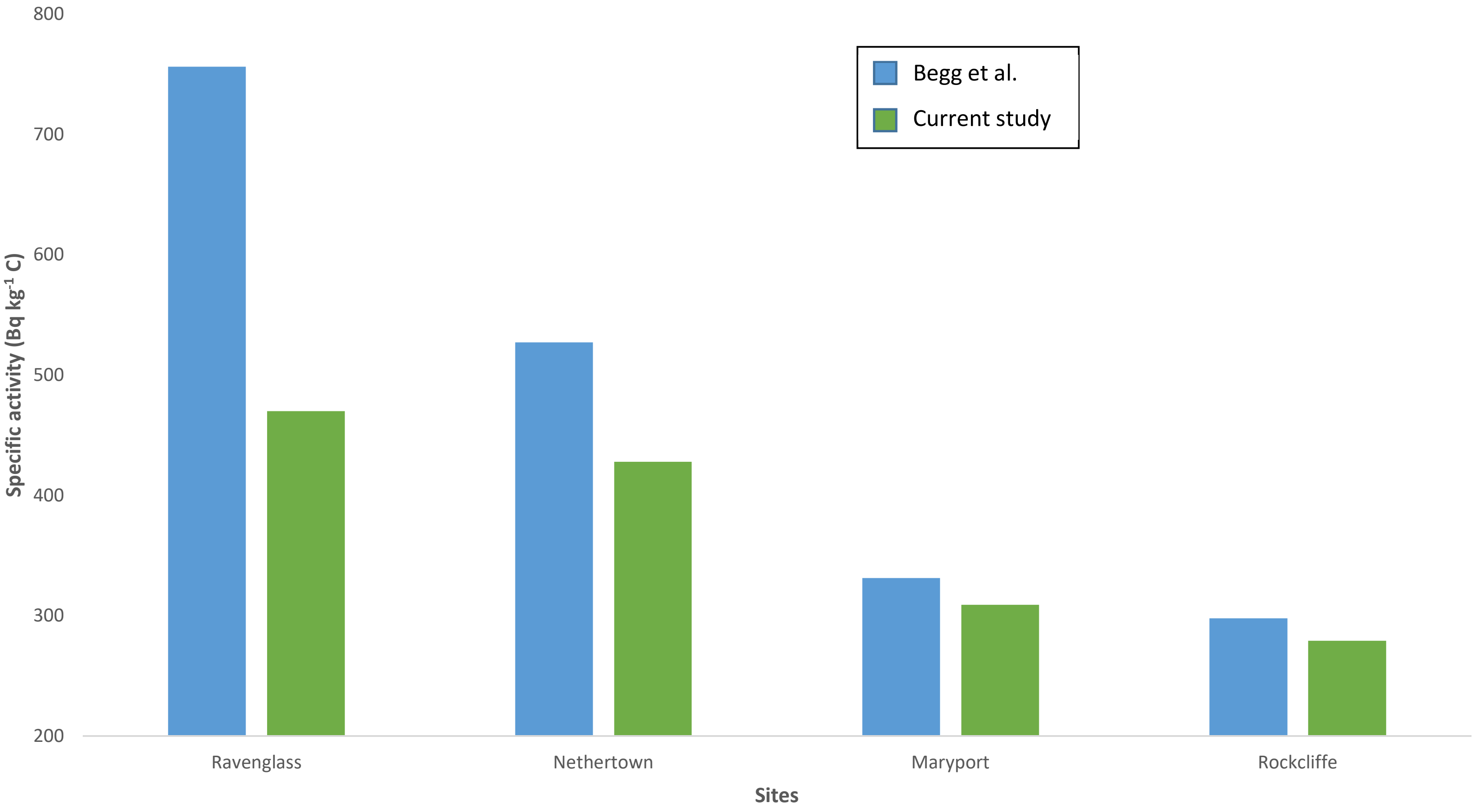

Figure 4-7: Comparisons of gross specific activity of ^{14}C in *Fucus* seaweed measured in this study (average values taken except for Ravenglass where only high water values were available) and Begg et al. (1992), error bars present but not visible due to small value.

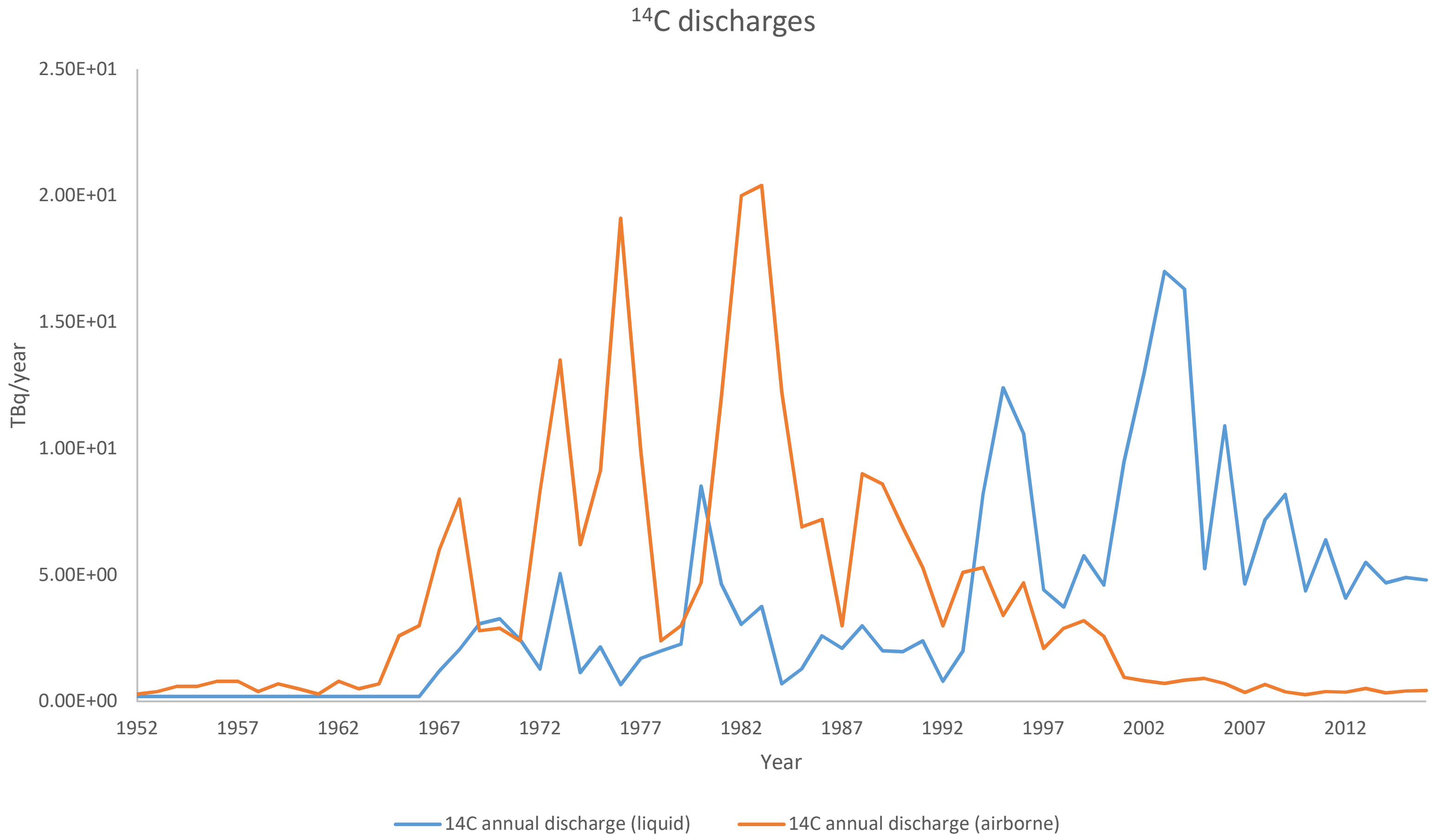

Figure 4-8: Airborne and liquid ^{14}C discharges from Sellafield between 1952 and 2016 (discharges between 1952 and 1985 are estimated (Muir et al., 2017)).

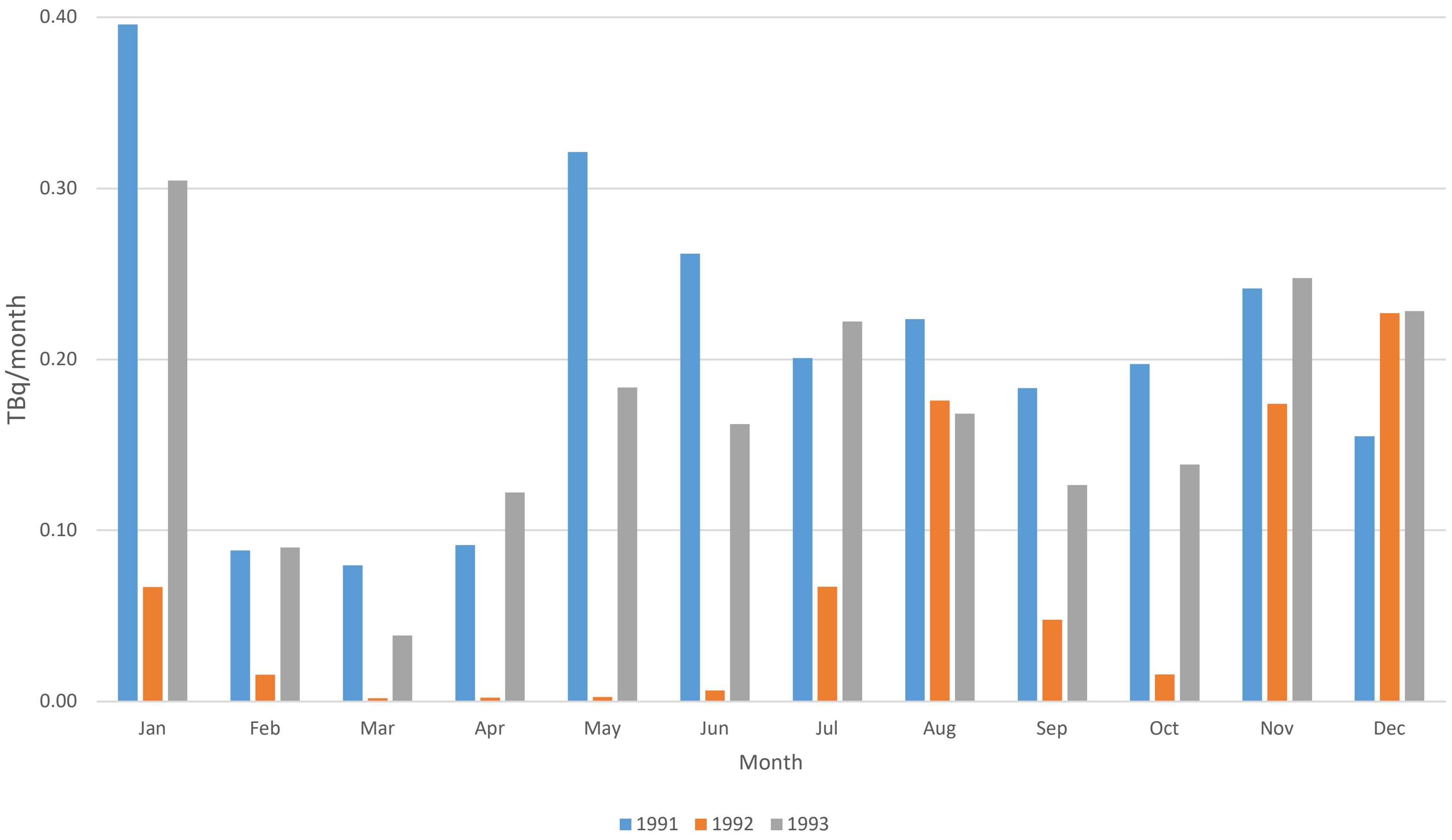

Figure 4-9: Monthly ^{14}C liquid discharges from Sellafield (1991 to 1993).

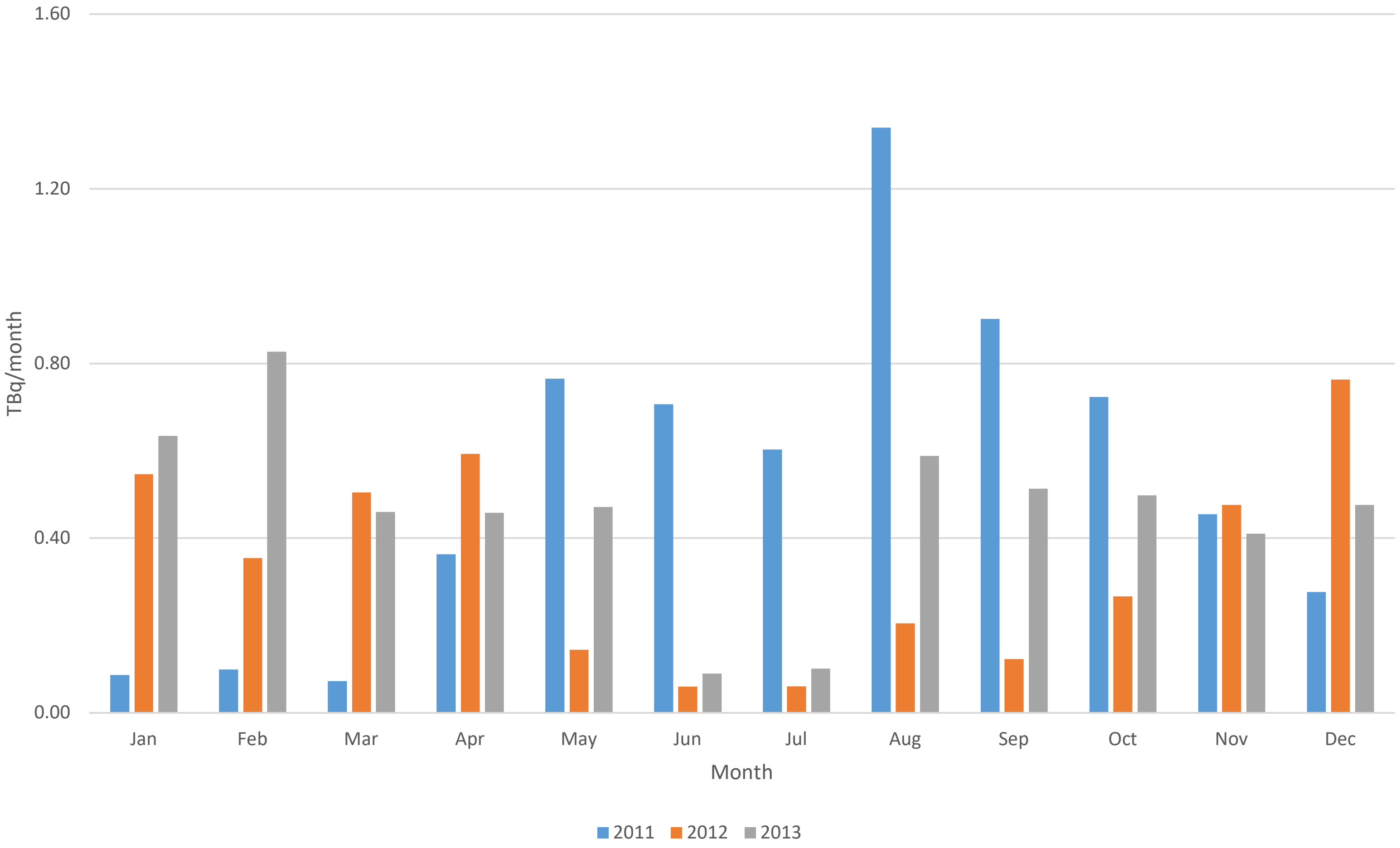

Figure 4-10: Monthly ^{14}C liquid discharges from Sellafield (2011 to 2013).

4.2 ^{14}C in Biota

4.2.1 Comparison of ^{14}C in individual limpets

Eight limpets of similar size were collected in close proximity to one another to compare variability in the specific activity of ^{14}C between individuals as other measurements of biota in this study were of multiple organisms. The specific activity of ^{14}C in the limpets ranged from 1054 Bq kg^{-1} C to 811 Bq kg^{-1} with a mean specific activity of ^{14}C of 894 Bq kg^{-1} and a standard deviation of 70 Bq kg^{-1} C. From the difference between individuals the % error was calculated as 8% which is equivalent to 1σ. This was used as a guide to estimating the variability between individuals where results were obtained from bulk sampling and has been included as an error on figures.

4.2.2 Organic ^{14}C and Inorganic ^{14}C

Where the specific activity of ^{14}C is compared between the organic and inorganic carbon of a sample (Figure 4-11), the organic fraction has the higher ^{14}C activity in almost all cases; for one mussel sample and the whelk sample the organic ^{14}C was significantly higher than the inorganic ^{14}C at 1σ while the difference between organic and inorganic ^{14}C in all other samples measured was within error. At 2σ there was no differences in the mussel and whelk sample, however, overall there is a noticeable trend of organic ^{14}C > inorganic ^{14}C. While a previous study of the west coast of the UK (Begg et al., 1992) also found organic tissue to have a higher ^{14}C activity than corresponding inorganic tissue, a study by Muir et al. (2015a) in the east coast of the UK found the inorganic carbon fraction to have the higher ^{14}C activity when compared to the organic tissue of biota. Muir et al. suggest that the difference between the inorganic and organic fractions is due to the form of carbon available to biota being organic rather than inorganic (DIC). In the Muir et al. (2015b) paper, looking at sites on the west coast on the UK, the seaweed had the lowest ^{14}C activity when compared to mussels and winkles, whereas seaweeds were found to have the highest activity at the Parton site in this study, from which it can be assumed that phytoplankton would also have a high ^{14}C activity as they are also primary producers and utilise DIC (Tortell and Morel, 2002). Another possible reason for the difference between organic and inorganic ^{14}C activity might be the difference in turnover time of carbon in the shell and flesh of biota (Begg et al., 1992). Shell carbonate is formed as the shell grows and does not exchange carbon once it is formed whereas the flesh of biota will continue to exchange with carbon from the biota's diet. As shell carbonate is fixed, if the DIC in the biota's environment had recently had a higher ^{14}C activity this would be seen in the seaweed and phytoplankton and become incorporated into the biota flesh as it fed but would not have as much effect on the shell as the majority of shell would already have been formed. Mussels produce shell material throughout the year but at a faster rate during summer whereas mussel flesh increases most during spring and stops during winter. These seasonal changes are caused foremost by changes in water temperature and to a lesser degree the availability of food (Stirling and Okumuş, 1995).

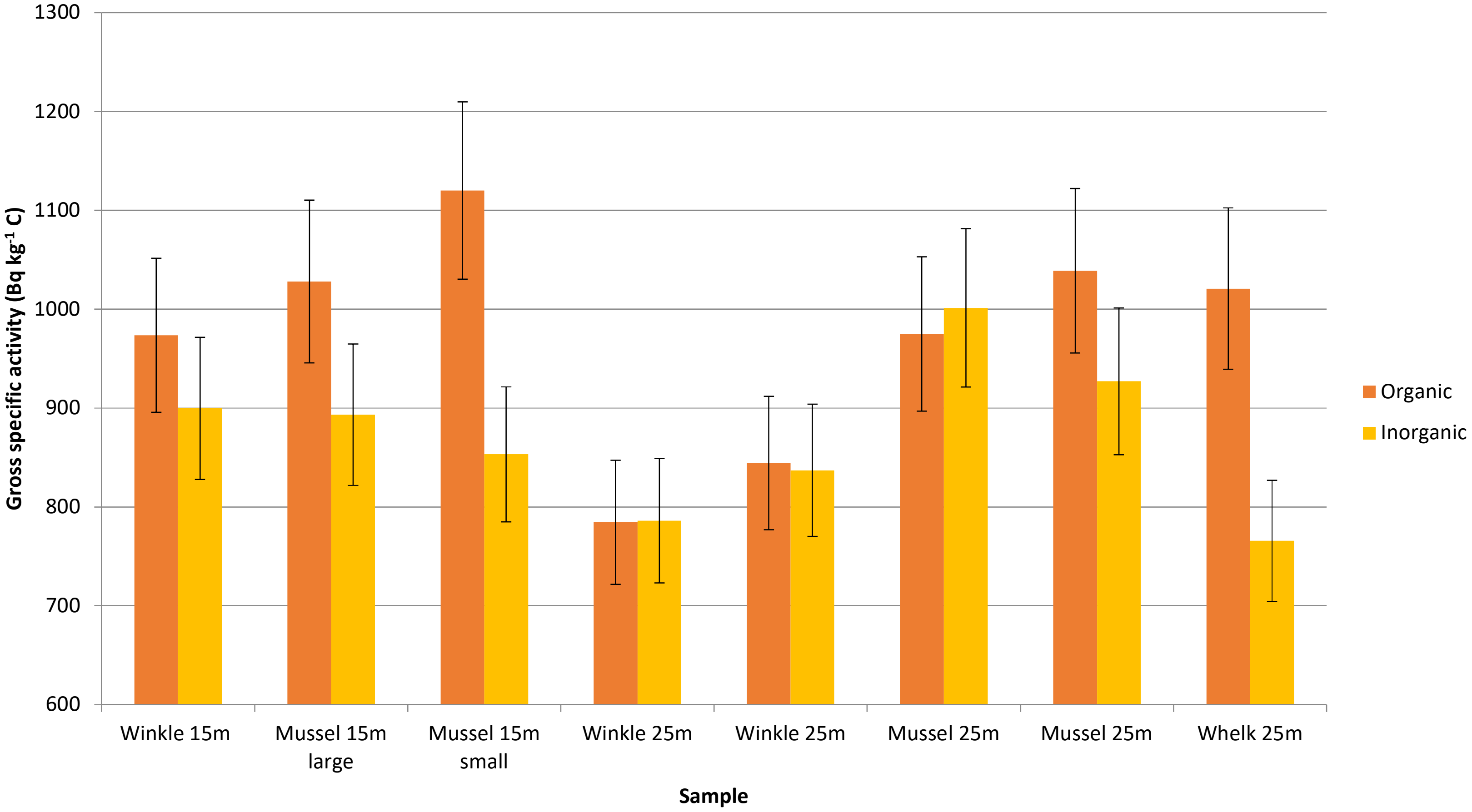

Figure 4-11: Comparison of gross specific activity of ^{14}C in organic and inorganic component of biota collected at various distances from the low water line from Parton including 8% error bar (± 1σ).

4.2.3 Parton

At the Parton site (Figure 4-12), seaweeds show the highest ^{14}C activity of the species sampled. Where it was possible to separate the same species by size there does not appear to be a clear difference between small and large members within a species; for limpets at 15 metres from the water's edge, the smaller members of the species appear to have a higher ^{14}C activity whereas further up the shore the opposite is seen. There is also a larger difference between two sets of large limpets at 15 metres than between small and large limpets at 15 metres. Again, with mussels, there is not much difference between small and large mussels at 15 metres when compared to the difference between mussels of a similar size to each other at 25 metres. It would appear that size of the individual organism does not have a correlation to ^{14}C activity.

On a similar note, there does not seem to be a correlation between distance from the low water mark and ^{14}C activity. Winkles seem to have a slightly higher ^{14}C activity closer to the low water mark while sea anemones show the opposite and mussels and limpets show no clear pattern and at 2 sigma error, there would be no within-species difference.

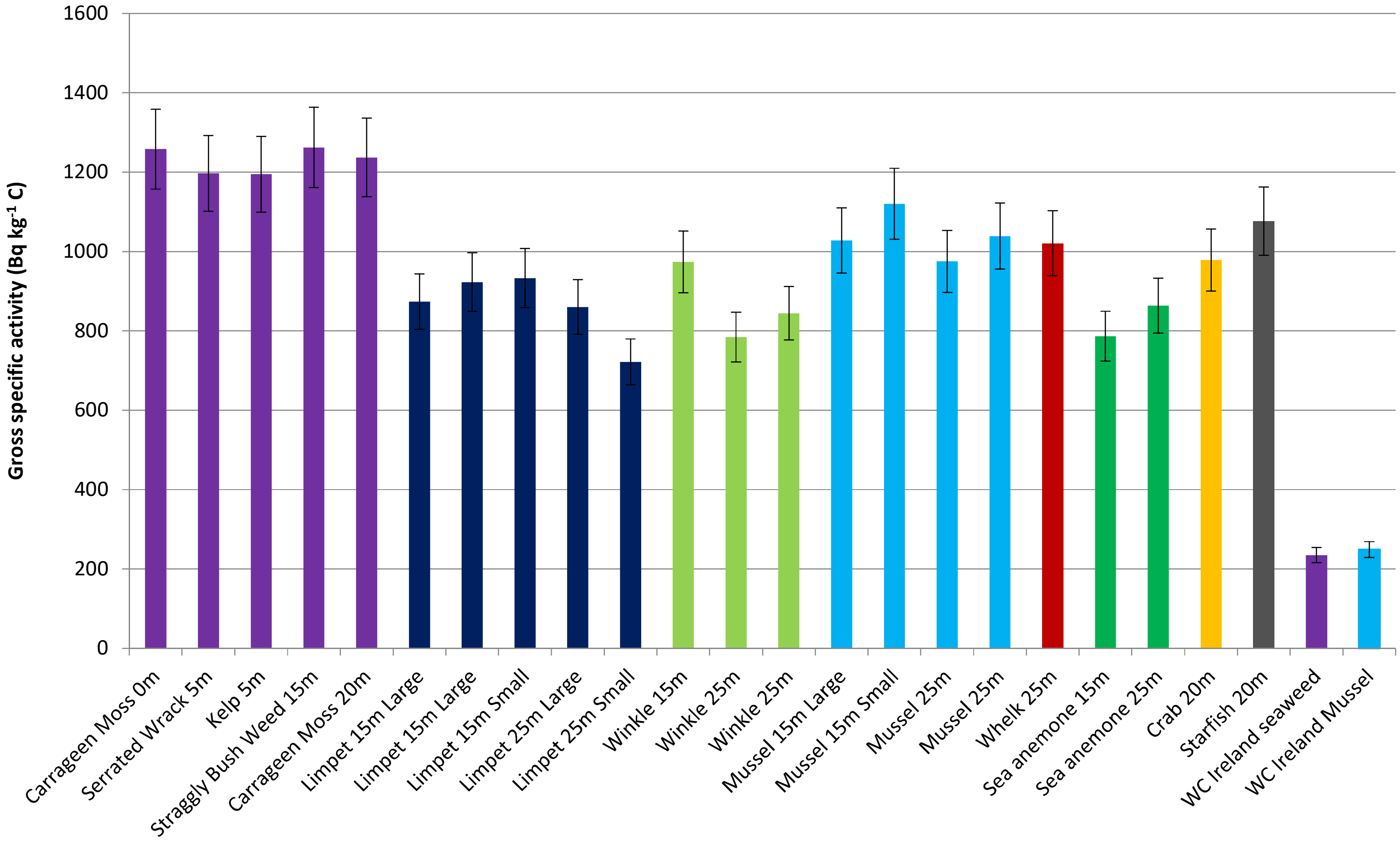

Figure 4-12: Gross specific activity of ^{14}C in biota collected at various distances from the low water line at Parton including background values for the west coast of Ireland including 8% error bar (± 1σ).

Figure 4-13 below shows the average ^{14}C activity where more than one measurement was made for a species. Seaweeds have the greatest ^{14}C activity in Parton at the time of sampling, followed by, in order of decreasing activity, starfish > mussels > whelks > crabs > winkles ≈ limpets > sea anemones. Previous studies at Parton have shown mussels > limpets > anemones ≈ winkles > seaweed (Cook et al., 2004a) which follows a similar pattern to this study with the exception of seaweeds, while Muir et al. (2015b) found a trend of winkle > mussel > limpet although they measured the ^{14}C in the inorganic shell of biota as opposed to the flesh, although the inorganic ^{14}C activities for Parton in this study (Figure 4-11) show mussels having a higher activity than winkles; mean inorganic mussel activity of 919 Bq kg^{-1} C versus mean inorganic winkle activity of 841 Bq kg^{-1} C, so it is not the difference between inorganic and organic ^{14}C that is causing this difference between this study and Muir et al. (2015b).

The difference in ^{14}C activities between the different species could be due to the differences in feeding habits. The seaweeds are primary producers, and convert CO_2 and DIC into biomass. As the seaweeds show the highest ^{14}C activities, this suggests that they are exposed to enriched DIC from the Sellafield plant. Mussels are filter feeders and mainly feed on phytoplankton which, like the seaweed, convert DIC to biomass. Limpets and winkles both feed on algae although winkles are known to occasionally consume small invertebrates; the fact that both limpets and winkles have comparable ^{14}C activities supports the argument that diet influences ^{14}C activity. Starfish, whelks, crabs and sea anemones are all predatory species. Starfish, whelks and crabs are all known to prey on mussels, although starfish and crabs will also scavenge for food; the ^{14}C activities of these predators are close to the activity of mussels.

Tierney et al. (2017) found no obvious trend between ^{14}C activity and position of biota in the food chain, rather it was suggested that life-span of an organism had a greater influence on the ^{14}C activity of an organism, with longer lived species integrating ^{14}C over a longer period of time, which included uptake during periods of higher ambient activity resulting in higher ^{14}C activity when compared to shorter-lived species. Sea anemones have one of the longest possible lifespans (up to 80 years) of biota from this study, while seaweeds have one of the shortest, between 4 and 10 years depending on species, but as the biota collected could have been at any stage of their lifespan (within reason) when collected, this could help to account for the variability in ^{14}C activities.

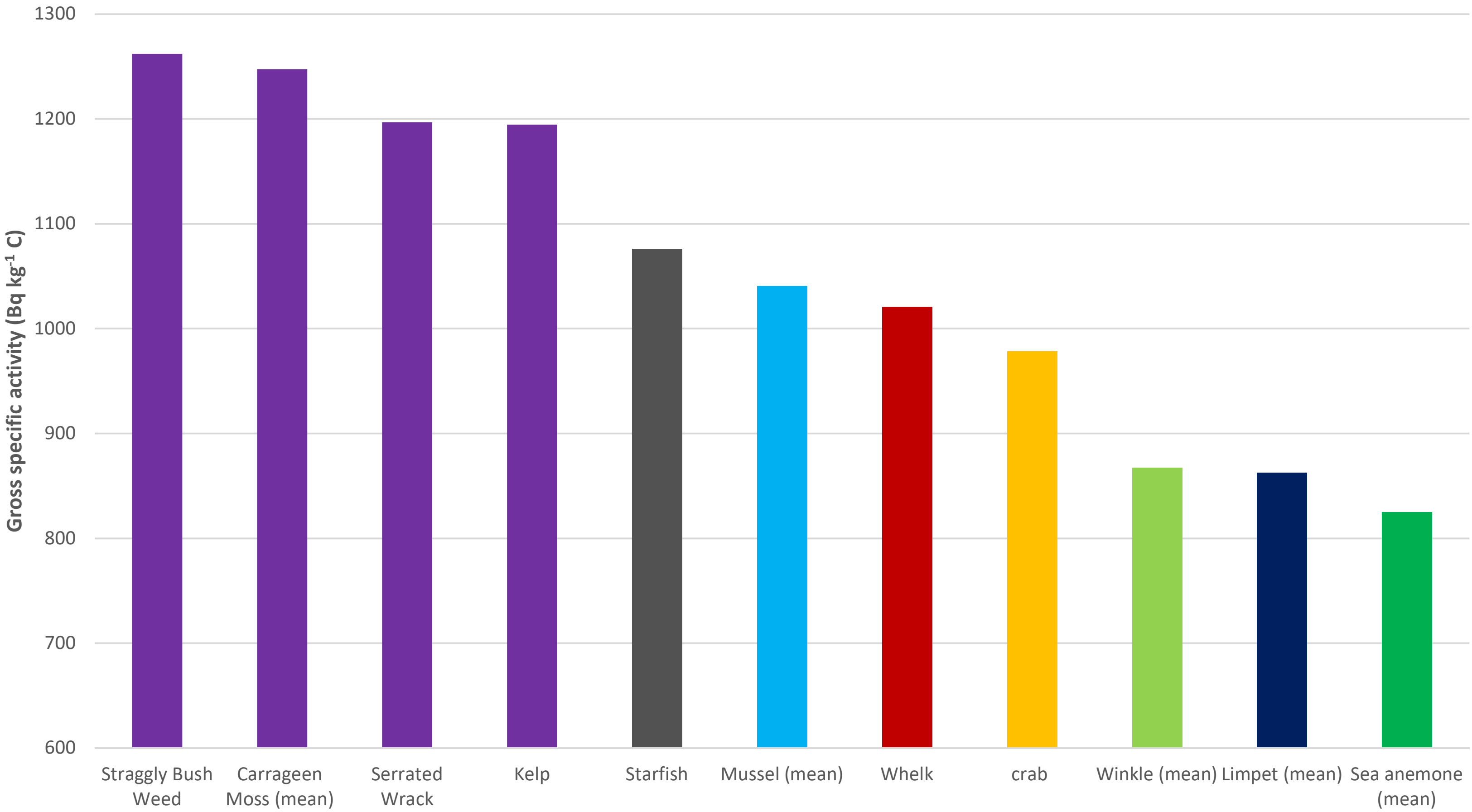

Figure 4-13: Gross specific activity of ^{14}C in biota collected from Parton – measurements from the same species averaged.

It can be seen from Figure 4-14 that seaweeds collected for the same site on different dates vary significantly in ^{14}C activity. The samples of serrated wrack collected in August 2015 and September 2016 are the only directly comparable samples, but given the similarity in activity shown in the variety of seaweeds collected in August 2015, it can be assumed that the ^{14}C activities between similar species of seaweed are relatively similar. The reason for the difference in ^{14}C activities found in seaweeds collected on different dates is not known, but one possible explanation could be that as Parton is close to the Sellafield site, the DIC released from the pipelines may not have been as well diluted in the seawater as it would be at sites further north of Sellafield. It is possible that ‘pockets’ of relatively high ^{14}C activity DIC could reach the seaweeds at Parton depending on recent releases causing an increase in ^{14}C activities in areas of new growth within seaweeds. This could also help explain why this study found seaweed to have the highest activity at Parton, while Begg et al. (1992) found seaweed to have the lowest ^{14}C activity at this site. At the other two sites studied, Garlieston and Port Appin, there are also differences between seaweeds sampled on different days, but the difference between seaweed collected at the high and low water mark on the same day is greater than the difference between seaweeds collected on different days.

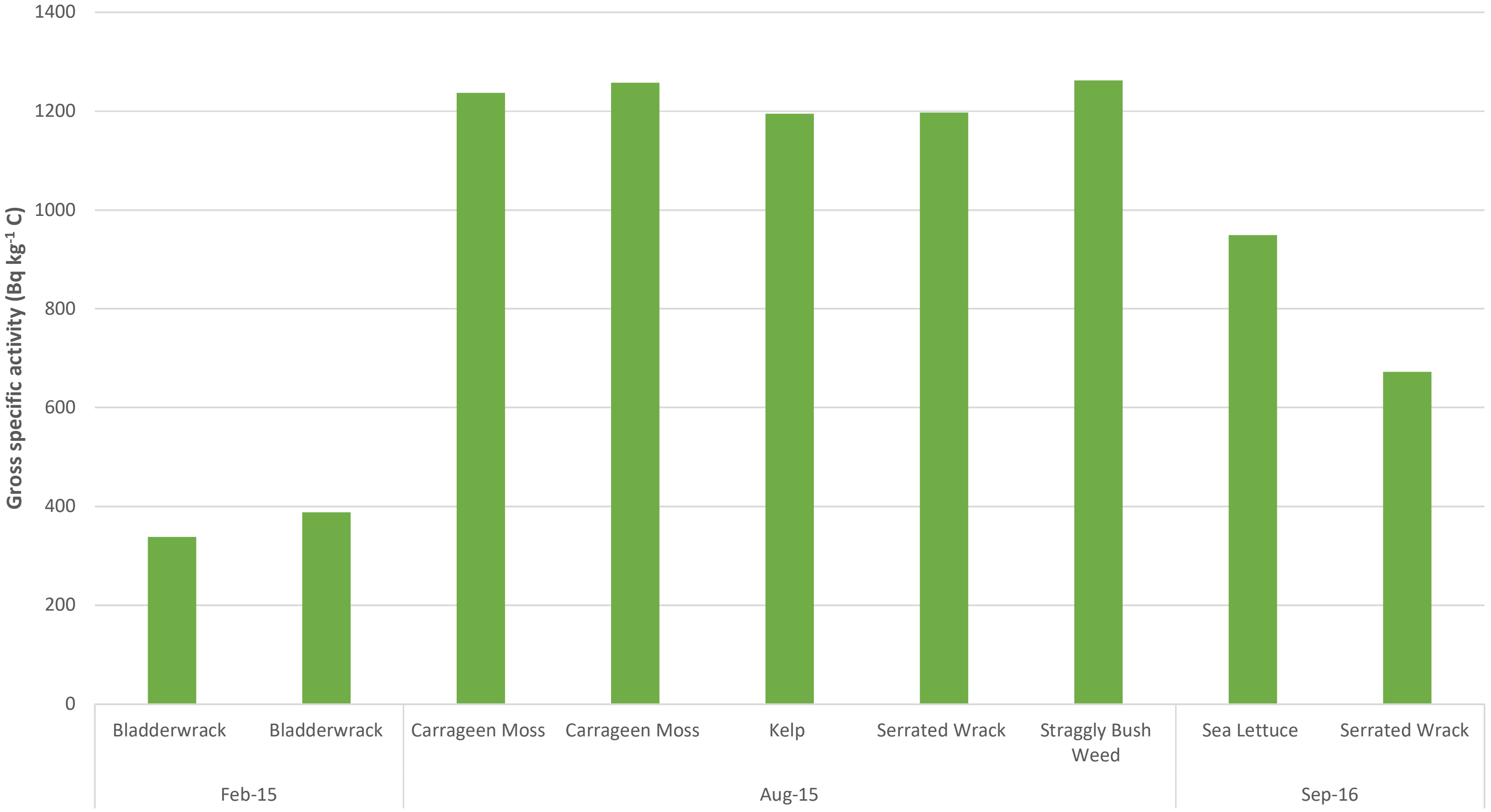

Figure 4-14: Comparison of gross specific activity of ^{14}C in seaweeds collected from Parton on different dates.

4.2.4 Garlieston

At the Garlieston site (Figure 4-15) mussels show the highest ^{14}C specific activity of the species sampled at this site which was also seen in a previous study by Cook et al. (2004a) although the site of that study was Parton. The seaweeds at Garlieston have some of the lowest ^{14}C activities of the biota sampled which is in contrast to Parton (Figure 4-12 and 4-13) where seaweeds had the highest activity. The range of ^{14}C activity is significantly lower at Garlieston compared to Parton; at Parton the ^{14}C activity varies from 600 to 1300 Bq kg^{-1} C, whereas at Garlieston the range is around 300 to 500 Bq kg^{-1} C. The spread of ^{14}C activity is also significantly lower at Garlieston when compared to Parton with the former having an approximate 200 Bq kg^{-1} difference between the highest and lowest value and the latter having an approximate 700 Bq kg^{-1} difference between the highest and lowest values. As the ^{14}C liquid discharges from Sellafield are diluted and dispersed as they travel up the coast of the UK there is a difference between sites that are different distances from Sellafield. There does not appear to be a relationship between the size of an organism and ^{14}C activity (Figure 4-15) whereas there is suggestion of a relationship between distance from the low water mark and ^{14}C activity, with samples closer to the low water mark having a higher activity for some species such as mussels and sea anemones but not for winkles over the same distance. When the error of 8% is taken into account this difference is within error with the exception of the sea anemones.

While Parton had a pattern of ^{14}C activity in biota in the following order; seaweed > starfish > mussels > whelks > crabs > winkles ≈ limpets > sea anemones, Garlieston does not have such a clear pattern. From the averages of gross ^{14}C activity (Figure 4-16); mussels > winkle ≈ sea anemone ≈ crab ≈ seaweed ≈ limpet. The similarity between the biota with the exception of mussels is likely due to the general lower ^{14}C activities found at Garlieston, as the ^{14}C activities fall closer to background levels, although they are still clearly above background, there are less observable difference between samples while the error remains the same.

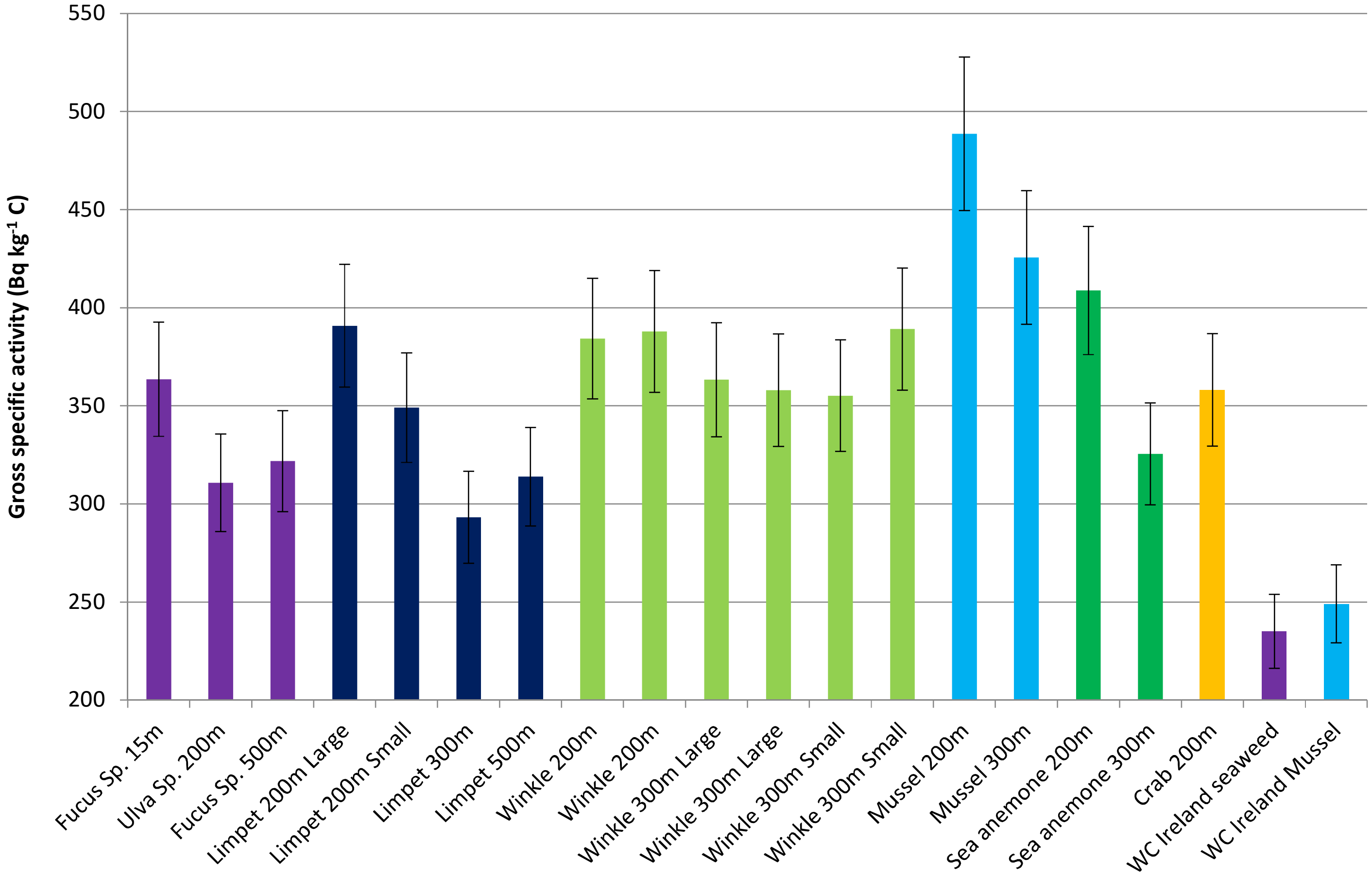

Figure 4-15: Gross specific activity of ^{14}C in biota collected at various distances from the low water line at Garlieston including background values for the west coast of Ireland including 8% error bar (± 1σ).

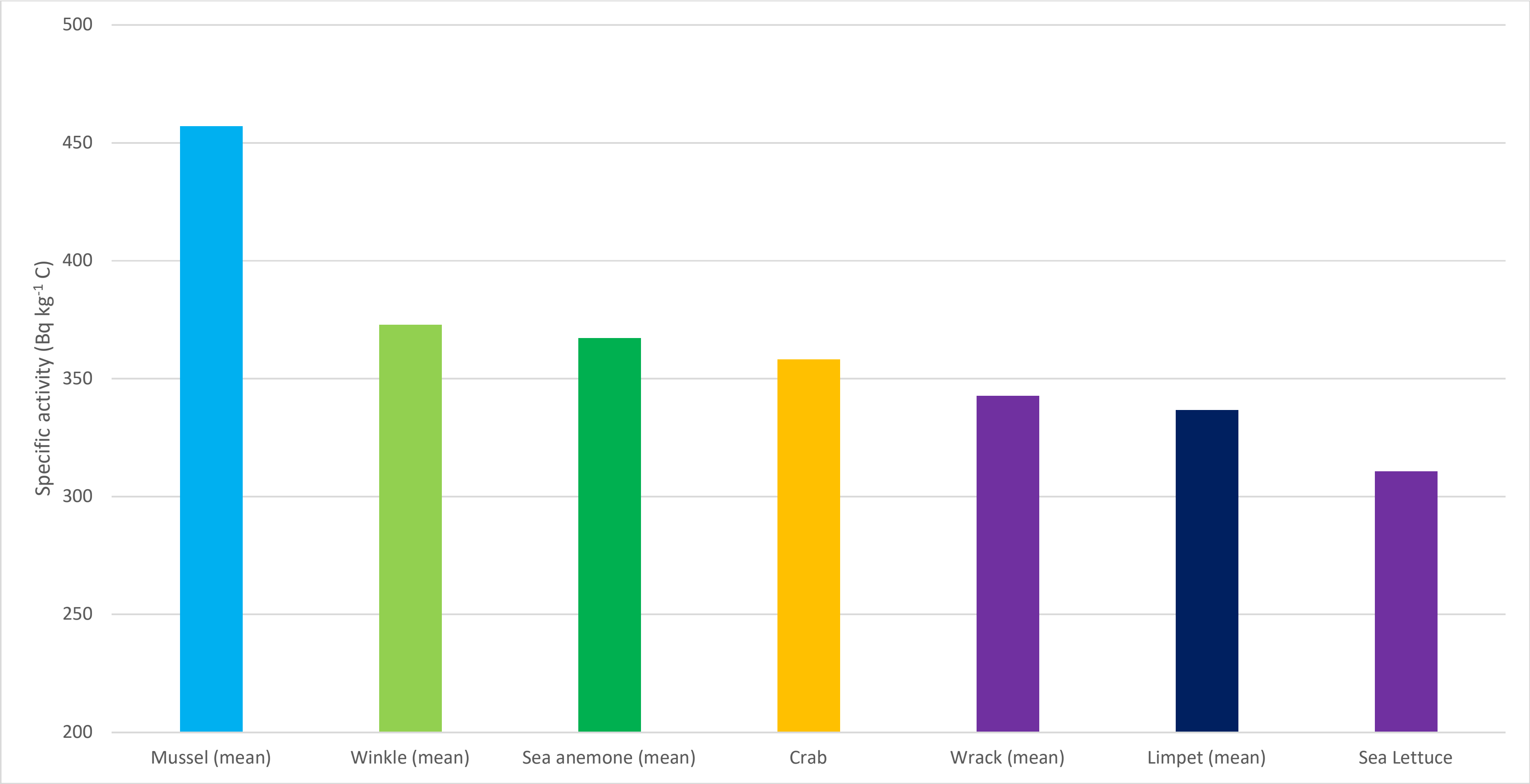

Figure 4-16: Gross specific activity of ^{14}C in biota collected from Garlieston – measurements from the same species averaged.

4.2.5 Port Appin

Port Appin is approximately 343 km from the Sellafield site and at this distance the specific activity of ^{14}C in biota collected from the site is close to the background value from the west coast of Ireland (Figure 4-17). With the 8% error on the measurements taken into account, the samples from Port Appin all fall within the same spread as one another. It is not possible to note any distinction between the species, distance from low water mark or size of organism in relation to ^{14}C activity. As shown in Figure 4-1, by 100 km, seaweed samples are close to background levels for ^{14}C and this is also true for other biota. As seaweed appears to give a fair representation of a site's ^{14}C enrichment, it is likely that by 100 km from Sellafield other biota are also showing ^{14}C activities close to background.

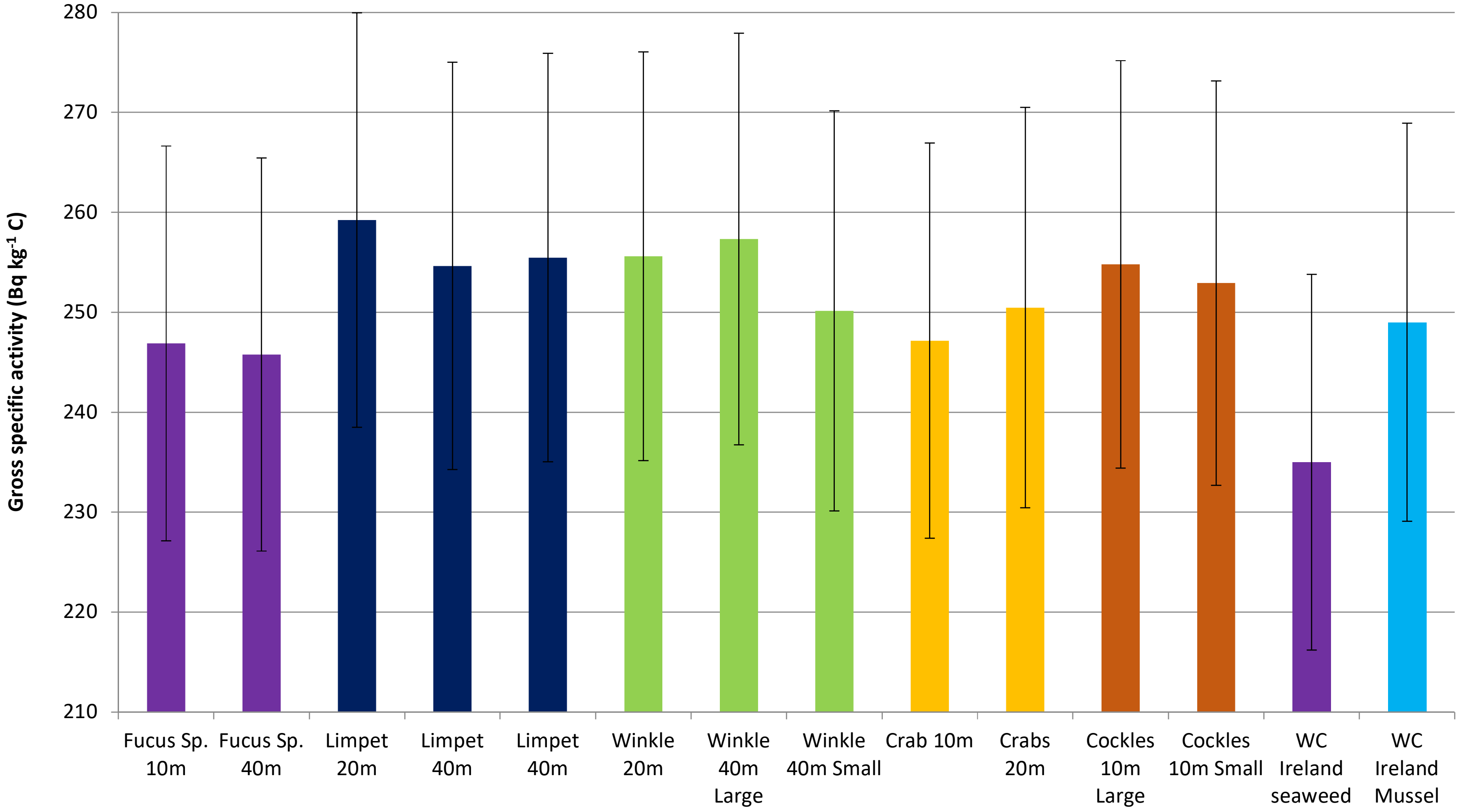

Figure 4-17: Gross specific activity of ^{14}C in biota collected at various distances from the low water line at Port Appin including background values for the west coast of Ireland including 8% error bar (± 1σ).

4.3 ^{129}I in Seawater

Figure 4-18 shows the ^{129}I concentration in seawater collected from sites on the west coast of the UK; at each site, two samples of seawater were collected from the same point and measured. Nethertown, the site closest to Sellafield, has a ^{129}I concentration more than ten times the values of any other site measured and also shows the greatest variability between the duplicate seawater measurements taken at the sites. As Nethertown is so close to the Sellafield site (less than 10 km) it is plausible that the liquid discharges from the twin 10 km pipelines have yet to mix well and to dilute and disperse in the Irish Sea, leading to pockets of heterogeneous, high Sellafield discharge concentrations which could account for the variability between the duplicate samples. The concentration of ^{129}I in seawater shows a general trend of decreasing concentration with increasing distance from Sellafield (Figure 4-18 and 4-19) and at most sites there is good agreement between the duplicate seawater measurements.

^{129}I is quite conservative in behaviour and remains dissolved in seawater for a long time, which makes it a good tracer. It is transported out of the Irish Sea with most joining discharges from La Hague (Figure 1-1) and moving up the Nordic coast into the Arctic Ocean, with a smaller portion moving south west into the Atlantic Ocean (Vivo-Vilches et al., 2018). To understand its behaviour on a more local scale, it is possible to estimate the halving distance from Sellafield (Figure 4-20) as follows:

$$\frac{\ln 2}{-0.0109} = -64 \text{ km}$$

Equation 5: Halving distance for the northward dispersion of ^{129}I from Sellafield.

This halving distance is in reasonable agreement with those calculated for ^{14}C (Equations 1, 2, 3 and 4).

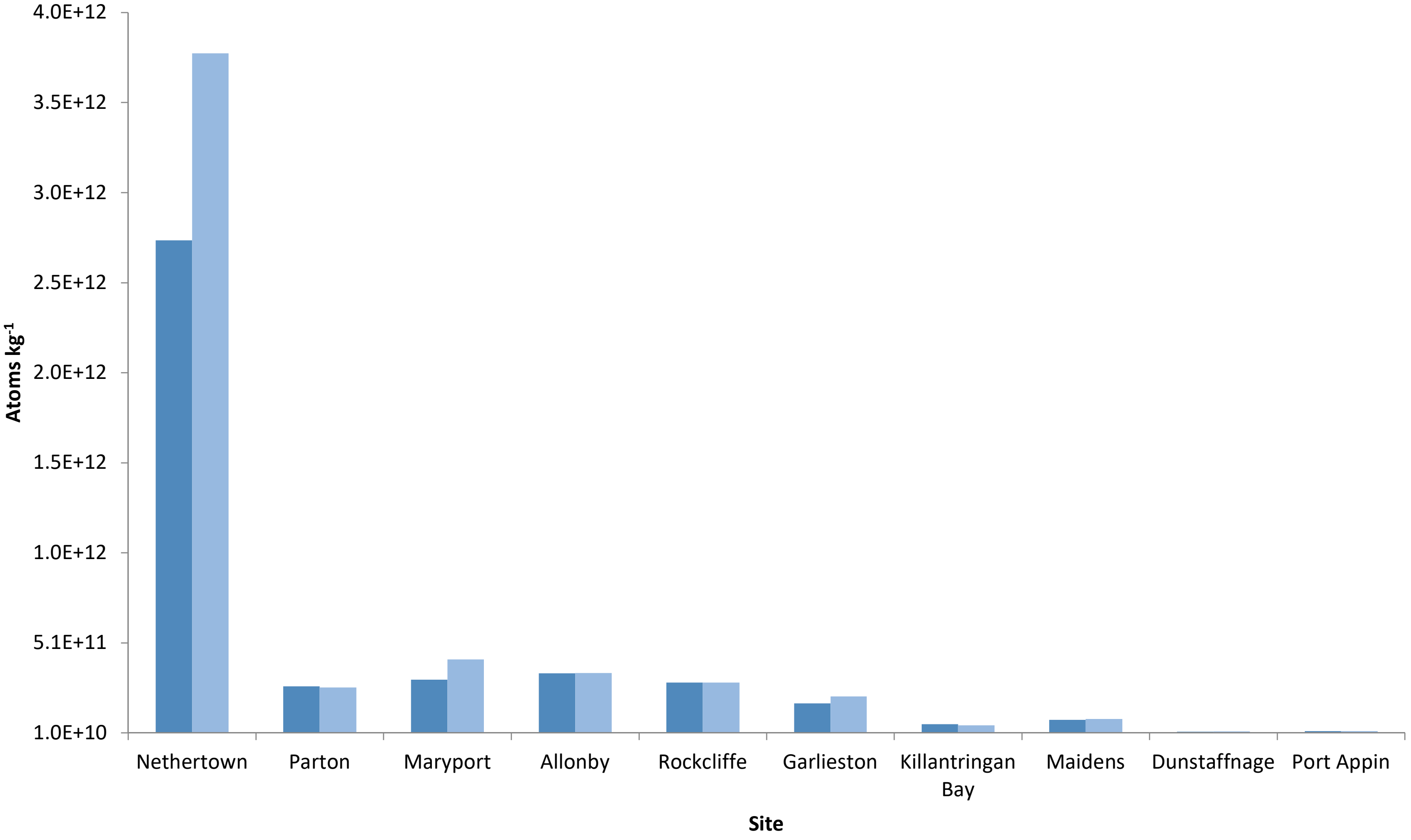

Figure 4-18: Duplicate ^{129}I measurements in seawater collected from ten sites on the west coast of the UK, error bars present but not visible due to small value.

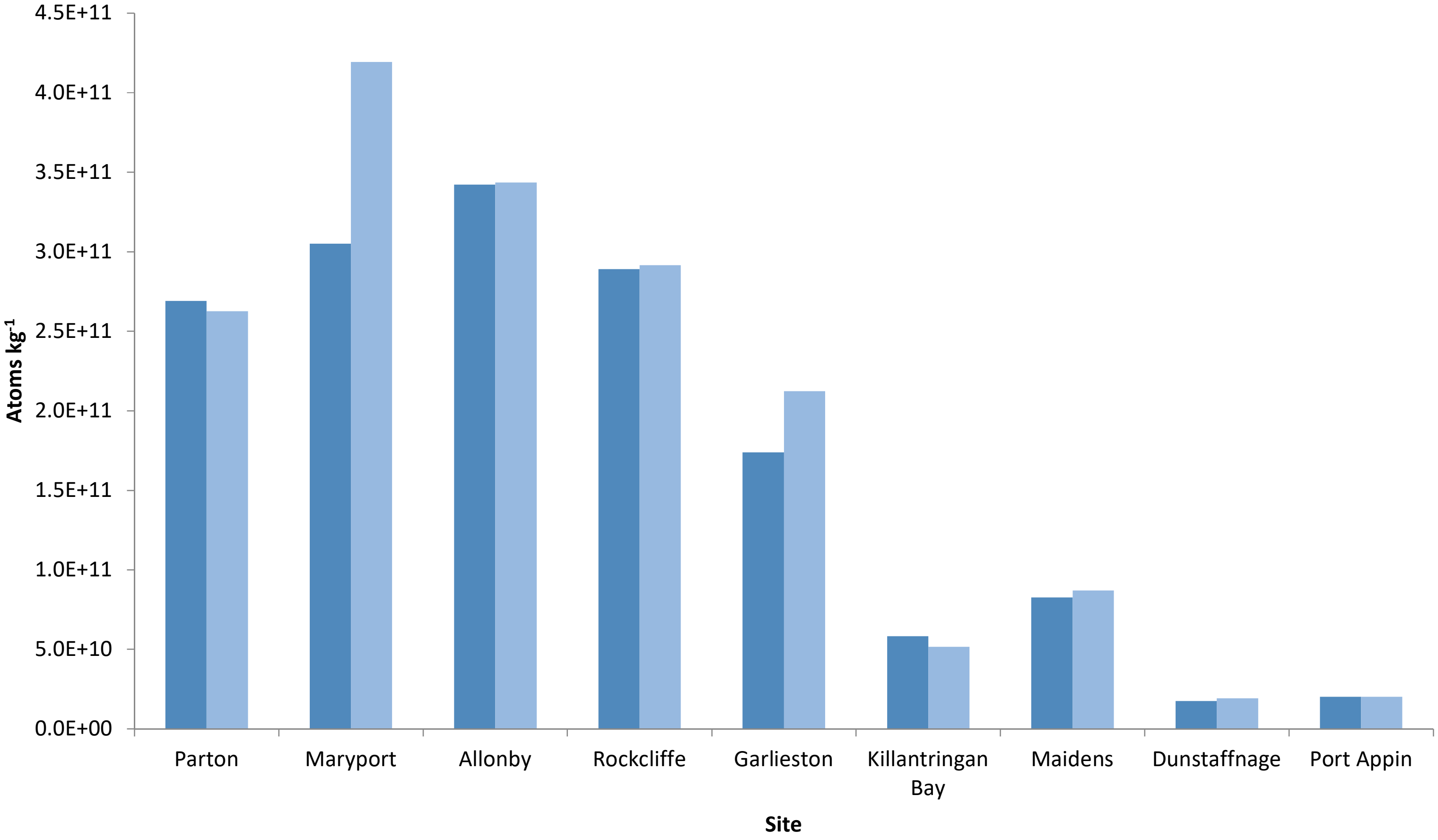

Figure 4-19: Duplicate ^{129}I measurements in seawater collected from nine sites on the west coast of the UK (Nethertown excluded), error bars present but not visible due to small value.

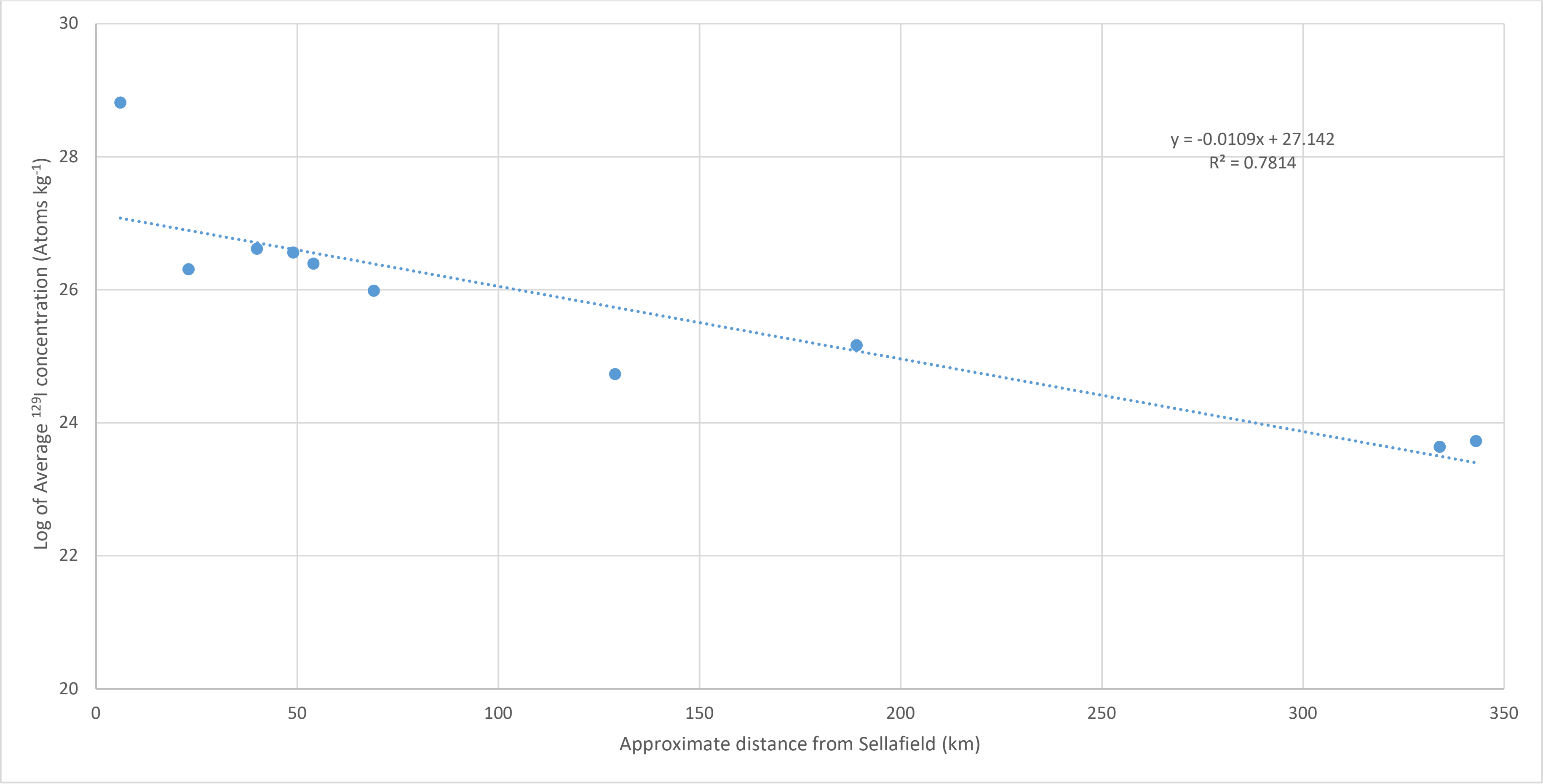

Figure 4-20: Natural log of average ^{129}I concentration in seawater against distance from Sellafield, including best fit equation of the line.

One of the original objectives of this research was to measure the ^{129}I concentrations in both the seaweed collected from each site and the biota collected from the three sites chosen for in-depth study. This objective was never fully completed as it was not possible to reproduce the published ^{129}I measurements in a range of Lithuanian soil samples and IAEA reference materials (Tables 3-9). Of the two IAEA reference materials measured, IAEA-375 (Russian soil) has a certified ^{129}I value and is the only sample which underwent alkali fusion and produced the expected ^{129}I concentration. Whereas IAEA-446 has no certified value for ^{129}I but has two published values ranging from 0.1 to 0.13 Bq kg^{-1} - the ^{129}I concentration measured in this study was 0.14 Bq kg^{-1}. The paper by Ežerinskis et al. (2016) does not state if the ^{129}I concentrations reported in soils are from a single AMS measurement or multiple measurements averaged. Although the results from the soils measured in this study did not correspond to the results Ežerinskis et al. measured in the same soils, the repeated measurements of the same soil gave relatively consistent results. There is a possibility that the published values for the soils may not be correct.

There are a variety of methods for measuring ^{129}I and if further study was undertaken it would be useful to measure samples using multiple methods to check the accuracy of the fusion extraction. When measuring ^{129}I by AMS there are two different methods used: the carrier method, where a known amount of a stable iodine carrier is added (in this study Woodward iodine was used as the carrier) and the sample has little stable iodine itself - the ^{129}I concentration can be calculated from the recovery of the carrier iodine and the iodine ratios; and the tracer method, which involves the addition of a ^{125}I tracer to determine yield and involves measuring the stable ^{127}I using ICP-MS before the carrier is added for AMS measurement. The tracer method was considered initially for this research but due to the relatively short half-life of ^{125}I (59.5 days) it was decided this was not feasible.

Alkali fusion has been shown to have a higher than 80% recovery for iodine but during the course of this research the alkali fusion method initially used produced results that did not agree with published values. A different method of alkali fusion was tested but failed to form a precipitate as expected and was quickly dismissed. Another method for extracting ^{129}I involves combusting a sample in oxygen at over

800°C and washing the resulting gases in an alkali solution or active charcoal which traps the iodine - but due to equipment and time constraints within this study it was not possible to undertake this.

Due to the time consuming processes involved in the alkali fusion and the subsequent extraction it was only possible to process 6 samples in a set, in a process that took several days. If the research were to be carried out again it would be beneficial to streamline the chemical process or to investigate a faster alternative methodology. It would also be beneficial to locate more certified standards for ^{129}I as it is not ideal to rely too heavily on using samples from previously published research as internal standards, especially when the published results lack clarity.

A study by Gómez-Guzmán et al. (2014) found a seawater concentration factor of iodine in *Fucus* to be (10563 ± 1038) while the IAEA recommended value is (10000). Unfortunately, due to the problems with the method, it is not possible to know how the results from this study would have correlated to these values.

4.4 Summary

It was found that both ^{14}C and ^{129}I, released from the Sellafield site as liquid discharges, decreased in concentration with increasing distance from Sellafield, and with similar halving distances, approximately 68 to 89 km for ^{14}C and 64 km for ^{129}I. For ^{14}C, there was a clear difference in activity between seaweed collected from the low water and high water areas of the intertidal environment, with low water seaweed having a higher activity. At the three sites chosen for a detailed study, the site closest to Sellafield, Parton, showed the highest degree of ^{14}C enrichment in biota with the greatest difference between different species, whereas the site furthest away from Sellafield, Port Appin, showed only slight enhancement in ^{14}C and there was little observable difference between biota. There was no relationship found between the size of an organism and its ^{14}C activity but at the mid-range site, Garlieston, there did appear to be a relationship between distance from the low water mark and ^{14}C activity in biota although this was not seen at the other sites. There appears to be some correlation between ^{14}C activity and feeding habit, with similar ^{14}C activities in species with similar diets and similar ^{14}C activities between predators and prey. It has also been shown in a previous study by Tierney et al. (2017) that there is a relationship between lifespan and ^{14}C activity due to longer lived species integrating ^{14}C over a longer period, including periods of higher ambient activity. This could explain the variability between biota at Parton which is closest to Sellafield and is more likely to experience pockets of higher activity ^{14}C seawater, whereas biota at sites further from Sellafield, where the ^{14}C in seawater would have been diluted, have a more uniform ^{14}C activity. It was not possible to measure the ^{129}I in solid samples due to an inconsistency between results for this study and those for measurements on IAEA standards and samples for which there are published results.

Chapter 5 – Conclusions

The research in this study was undertaken to achieve the following aims:

- To understand the fate of ^{14}C in the intertidal environment
- To understand the fate of ^{129}I in the intertidal environment
- To compare the behaviour of ^{14}C and ^{129}I

While it was possible to carry out the ^{14}C analysis on the collected biota, the ^{129}I analysis was only conducted on the seawater samples, resulting in an incomplete picture for the fate of ^{129}I in the intertidal environment. This also meant that it was not possible to complete a direct comparison of the behaviour of ^{14}C and ^{129}I but a partial comparison can be made by comparing the ^{14}C in seaweed to the ^{129}I in seawater. The main conclusions of the study are as follows:

- Both ^{14}C and ^{129}I show an approximate exponential decreases in activity in the intertidal environment of the west coast of the UK with increasing distance from the Sellafield site due to the 'dilute and disperse' mechanism.
- The halving distance for the dispersion of ^{14}C was found to be between 68 km and 89 km while the halving distance for ^{129}I was 64 km.
- There is a higher ^{14}C activity in seaweed inhabiting the area of the intertidal environment near the low water mark when compared with seaweed inhabiting the area at the high water mark due to the seaweed at the high water mark being exposed to the atmosphere for longer periods of time than the low water seaweed, with atmospheric ^{14}C having a lower activity than the ^{14}C in seawater, but this was rarely seen in other biota studied.
- All biota samples were found to be above background level for ^{14}C although at the site furthest from Sellafield, Port Appin, the activities measured were close to background.
- There was no relationship between the size of an organism and the ^{14}C activity of the organism.

- When seaweed samples from this study were compared to samples collected from 1988/1989, the ^{14}C activities had decreased, despite the fact that the aqueous discharges are now higher. It is suggested that this is due to differences in the annual discharge pattern but further work is required on this. The difference between the ^{14}C activities in the two studies decreased as distance from Sellafield increased.
- The organic fraction of biota tended to have the higher ^{14}C activity when compared to the inorganic fraction.
- At Parton, a pattern of decreasing activity was found in the biota as follows; seaweed > starfish > mussels > whelks > crabs > winkles ≈ limpets > sea anemones. At Garlieston, mussels had the highest activity and all other biota sampled were of similar ^{14}C activities while at Port Appin there was no discernible difference between ^{14}C activities in biota.
- There appeared to be a relationship between diet and ^{14}C activity with biota with a similar diet having similar ^{14}C activities and similar ^{14}C activities between organisms and their food source.
- It was observed that there was a large difference in ^{14}C activities measured in seaweed samples collected from the same site at different points in time with the difference being most notable at Parton, close to Sellafield.
- It was not possible to measure the ^{129}I in solid samples due to inconsistent results when developing the extraction method.

The results of this study indicate that ^{14}C released from Sellafield is incorporated into intertidal biota on the west coast of the UK. This is most clearly seen at sites closest to Sellafield but due to the dilute and disperse mechanism, both ^{129}I and ^{14}C concentrations decrease rapidly as the currents in the Irish Sea move the discharges north.

As ^{14}C activities in seaweed at Parton were shown to vary greatly depending on the time of sampling it would be of interest to carry out a more routine sampling regime at this site, possibly including monthly sampling and sampling at several positions on the beach, of seaweed, where feasible.

It is unfortunate that the study did not include ^{129}I concentrations in biota and further work should be undertaken to develop a reliable method for extracting ^{129}I from solid samples. With this in place it would be possible to directly compare the ^{129}I and the ^{14}C in samples of seaweed and intertidal fauna and it would also improve the understanding of the transport of ^{129}I in the intertidal food web.

It is intended that in the future this data can be incorporated into an Ecopath model developed to better understand the dispersion of ^{14}C from Sellafield into the ecosystem of the west coast of the UK (Tierney et al., 2018).

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