Caborn, Jane A.; Howard, Brenda J.; Blowers, Paul; Wright, Simon M.. 2016.
**Spatial trends on an ungrazed West Cumbrian saltmarsh of surface contamination by selected radionuclides over a 25 year period.**


10.1016/j.jenvrad.2015.09.011

# Spatial trends on an ungrazed West Cumbrian saltmarsh of surface contamination by selected radionuclides over a 25 year period

[a, b]*Jane A. Caborn*, [a]*Brenda J. Howard*, [c]*Paul Blowers*, [a]*Simon M. Wright,*

[a]Centre for Ecology & Hydrology - Lancaster, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP, UK.

[b]NNL, Preston Laboratory, A709, Springfields, Salwick, Preston, PR4 0XJ, UK.

[c]Cefas Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk, NR33 0HT, UK.

**KEYWORDS**

saltmarsh, radionuclides, spatial variation, temporal variation, sedimentation, monitoring

**ABSTRACT**

Long term spatial and temporal variations in radionuclide activity have been measured in a contaminated ungrazed saltmarsh near Ravenglass, Cumbria. Over a twenty-five year period there has been a decrease in activity concentration with $^{106}$Ru and $^{137}$Cs showing the highest rate of change followed by Pu alpha and $^{241}$Am. A number of factors contribute to the reduction with time; including radiological half lives, discharge and remobilisation. For $^{241}$Am the lower reduction rate is partially due to ingrowth from $^{241}$Pu and partially as a result of transport of sediment from the offshore Irish Sea mud patch. Considerable spatial variation for the different radionuclides was observed, which with time became less defined. The highest activity concentrations of long-lived radionuclides were in low energy areas, typically where higher rates of sedimentation and vegetation occurred. The trend was reversed for the shorter lived radionuclide, $^{106}$Ru, with higher activity concentrations observed in high energy areas where there was frequent tidal inundation.

Surface scrape samples provide a pragmatic, practical method of measuring sediment contamination over large areas and is a sampling approach adopted by most routine environmental monitoring programs, but it does not allow for interpretation of the effect of variation in sedimentation rates. This paper proposes a method for calculating indicative sedimentation rates across the saltmarsh using surface scrape data, which produces results consistent with values experimentally obtained.

## 1. INTRODUCTION

Between 1952 and 1992 the reprocessing facilities on Sellafield Limited nuclear site in NW England have, under authorization, released liquid effluents containing low levels of activity into the Irish Sea. The liquid effluents contained actinide and fission elements which are discharged via pipeline and are comprised of the purge water from waste storage ponds and process liquors from spent fuel reprocessing. Discharge histories showed the activity concentrations for radionuclides including $^{137}$Cs, Pu-α and $^{241}$Am reached a maximum in the 1970s and then substantially declined (Gray et al., 1995).

Once discharged, the radionuclides become attached to varying degrees dependent on particle reactivity to sedimentary particles with some becoming incorporated by sedimentary deposition and suspension processes into intertidal and estuarine environments resulting in the saltmarshes being contaminated with a wide range of radionuclides (Howard et al., 1986). Parallel to the coastline is an area of mud and muddy sediments (approximately 15km long x 3 km wide) commonly known as the ‘mud patch’ (Kershaw *et al.,* 1992; MacKenzie *et al.,* 1994; Pentreath *et al.,* 1984). Fine grained particles with associated radionuclides accumulate on the patch as a result of tidal movement and currents in the shallow Western Irish Sea basin (depth approximately 30m) (Hetherington, 1978; MacKenzie *et al.,* 1994). Particulates are redistributed and deposited onto the saltmarsh as a result of tidal processes and storm events.

The Ravenglass estuary (NW, England) is one of the most radioactively contaminated saltmarshes within the Irish Sea and provides a unique resource for understanding the behavior of radionuclides in the environment. This study focuses on the spatial and temporal changes in the activity concentrations of deposited radionuclides in surface sediment over a period of 25 years, determines sedimentation rates across the ungrazed saltmarsh and relates the data to discharge history.

## 2. EXPERIMENTAL SITE AND SAMPLING DETAILS

A survey in 1980 described the spatial distribution of activity concentrations for various radionuclides in the surface silts of an ungrazed saltmarsh in the River Esk estuary, Cumbria (Horrill, 1983). Further surface samples were taken in 1992 and 2005 by the Centre for Ecology and Hydrology (CEH), based on the sampling grid established in 1980, to enable assessment of the long term environmental processes for the 25 year period. Additional reported data from a study conducted in 1997 by Oh (2009) have also been included.

Ravenglass saltmarsh is situated approximately 10km south of the Sellafield site in the River Esk Estuary in Cumbria, UK. The site is on the northern shore of the River Esk (National Grid reference SD089948), inland of a railway viaduct (

Figure 1). The sampling area was 300 x 250m.

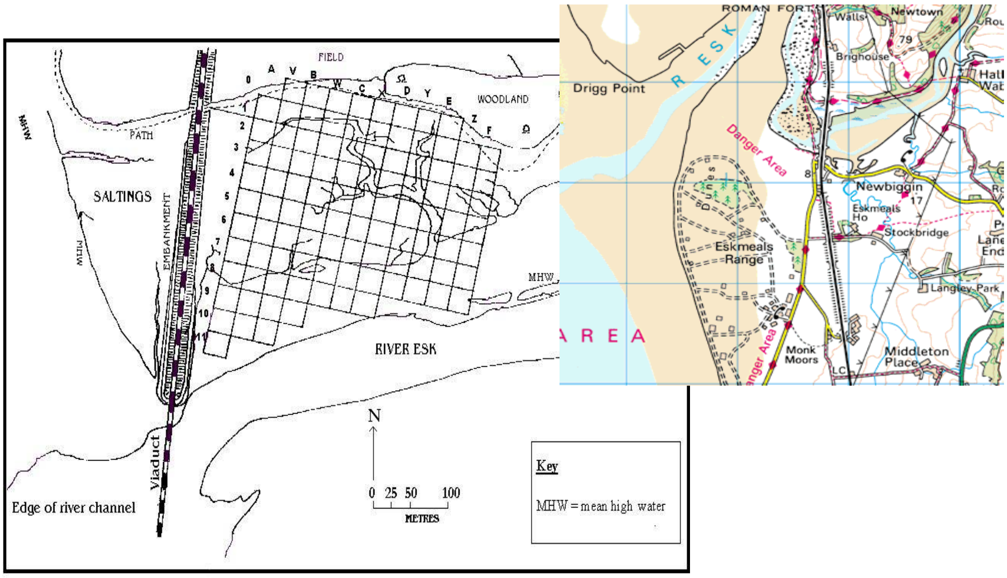



Figure 1: Location of saltmarsh and sampling grid (Ordnance Survey, 2006; Horrill, 1983)

## 2.1 Site sampling

The site was originally selected in 1980 on the basis that the total gamma radiation levels, using a field ratemeter, were relatively high compared with other saltmarshes in the estuary. In 1980 a permanent 25m survey grid was established on the marsh ( Figure 1) with a total of 100 sampling points. In August 1992 and March 1997 a survey of all the sample points was carried out similar to that of the original study of July 1980 (Horrill, 1983). A subsequent, less intensive survey was carried out in July 2005 comprising of 26 sampling points (alternate rows and columns).

For each of the surveys, a 250 x 250 mm quadrant was placed at the grid point. The vegetation within the quadrant clipped and collected taking care to avoid the inclusion of surface silt. The surface silt was then removed over the quadrant area by scraping to a depth of approximately 20 mm. In many cases the sample silt included a considerable portion of root mat.

## 2.2 Site characteristics

A diagram of the saltmarsh in 1980 and the associated sampling grid is given in

Figure 1. Horrill (1983) reported a linear trend in vegetation distribution across the saltmarsh. The size and shape of the saltmarsh has changed over time due to continuous accretion and erosion. By 1992, an erosion bank had developed at the lower end of the marsh and three sampling sites were lost (B10, X8 and D8). The vegetation cover on the saltmarsh was similar to that recorded during the original survey (Horrill, 1983).

By 2005 it was observed that the degree of erosion had increased significantly, markedly reducing the number of available sampling points near the river. A new triangular area of saltmarsh covered in vegetation was present at the lower end of the sampling transect (Figure 2). Over the sampling period, the extent of vegetation biomass on the remaining saltmarsh has markedly increased except at sites B5, C5 and C7 where there was no vegetation coverage.

Figure 2: Aerial map of Ravenglass saltmarsh (Google Maps, 2015).

## 3. RADIOCHEMICAL ANALYSIS

Following collection, the samples were dried at 105ºC, ground and analysed for radionuclide content. CEH Lancaster (formerly ITE Merlewood) performed the analysis for the 1980, 1992 and 2005 surveys. The 1997 survey was conducted by the Geosciences Advisory Unit (GAU), Southampton (Oh, 2009).

The measurement of gamma-emitting radionuclides ($^{106}Ru$ $^{137}Cs$ and $^{241}Am$) was carried out by gamma spectrometry using germanium detectors coupled to a computerised analytical system. The detectors were calibrated for efficiency using traceable, certified, mixed radionuclide standards. Limits of detection ranged from 0.5 to 10 Bq $kg^{-1}$ in oven dried samples (75 to 100g dry weight) for count times ranging from 1 to 2 days.

The Pu alpha analyses were carried out radiochemically, specifically by the addition of appropriate yield tracers to between 0.3 and 0.5g of sample, ashing and acid leaching. Ion-exchange chromatography was used to purify the plutonium which was then electrodeposited onto stainless-steel discs. Measurement of the isotopes was undertaken by alpha-spectrometry using passivated ion-implanted planar silicon (PIPS) detectors in conjunction with a multi-channel analyser.

All results are reported as dry weights (dw). Quality control samples were analysed along with the samples. CEH and the GAU have successfully participated in recognised proficiency testing schemes e.g. NPL and IAEA.

## 4. STATISTICAL ANALYSIS

The average annual percentage change (r) was used to quantify the rates of change in radionuclide activity concentration with time from the data at the four irregularly spaced monitoring times; 1980, 1992, 1997 and 2005. For individual periods this was given by using Eq. (1):

$$r = 100 \times \left(1 - \frac{m_2}{m_1}\right)^{1/t} \qquad (1)$$

where $m_1$ and $m_2$ are the measurements of activity concentration at times 1 and 2 and t is the period, in years, between these times.

A regression line was used to calculate rates of change covering more than two measurements. The natural logarithm of the activity concentration was regressed against time since the start of monitoring (in years). The slope, s, of the regression line was then converted to an average annual percentage change by applying Eq. (2):

$$r = 100 \times (1 - e^s) \qquad (2)$$

## 5. RESULTS AND DISCUSSION

Saltmarshes are highly dynamic environments with the extent of sediment, and therefore radionuclide deposition onto the saltmarsh, dependent on a number of factors including sediment type and particle size, sediment chemical and physical characteristics, ingress and egress routes of sediment during the tides, remobilisation, and effect of vertical mixing processes and presence of vegetation. To understand the temporal and spatial variation, this study focused on the $^{106}$Ru, which is a short lived isotope (371.5 days) and as such will reflect recent sedimentation, and the long lived radionuclides $^{137}Cs$ (30.05 years), Pu alpha ($^{238}Pu$, 87.74 years and $^{239+240}Pu$, 24100 years and 6561 years respectively) and $^{241}Am$ (432.6 years) which have contrasting environmental mobilities and sediment association characteristics.

Surface scrapes are routinely used for environmental monitoring and are highly influenced by the dynamic processes affecting sediment movement and deposition rates. Sedimentation rates for the saltmarsh of between 5.0 and 11.6 mm $y^{-1}$ have previously been reported (Marsden et al., 2006; Morris et al., 2000; Oh., 1999) therefore the samples taken for this study at a depth of 20 mm reflect short term deposition (1.7 to 4.0 years). The assessment of temporal and spatial sedimentation data allows the processes affecting the radionuclide distribution in saltmarshes and correlations with the history of Sellafield discharges to be determined. Previous work (Marsden et al., 2006, Morris et al., 2000) showed a high correlation between radionuclide activity and Sellafield discharge history for sediment cores from the saltmarsh; however, this observation is limited to a single fixed sampling point. Using detailed sedimentation rate data from sediment cores, we estimated the temporal and spatial variation in sedimentation rates across the entire saltmarsh and studied the effect on environmental processes and the relationship with discharge history.

This is a long term, comprehensive study with analysis carried out by a number of people at two organisations; therefore, there are constraints which limit the data set and prevent calculation of inventories. Nevertheless the data have value establishing the spatial and temporal variation across the saltmarsh. The samples were dried and ground prior to analysis, therefore analysis of the physical properties of the sediments was not possible. The 1980 and 1997 data have previously been published by Horrill (1983) and Oh *et al.*, (2009) respectively. Results are reported as geometric means along with minima, medians, maxima and arithmetic standard deviations.

**Mechanisms for Radionuclide Transport**

The Ravenglass saltmarsh is a sink for radionuclides with their mobility and distribution effected by a number of parameters. Pu-239/240 and $^{241}$Am activity concentrations in the North Eastern Irish Sea surficial sediments peaked in the late 1970's and early 1980's respectively and have decreased steadily, but to a lesser degree than that of $^{137}$Cs (Kershaw et al., 1999; Mitchell et al., 1999). Also as the distance from Sellafield to intertidal mud and saltmarsh sites increases, the activity concentrations of long lived radionuclides generally decrease (Kershaw et al., 1999; Mitchell et al., 1999; Sanchez et al., 1997). Radionuclide depth distributions reported in sediment profiles have shown that peak activity concentration, associated with the highest discharge rates from Sellafield, tends to occur at different depths and are dependent on the distance of the profile site from the saltmarsh seaward boundary (Oh., 1999). In this study, the activity concentrations of those radionuclides and $^{106}$Ru were considered. All have decreased significantly over the 25 years mainly due to the sedimentation of 'new' silt onto the saltmarsh which has lower associated activity due to the reduction in discharges from Sellafield.

Within the Ravenglass saltmarsh there are areas of low energy (calm, shallow water) which are only inundated by high Spring tides and are less prone to re-suspension. Fine particles settle more readily in low energy conditions and have the greatest sediment deposition (Howard et al., 1986; Chapman, 1941). High energy areas are inundated by daily tidal flow with less sedimentation occurring, particularly to the seaward part of the saltmarsh and adjacent to the railway bridge.

Colloidal and particulate radioactivity is deposited onto the saltmarsh during high tide. This sampling site has a highly asymmetrically tidal range pattern (Carr and Blackley, 1986) with the landward part of the marsh inundated infrequently by high Spring tides resulting in varying energy areas across the saltmarsh. The low energy areas are at the landward end of the saltmarsh and to a lesser extent the mid, elevated region. The seaward areas are classed as high energy areas where tidal inundation occurs daily with the channels across the saltmarsh becoming inundated almost as frequently dependant on the distance from the sea and the tidal phase.

The higher activity concentrations tend to occur lower down the saltmarsh depth profile near to the seaward edge and higher up the profile towards the landward edge (Oh., 1999). Generally, the pattern is due to lower sedimentation rates at the landward edge of saltmarshes and constant tidal reworking of sediments near to the main tidal channels (Friddlington et al., 1997) with the highest activity concentration in the surface sediments located in the areas of low energy where finer sediment is deposited. However, this increase in activity may only be temporary because there is a greater tendency for the associated small particles to become resuspended and distributed elsewhere (Friddlington *et al.,* 1997; Mackenzie *et al.,* 1999).

Stanners and Aston (1981) showed that grain size distribution of estuarine sediments influenced radionuclide activity, with fine grained sediments having high radionuclide absorptive capabilities. The sediment at sampling point B5 on the Ravenglass saltmarsh was found to be uniform material to a depth of ~1m, dominated by silt sized particles (40% 63-125µm; 24% 32-63µm; 21% 8-32µm; 4% 2-8µm; 7% <2µm). Due to the presence of plant roots, the top 50mm had an elevated organic content of 3.1% (Marsden et al., 2006). This agrees with Carr and Blackley (1986) who described the sediment on the saltmarsh as comprising mainly of sand and gravel with areas of silt and clay. Preferential accumulation of fine grained sediments was reported at the landward edge of the marsh (Oh et al., 1999). These sediments contained higher levels of $Al_2O_3$ in the top surface layer and a greater clay content. As particle size decreases, the activity concentrations of $^{137}Cs$, $^{241}Am$, $^{238}Pu$ and $^{239+240}Pu$ in sediments increases (Livens et al., 1988; MacKenzie et al., 1999). However particles less than 10µm exhibit cohesive behaviour, forming aggregates and associating with larger particles, which hinders re-suspension especially in low energy areas where there is less disturbance. If the sediment is disturbed by physical processes, high current velocities and/or bioturbation then the cohesiveness of sediment particles decrease (MacKenzie et al., 1999).

Vegetation on the saltmarsh acts as a physical trap for contaminated sediments, increasing activity concentration in associated sediments underlying vegetated areas. Horrill (1984) considered that the greater the period of time that the vegetation is immersed by the tide the higher the potential for deposition of radionuclide bearing sediment. The activity concentrations for all radionuclides measured in sediment were higher than for an adjacent grazed saltmarsh with a much lower vegetation biomass compared with our study ungrazed saltmarsh (Horrill, 1984). The actinide activity concentration was lower by a factor of three; however, factors such as the position, elevation and other characteristics of each saltmarsh relative to the tidal movement may greatly affect the extent of sediment deposition limiting the comparisons that can be made.

Livens and Baxter (1988a) and Livens and Baxter (1988b) stated that for surface sediments the chemical and physical association of a radioactive element were the major factors determining the bioavailability of a radionuclide. The degree of association of each radionuclide with sediment is governed by parameters such as geochemical behaviour of the elemental composition, chemical form of radionuclide, oxidation state, pH, salinity and organic content. Once associated with the sediment, deposition of radionuclides onto the saltmarsh is determined by many factors which influence the extent and site of sediment accretion.

### 5.1.1 Short lived nuclide: $^{106}$Ru

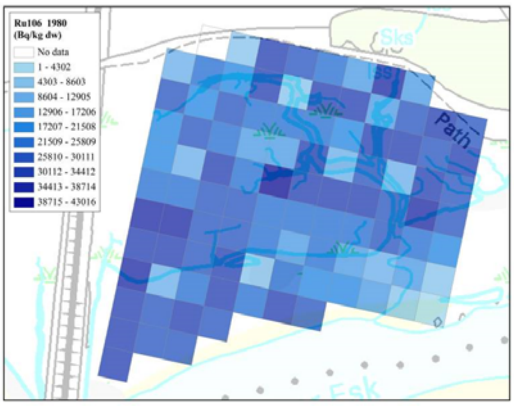
Ru-106 is a short lived radionuclide with a half-life of 368.2 days and exists in many complex species with the +2, +3 and +4 the most common. It is discharged from the pipeline as a nitrosyl complex which has high solubility characteristics. Stanners and Aston (1981) predicted it would take one month for this radionuclide to reach the estuary post discharge, therefore the activity concentrations reflect recent sedimentation. Ru has a strong association with soils/sediments with reported distribution coefficients ($K_d$) of $4 \times 10^4$ L kg$^{-1}$ (IAEA, 2004).

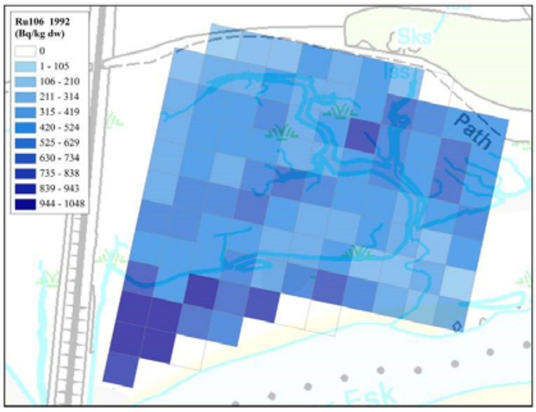
Over the 25 year period, for all the sampling points, the activity concentration decreased with an annual rate of change of almost 20%. The greatest rate of change occurred between 1980 and 1992 with a 27% per year activity reduction. Between 1992 and 2005 the activity concentrations decreased fivefold with an annual rate of change of 12%. The geometric mean and median for the 1992 and 2005 data are similar; however, for the 1980 results the distribution was biased towards the higher activity concentrations. (Table 1). Ru-106 was not determined in the 1997 samples.

Table 1: Ru-106 activity concentrations (Bq kg$^{-1}$ dry weight) across the saltmarsh for the different sampling periods

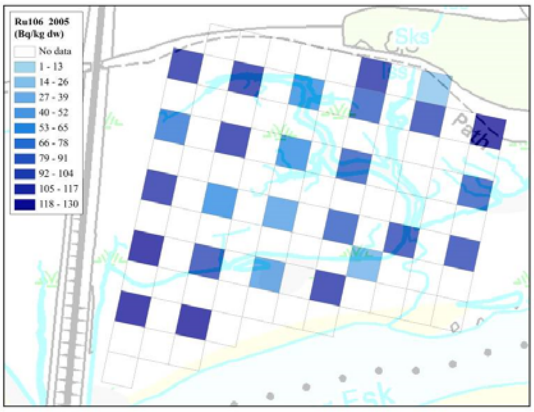
| Year | 1980 | 1992 | 2005 |
|---|---|---|---|
| Geometric Mean | 17200 | 468 | 82.2 |
| Median | 20300 | 463 | 96.8 |
| Minimum | 1620 | 110 | 22.4 |
| Maximum | 29300 | 1050 | 130 |
| Standard deviation | 6450 | 195 | 30.2 |
| Number of samples | 99 | 97 | 26 |

The spatial maps show enhanced $^{106}Ru$ content in the seaward saltmarsh and, to a lesser extent, in a band across the middle of the saltmarsh where there is also regular tidal ingress due to the presence of channels (Figure 3). The activity reflects recent sedimentation with the lower concentrations present in the less frequently inundated landward side of the saltmarsh. The spatial differences in activity concentration become less evident as time progresses consistent with decreased discharges. During the time period of 1980 to 1992, the activity of $^{106}Ru$ significantly decreased, most noticeably at the landward end of the saltmarsh and the least towards the seaward regions. Between 1992 and 2005 there was no significant spatial variation in the rate of change over the monitoring period.




**Spatial variation of $^{106}Ru$ (1980)** **Spatial variation of $^{106}Ru$ (1992)**




**Spatial variation of $^{106}$Ru (2005)**

Figure 3: Spatial distribution of the short lived radionuclide, $^{106}$Ru, at three time points (1980, 1992, 2005) at Ravenglass saltmarsh. The activity concentration is shown in Bq kg$^{-1}$ dry weight.

### <u>5.1.2 Labile nuclide: $^{137}$Cs</u>

Caesium exists as the monovalent cation in the environment which is not readily hydrolysed therefore highly soluble and mobile forming aqueous complexes. At the peak of the Sellafield discharges in 1975, $^{137}$Cs distribution coefficients ($K_d$) were reported to be 350 L kg$^{-1}$ (Baxter et al., 1979) which increased over time to 2 x $10^5$ L kg$^{-1}$ (Pulford et al., 1998). This was attributed to the significant decrease in activity discharged and the migration of the labile Cs fraction out of the Irish Sea basin (Marsden et al., 2006).

Sequential extraction studies showed the association of Cesium in surface layer of Cumbrian soils declined in the following order Residual>Exchangeable> Organic>Oxide>Adsorbed with Cs strongly associated with silicates, notably clay, becoming trapped within clay mineral lattices due to edge closure preventing ion exchange with leaching solutions (Livens and Baxter, 1988a and

Livens and Baxter, 1988b ). Oh (1999) reported variable concentrations of $SiO_2$ with the elevated levels in the mid to seaward (E3, F5 and Y3) regions.

Within saltmarsh systems, contaminated sediments are recycled and re-distributed (Kelly and Emptage, 1992), a phenomenon that has been reported in the Esk estuary (Bradley and Clapham, 1998). Morris at al. (2000) reported that due to the poor correlation with discharge data significant post-depositional remobilization of $^{137}Cs$ has occurred. During the period of maximum discharges, the saltmarsh mud patch sediments trapped approximately 10% of $^{137}Cs$ discharged, but by 1991 significant re-dissolution had occurred with ~75% of $^{137}Cs$ lost from the surface (<10cm depth) sediment (MacKenzie et al., 1999).

In the surface scrape samples analysed, the $^{137}Cs$ activity concentration reduced considerably over the 25 year time period from a geometric mean of 15 kBq $kg^{-1}$ dw in 1980 to 0.62 kBq $kg^{-1}$ dw in 2005 (Table 2). Over the 25 year period, for all the sampling points, the activity concentration decreased with an annual rate of change of almost 15%. The greatest rate of change occurred between 1980 and 1992 with a reduction in activity of 16% per year, similar for between 1992 and 1997 (14%). The decrease was less significant between 1997 and 2005 (rate of change of approximately 5%). The rates were typically consistent across the saltmarsh except for the landward sampling points B0 and E0, where the 1997 values were higher than those of 1992.

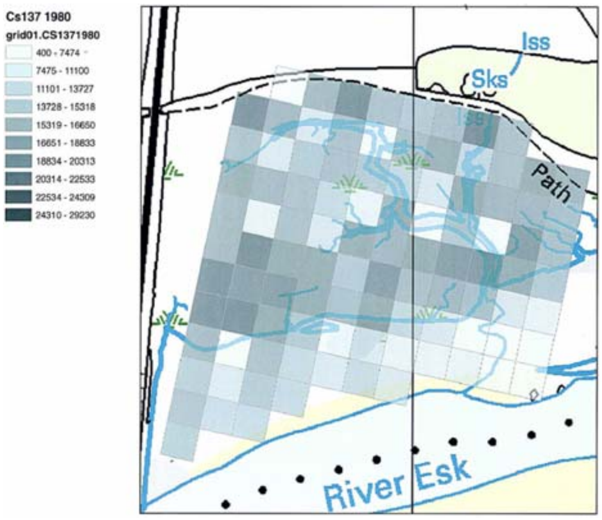
For the 1992 and 1997 time points the calculated geometric mean and median for the results were in good agreement, however there is bias towards the higher and lower activities for 1980 and 2005 respectively.

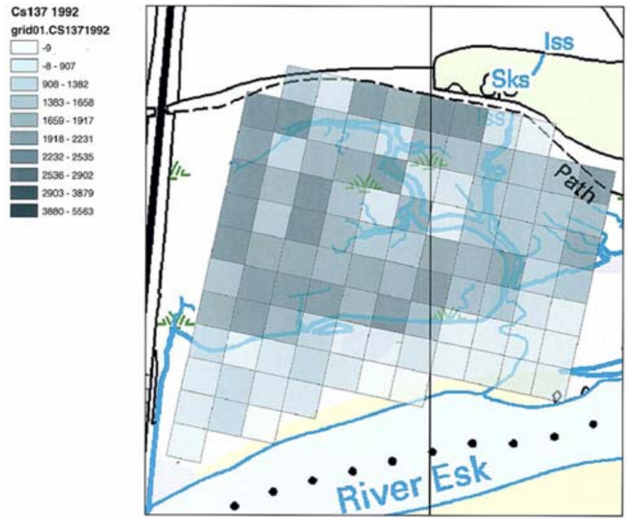
Table 2: Cs-137 activity concentrations (Bq $kg^{-1}$ dry weight) across the saltmarsh for the different sampling periods

| Year | 1980 | 1992 | 1997 | 2005 |
|---|---|---|---|---|
| Geometric Mean | 15100 | 1822 | 987 | 619 |
| Median | 17900 | 1894 | 989 | 581 |
| Minimum | 400 | 432 | 333 | 365 |
| Maximum | 29200 | 5560 | 5480 | 2090 |
| Standard deviation | 5900 | 1140 | 612 | 360 |
| Number of samples | 100 | 97 | 97 | 26 |

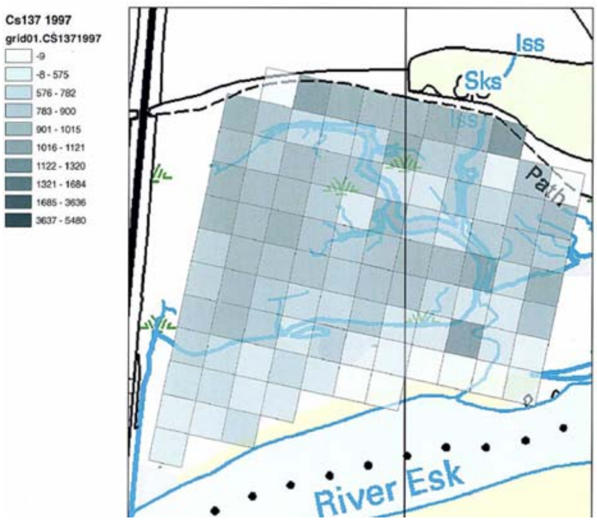
Substantial spatial variation in $^{137}Cs$ activity concentration occurred on the saltmarsh (Figure 4) with the highest activity concentrations in the low energy areas, at the landward end of the saltmarsh and the slightly elevated middle area. The sediments in these regions experience less tidal movement reducing the potential for remobilization of $^{137}Cs$, have a higher clay content which has a strong association with Cs and comprises of fine grain sediment that have high activity concentrations. Consistent with our data, Tyler (1999) reported high activity concentration of $^{137}Cs$ towards the landward side of the Caerlaverock saltmarsh in Scotland and considerable spatial variation in levels over the saltmarsh.

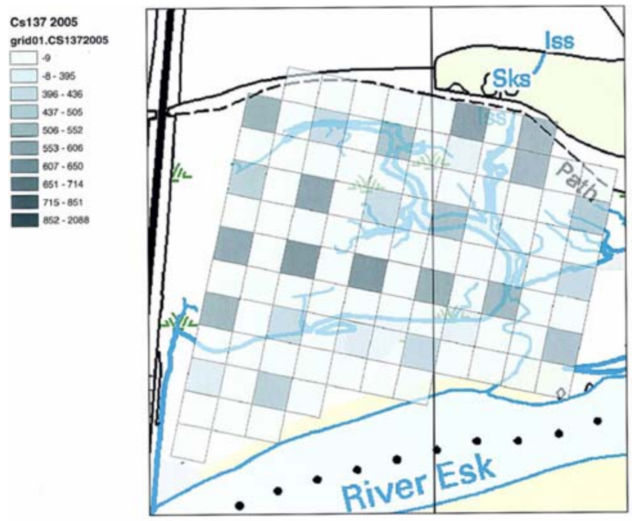
The spatial rate of change showed systematic trends over time. Between 1980 and 1992 the highest rates were observed at the seaward and eastern sides of the saltmarsh. This pattern was reversed during 1992 to 1997 with the most variation in rate of change at the middle and landward westerly side of the saltmarsh. The rate of change was lower between 1997 and 2005, with the greatest reductions in activity concentrations occurring at the landward easterly side of the saltmarsh.




**Spatial variation of $^{137}$Cs (1980).**




**Spatial variation of $^{137}$Cs (1992).**

**Spatial variation of $^{137}$Cs (1997).** **Spatial variation of $^{137}$Cs (2005).**

Figure 4: Spatial distribution of the labile radionuclide, $^{137}$Cs, at four time points (1980, 1992, 1997, 2005) at Ravenglass saltmarsh. The activity concentration is shown in Bq kg$^{-1}$ dry weight.

### 5.1.3 Actinides: Pu alpha and Am-241

The oxidation state of plutonium influences the radionuclides behaviour in the environment potentially existing in multiple states (predominantly +3 to +5) and affected by $E_h$, pH and ligand concentration (Choppin, 2006). The mobile and soluble pentavalent species, $PuO_2^+$, dominates in coastline or surface waters (Choppin and Wang, 1998) whilst in the marine environment it is present in the +3 and +4 oxidation states, hydrolysing with water to produce hydroxide precipitates. The complex chemistry enables plutonium transport in both the aqueous and particulate phases.

Americium is less redox active, existing as $Am^{3+}$, in the environment which like Pu hydrolyses to form hydroxide precipitates with transport due to attachment to particulates. Day and Cross (1981) estimated from discharge records that in 1980 27% of the total $^{241}$Am activity in the Irish Sea originated from the decay of $^{241}$Pu (half-life 14.4 years). Estimates showed that 95% of the Pu and the majority of Am within 12 hours of discharge associated with the sediment on the Irish Sea floor (Hetherington et al., 1978).

Both Pu and Am strongly associate with organic complex fractions in sediments (McDonald et al., 2001) with Pu (III/IV) is adsorbed to a greater extent than Pu (V/VI) (Nelson and Lovett, 1978). Measured distribution coefficients ($K_d$) in coastal waters have been reported as $10^6$ L kg$^{-1}$ for Pu (III/IV) and $10^4$ L kg$^{-1}$ for Pu (V/VI) with Am having similar values to Pu (III/IV) at 2.2-2.4x$10^6$ L kg$^{-1}$ (Marsden et al., 2006). The $K_d$ of Pu at three zones across the Ravenglass saltmarsh was determined by Livens et al. (1994) and varied between $10^4$ and $10^6$ L kg$^{-1}$.

Resolubilization at the saltmarsh was not considered to be a significant factor with other physical processes dictating Pu and Am movement (Livens and Baxter, 1988a and Livens and Baxter, 1988b). Consistent with this, the distribution of Pu and Am with sediment depth showed a good correlation with Sellafield discharge history data (Morris et al., 2000). Activity remobilised from the Irish Sea mud patch may be deposited onto saltmarsh sediment and retained in this ecosystem.

Over the 25 year period, the Pu alpha activity steadily declined from a geometric mean of 11 kBq $kg^{-1}$ dw in 1980 to 0.8 kBq $kg^{-1}$ dw with the highest rate of change between 1980 and 1992 showing a reduction of 16.2% (Table 2). For time periods 1992 to 1997 and 1997 to 2005 the rate of change was less significant showing a reduction of 5.4% and 3.3% per annum respectively with a 14-fold decrease in activity over the 25 years equivalent to an average of 9.54% per year. The geometric mean and median for the 1992, 1997 and 2005 data were similar, however the distribution is biased towards the higher activity concentrations for the 1980 results. There were five sample points where the activity concentrations increased between 1992 and 2005, of which two, E6, and F6, increased by 3.1- and 6.4-fold respectively. Two of these five sampling sites also had an increase in $^{241}$Am activity concentration suggesting that there have been similar environmental influences on both transuranic radionuclides, but not $^{106}$Ru and $^{137}$Cs. Both sites are at the seaward area of the saltmarsh where tidal movement is highest and the most likelihood of deposition from both the pipeline and as a result of transport of sediment form the offshore mud patch.

As with the other radionuclides, the activity of $^{241}$Am decreased over the 25 year period (Table 3), however the reduction was less significant compared to Pu alpha, $^{137}$Cs and $^{106}$Ru. In the saltmarsh, the $^{241}$Am activity concentration reduced from a geometric mean of 5.0 kBq $kg^{-1}$ dw in 1980 to 1.6 kBq $kg^{-1}$ dw in 2005. The highest annual percentage rate of change was in period of 1992 to 1997 (reduction of 12% per year); twice the rate of the preceding period (-5.9% per annum) and significantly higher than for 1997 to 2005. The geometric mean and median for the 1997 were similar, however for the distribution is biased towards the higher activity concentrations for the 1980 and 1992 results and lower activities for 2005.

The slower rate of reduction is partially due to decline in activity concentrations of sediments being offset by the ingrowth of $^{241}$Am from the decay of its parent nuclide, $^{241}$Pu. Marsden *et al.,* (2006) estimated that 17% of the current sediment inventory for $^{241}$Am activity was due to the in situ decay of $^{241}$Pu, with the highest rate of ingrowth between the late 1960's and 1980 due to the high $^{241}$Pu discharges and lapsed time for decay to occur. The observed activity was concluded to comprise of pipeline and ingrowth sources and $^{241}$Am from the off shore mud patch. Storage in mud patch sediments is likely due to the high affinity for Irish Sea Sediments compared to Pu and strong association with particulate material with geochemical differential of Pu and Am reported by Marsden *et al.,* (2006) and Day and Cross (1981).

Table 3: Pu alpha and Am-241 activity concentrations (Bq kg$^{-1}$ dry weight) across the saltmarsh for the different sampling periods

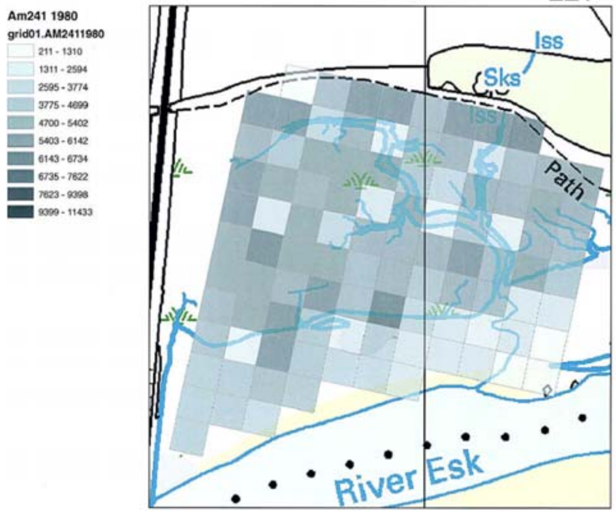
| Radionuclide | Year | 1980 | 1992 | 1997 | 2005 |
|---|---|---|---|---|---|
| Pu alpha | Geometric Mean | 11500 | 1540 | 1190 | 806 |
| | Median | 14700 | 1580 | 1190 | 840 |
| | Minimum | 229 | 519 | 412 | 494 |
| | Maximum | 26000 | 9410 | 4300 | 2100 |
| | Standard deviation | 5490 | 1060 | 496 | 342 |
| | Number of samples | 54 | 97 | 95 | 26 |
| Am-241 | Geometric Mean | 5040 | 2060 | 1460 | 1590 |
| | Median | 5980 | 2620 | 1470 | 1460 |
| | Minimum | 211 | 326 | 807 | 790 |
| | Maximum | 11400 | 8060 | 3960 | 4640 |
| | Standard deviation | 2160 | 1180 | 496 | 779 |

| | | | | |
|---|---|---|---|---|
| Number of samples | 100 | 97 | 95 | 26 |

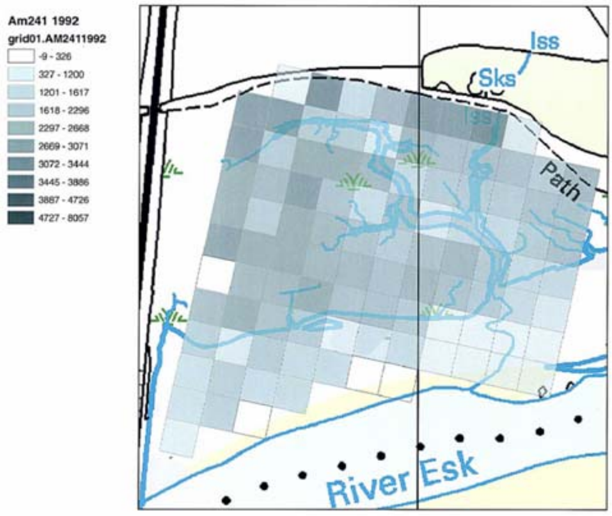
The spatial trends were similar to that of $^{137}Cs$ but less distinct, with the areas of lowest Pu alpha and $^{241}Am$ activity occurring in, or near, areas of high energy (and low sedimentation) areas. The highest activity concentrations were in the low energy areas where there is high sedimentation and vegetation trapping occurs especially towards the back of the marsh. The spatial data are given for $^{241}Am$ only in Figure 5 as these are the most complete data set with the same trends shown for Pu alpha. Consistent with our data, Tyler (1999) reported high activity concentrations of $^{241}Am$ in surface sediment towards the landward side of the Caerlaverock saltmarsh in Scotland and also elevated activity in the central area of the saltmarsh. The observed distribution was attributed to the age of the deposit, sedimentation rate and particle size characteristics.

For each of the three individual monitoring periods, there was a relatively uniform rate of change with no clear tendency for higher rates in particular areas of the saltmarsh. No significant spatial trends with time were apparent for any of the individual periods or for the complete monitoring period. There was a non significant tendency for the rate of change in Pu alpha and $^{241}Am$ activity to be greatest in high energy areas, but reduced more slowly than that of Cs resulting in less marked spatial variation with time.

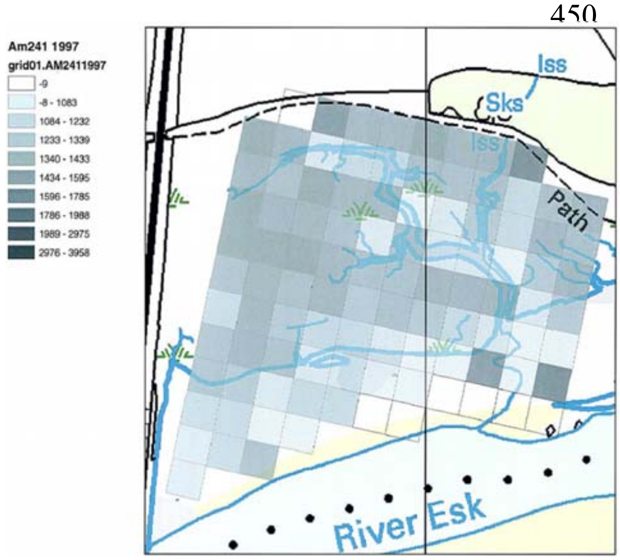
The rate of change in spatial variation has a higher tendency for Pu alpha compared with Am. This may be due to three factors (i) if Pu is present in the (III/IV) state it will be more strongly associated with particles than Am (ii) Pu is not continuously enhanced by nuclide ingrowth as is Am and (iii) the $^{238}Pu$ component of the Pu alpha has a physical half life of 87.7 years which is much shorter than that of Am.



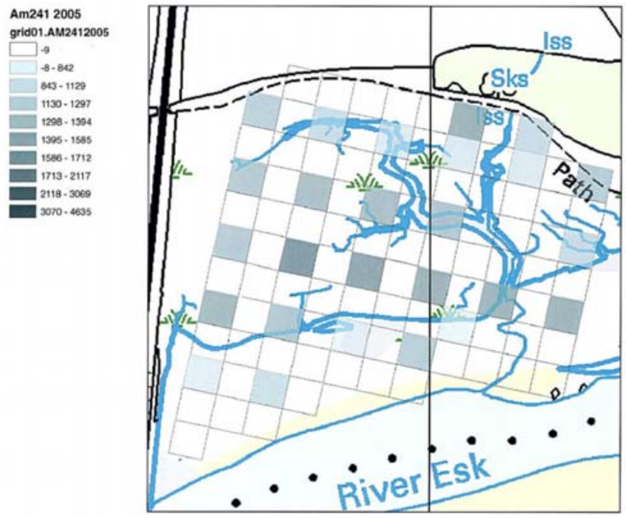

**Spatial variation of $^{241}$Am (1980).**




**Spatial variation of $^{241}$Am (1992).**




**Spatial variation of $^{241}$Am (1997).**




**Spatial variation of $^{241}$Am (2005).**

Figure 5: Spatial distribution of $^{241}$Am, at four time points (1980, 1992, 1997, 2005) at Ravenglass saltmarsh. The activity concentration is shown in Bq kg$^{-1}$ dry weight.

The rate of reduction with time, over the whole period, declined in the order: $^{106}$Ru>$^{137}$Cs>Pu alpha>$^{241}$Am and was markedly higher for $^{137}$Cs than for the other long-lived radionuclides. A number of factors contribute to the difference, including rates of discharge, physical half lives, chemical and physical association and higher rates of remobilisation of $^{137}$Cs, discussed below. The lower reduction rate for $^{241}$Am is partially due to ingrowth from $^{241}$Pu.

## **5.2 Sedimentation rates**

The Ravenglass saltmarsh has both high (seaward and to a lesser extent in the channels) and low energy areas (landward). The surface sediment samples taken from the seaward part of the marsh (

Figure 1, rows 6- 11) and, to a lesser extent, the creeks across the saltmarsh will incorporate more recently deposited sediment compared to the back of the marsh (row 0). Rates of accretion will also vary according the density and type of vegetation, height of the marsh relative to sea level and the distance from creeks (Aston and Stanners, 1979).

The correlation of sediment profiles and discharge rates from Sellafield varies due to the rate of sedimentation and redistribution of sediments (Friddlington et al., 1997). Sedimentation rates are a key parameter in understanding the spatial and temporal variation in radionuclide activity concentrations of the saltmarsh with varying values reported across the UK (Table 4).

Table 4: Sedimentation rates for saltmarshes across the UK

| Reference | Location | Method of calculation | Sedimentation rate (mm/yr) |
|---|---|---|---|
| Aston & Stanners (1979) | R Esk, Ravenglass | $^{134}Cs$:$^{137}Cs$ ratio | 65 |
| | | $^{134+137}Cs$, $^{106}Ru$, $^{144}Ce$, $^{95}Zr/Nb$ | 50-80 |
| Aston & Stanners (1981) | R Esk, Ravenglass | Pu isotope ratio | 13, 10 & 62 |
| Kelly and Emptage (1992) | R Esk, Ravenglass | Physical data | 4 |
| Marsden et al., (2006) | Ravenglass | Discharge data | 6.86 |
| Morris et al., (2000) | Ravenglass | Discharge data | 5.0 & 5.6 (Pu), 5.2 (Am), 4.8 (Cs) |
| Oh (1999) | Ravenglass | Model | 5.7 to 11.6 |
| Clifton & Hamilton (1982) | Newbiggin | | 5 to 34 |
| Hetherington (1978) | Newbiggin | $^{239}Pu$:$^{238}Pu$ ratio | 12 to 20 |
| Brown et al., (1999) | Longton, Ribble | Pu and Cs ratios | 7 (Pu) 7.9 (Cs) |
| Stanners & Aston (1981) | Cumbria and Lancashire coast line | $^{134}Cs$, $^{137}Cs$, $^{106}Ru$ | 0.25 to 71 |
| Harvey et al., (2007) | Southwick Merse & Orchardton Merse | Discharge data | Southwick:13-93 Orchardton:0 to 81 |
| MacKenzie & Scott (1982) | Scottish coast | Discharge data | 20-30 |
| MacKenzie et al., (1994) | Solway sediment | Discharge data | 65 and 32 |

To calculate the indicative sedimentation rates across the saltmarsh from surface scrape samples data, from a sediment core previously analysed by Morris et al., (2000) were used. A number of assumptions were also made:

- The saltmarsh as a whole has the same input source as the core at sampling point B5.
- Lag times across the saltmarsh are identical.
- Post depositional migration of radionuclides is insignificant.
- Fine particle distribution will be the same across the saltmarsh.

The only other input sources that affects the saltmarsh is from the River Esk, which will have had $^{137}Cs$ deposited due to the Chernobyl accident after the 1986 deposition as well as global fallout.

To calculate the lag times across the saltmarsh, the hypothesis stated in Stanners and Aston (1981) was used and the ratios of $^{134}Cs$ to $^{137}Cs$ and $^{106}Ru$ to $^{137}Cs$ at each sampling point and time period calculated. Where both ratios were low the sediment was classed as being deposited for some time or there was a long lag time from discharge of the effluent radionuclide to sediment deposition. Low $^{134}Cs$ to $^{137}Cs$ ratios and high $^{106}Ru$ to $^{137}Cs$ ratios indicated the sediment was recently contaminated and deposited with discharges less than half a year old. When applied to the 1980 data, the majority of the sampling points fell into the second category with lag times less than 0.5 years and recently contaminated. In the low energy areas (sampling points A1, A3, A4, V0, V4, V5, C1, X6, Y1 and E0) both ratios were low, indicating longer lag times or that the sediment had been deposited for a relatively long period of time. The ratios were also low for the 1992 and 2005 data (with the sole exception for B11 sampling point in 1992).

The sedimentation rates for a core taken at sampling position B5 (Livens pers comm.) of the Ravenglass saltmarsh where determined as 6.86mm/year and between 4.8 and 5.6mm/year (Marsden *et al.,* 2006; Morris *et al.,* 2000). The activity concentrations of the surface data from this study and for the two sets of sediment core data for B5 show a good correlation for $^{241}Am$, $^{137}Cs$ (Figure 6) and $^{238+239/240}Pu$.

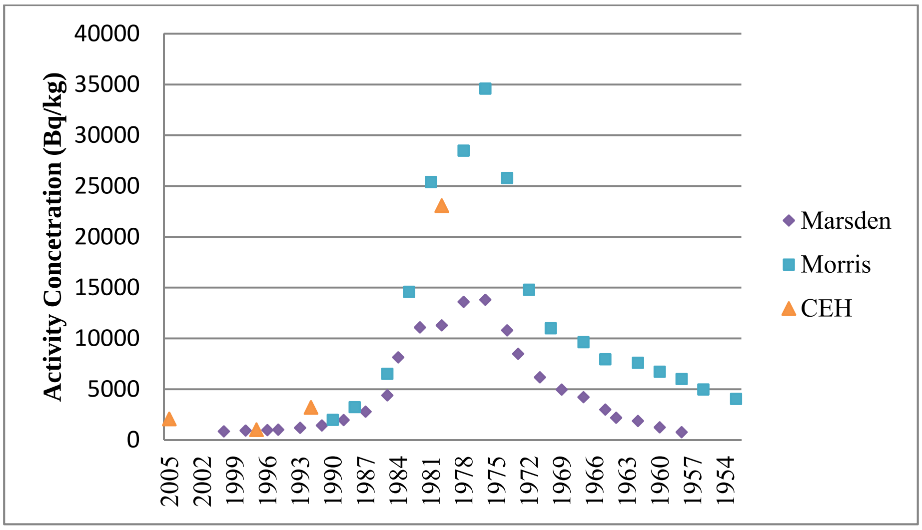



Figure 6: Comparison of $^{137}$Cs activity concentrations in surface scrape and sediment core data at sampling point B5.

The indicative sedimentation rates were calculated using the surface sample data. The ratio of activity concentration at a sampling point (e.g. A0) for two different times point (e.g. 1980 and 2005) using Eq. (3) for each radionuclide was calculated. Ru-106 was not used in the calculations due to the short half-life and data were not reported by Marsden *et al.*, (2006) and Morris *et al.*, (2000). Neither was Am-241 due to the ingrowth from the decay of its parent nuclide, $^{241}$Pu.

$$\text{Difference factor} = \frac{\text{Activity at sampling point A0 at } t_1}{\text{Activity at sampling point A0 at } t_2} \qquad (3)$$

Each difference factor (Eq. 3) was then divided by the difference factor at sampling point B5 for the same time interval (e.g. 1980 and 2005) and radionuclide producing a sedimentation factor. It was assumed that the difference factor at B5 was equivalent to the sedimentation rate over the period $t_1$ and $t_2$ using Eq. (4):

$$\text{Sedimentation factor} = \frac{\text{Difference factor}}{\text{Difference factor at B5}} \qquad (4)$$

To calculate the sedimentation rate (mm/year) at each sampling point for a specific time period, the sedimentation factor was multiplied by the corresponding sedimentation rate for B5 as quoted by Morris *et al.* (2000), including with and without mixing rates for plutonium and listed in Table 4 using Eq. (5):

$$\text{Sedimentation rate} = \text{Sedimentation factor} \times \text{Sedimentation rate at B5} \qquad (5)$$

To verify the method, the calculated sedimentation rates were compared with those at sampling points A3, B7/W7 and X6/X7 taken in 1996/1997 by Oh (2000) (Table **5**). Generally, the correlation is good between the sedimentation rates calculated using the values stated for the cores, for the time intervals 1992 to 1997 and for $^{137}Cs$ and $^{238+239/240}Pu$ with the rates reported by Oh (2000) are generally higher, but the same trends are evident.

| Nuclide | Time interval | Data Source | Sampling point | | |
|---|---|---|---|---|---|
| | | | A3 | B7/W7 | X6/X7 |
| Cs | 1997 | J'Oh no mixing | 5.50 | 9.00 | 9.60 |
| | 1997 | J'Oh with mixing | 7.00 | 12.0 | 12.0 |
| | 1980-1992 | CEH | 2.91 | 4.82 | 8.80 |
| | 1992-1997 | CEH | 5.14 | 4.94 | 5.93 |
| | 1980-2005 | CEH | 17.5 | 19.2 | |
| Pu239/240 | 1997 | J'Oh no mixing | 8.60 | 8.60 | 10.4 |
| | 1997 | J'Oh mixing | 10.6 | 10.6 | 12.7 |
| | 1980-1992 | CEH no mixing | 7.56 | 5.12 | 4.09 |
| | 1980-1992 | CEH mixing | 8.47 | 5.73 | 4.58 |
| | 1992-1997 | CEH no mixing | 2.13 | 5.33 | 7.44 |
| | 1992-1997 | CEH with mixing | 2.39 | 5.97 | 8.34 |
| | 1980-2005 | CEH no mixing | 8.89 | 14.0 | |
| | 1980-2005 | CEH with mixing | 9.96 | 15.6 | |

Table 5: Comparison of sedimentation rate (mm/yr) reported in the literature for cores taken at four sampling points

The sedimentation rates were then estimated for each data point and time period. This showed a high degree of variation in sedimentation rates (

Table 6) ranging from 0.12 mm $yr^{-1}$ to 37.2 mm $yr^{-1}$, which is similar to the variation reported by Stanners & Aston (1981). Using the calculated rates, the 20mm surface scrape samples taken correspond to between just over half a year to greater than 100 years of sediment accumulation. The geometric mean and median were in general good agreement with an average sedimentation rate for the 25 years of between 7.7 and 11 mm $yr^{-1}$.

| Nuclide | Time interval | Sedimentation rate mm $year^{-1}$ | | | | |
|---|---|---|---|---|---|---|
| | | Geometric Mean | Median | Minimum | Maximum | SD |
| Cs | 1980-1992 | 4.72 | 4.94 | 0.12 | 15.3 | 2.33 |
| | 1992-1997 | 3.45 | 3.64 | 0.24 | 9.90 | 1.70 |
| | 1997-2005 | 15.8 | 14.6 | 15.5 | 4.80 | 27.0 |
| | 1980-2005 | 10.9 | 12.4 | 2.73 | 26.7 | 5.33 |
| Pu (mix) | 1980-1992 | 3.86 | 4.35 | 0.70 | 11.0 | 1.97 |
| | 1992-1997 | 5.07 | 5.13 | 0.62 | 20.7 | 2.62 |
| | 1997-2005 | 13.1 | 13.5 | 5.60 | 37.2 | 6.26 |
| | 1980-2005 | 8.60 | 9.51 | 3.55 | 15.7 | 4.02 |
| Pu (no mix) | 1980-1992 | 3.45 | 3.89 | 0.62 | 9.87 | 1.76 |
| | 1992-1997 | 4.52 | 4.58 | 0.55 | 18.5 | 2.34 |
| | 1997-2005 | 11.7 | 12.0 | 5.00 | 33.2 | 5.59 |
| | 1980-2005 | 7.68 | 8.49 | 3.17 | 14.0 | 3.59 |

Table 6: Sedimentation rates across the saltmarsh for the different sampling periods

The data for the 1980 to 2005 time periods produced sedimentation rates which generally increased fourfold, which is due to an increase during 1997 to 2005. During this time period the vegetation present on the saltmarsh had markedly increased and a new triangular area of saltmarsh covered in vegetation was present at the lower, seaward end of the sampling transect.

## 6. CONCLUSIONS

The Ravenglass saltmarsh is a highly dynamic ecosystem with spatially varying rates of deposition of different radionuclides which also vary with time. The activity concentrations of all the nuclides on the Ravenglass saltmarsh have significantly decreased over the past 25 years as the discharges have decreased with the rate of change dependant on the radionuclide and location in the saltmarsh. The decline was in the following order: $^{106}$Ru> $^{137}$Cs> Pu alpha >$^{241}$Am. The low reduction rate for $^{241}$Am is partially due to ingrowth from $^{241}$Pu and as a result of transport of sediment from the offshore Irish Sea mud patch.

All the radionuclides considered showed spatial variation across the sampled site which became less distinct with time as activity concentrations declined. Ru-106 accumulated in areas of high energy, whereas the other long-lived radionuclides were more prevalent in low energy areas. However only $^{137}$Cs and, to a lesser extent, $^{241}$Am, showed statistically significant spatial variation in the rate of change over the monitoring period.

The time from discharge from the Sellafield pipeline to reaching the saltmarsh (lag time) was calculated using Cs and Ru ratio data and for the 1980 data set was predicted to be less than 0.5 years indicating recent contamination. However, for 1992 and 2005 the Cs and Ru ratios changed indicating the sediment had been deposited for some time or there was a long lag time from discharge of the effluent radionuclide to sediment deposition.

Surface scrape samples provide a pragmatic, practical method of measuring sediment contamination over large areas and a sampling approach adopted by most routine environmental monitoring programs. A method for calculating sedimentation rates across the saltmarsh using surface scrape and limited core data were presented. This approach has the advantage of estimating the degree of sediment deposition and reworking over a time period and large sampling area without the need for taking numerous core samples. The sedimentation data determined a rate of between 0.12 mm $yr^{-1}$ and 37.2 mm $yr^{-1}$ which is similar to the variation reported by Stanners & Aston (1981) for sites around the Cumbrian and Lancashire coastline. The geometric mean showed that the sedimentation rate across the saltmarsh for the 25 years is between 7.7 and 11 mm $yr^{-1}$ with the sampling site showing high levels of variation.

## AUTHOR INFORMATION

### Corresponding Author

Jane A Caborn

NNL Preston Laboratory

A709, Springfields,

Salwick,

Preston, PR4 0XJ

E-mail address: jane.a.caborn@nnl.co.uk

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Funding Sources

This work was part funded by the NNL's IR&D program.

## ACKNOWLEDGMENT

The authors would like to thank Dave Horrill, Professor Francis Livens and Valerie Kennedy for useful discussions and acknowledge their previous contribution to work reported here. Additional thanks to Kins Leonard (Cefas) for his scientific input.

## ABBREVIATIONS

dw, dry weight

CEH, Centre of Ecology and Hydrology

GAU, Geosciences Advisory Unit

NPL, National Physical Laboratory

IAEA, International Atomic Energy Authoirty

PIPS, passivated implanted planar silicon

## REFERENCES

Gray, J; Jones, S. R; Smith, A. D. Discharges to the environment from the Sellafield site 1951-1992. *J. Radiol. Prot.* **1995,** *15*, 99-131.

Howard, B. J.; Livens, F. R.; Walters, C. B. A review of radionuclides in tide washed pastures on the Irish sea coast in England and Wales and their transfer to food products. *Envir. Pollut.* **1986**, *93*, 63-74.

Kershaw, P.J., Pentreath, R.J., Woodhead, D.S., Hunt, G.J. A review of radioactivity in the Irish Sea. Aquatic Environment Monitoring Report No. 32, Ministry of Agriculture, Fisheries and Food, Lowestoft, **1992,** 65 pp.

Mackenzie, A. B; Scott, R. D; Allan, R. L; Shaban, B; Cook, Y. A; Cook, G. T; Pulford, I. D. Sediment radionuclides profiles implications fr mechanisms of Sellafield waste dispersal in the Irish Sea. *Journal of Environmental Radioactivity*. **1994.** 23, 36-69.

Pentreath, R. J, Lovett, M. B, Jefferies, D. F, Woodhead, D. S, Tarbot, J. W, Mitchell, N. T, Impact on public radiation exposure of transuranium nuclides discharged in liquid wastes from fuel element reprocessing at Sellafield, United Kingdom. Radioactive Waste Management. Vol. 5. Vienna: IAEA. **1984.**

Hetherington, J. A. The uptake of plutonium nuclides by marine sediments. *Mar. Sci. Commun.* **1978.** 4, 239-274.

Horrill, A. D. Concentrations and spatial distribution of radioactivity in an ungrazed salt marsh. In: *Ecological Aspects of Radionuclide Release. Brit. Ecol. Soc. Spec.* Coughtrey, P. J; Eds.; 1983, *3*, 199-215.

Oh, J-S.; Warwick, P. E.; Croudace, I. W. Spatial distribution of $^{241}$Am, $^{137}$Cs, $^{238}$Pu, $^{239,240}$Pu and $^{241}$Pu over 17 year periods in the Ravenglass saltmarsh, Cumbria, UK. *Applied Radiation and Isotopes* **2009,** *67* (7-8), 1484-1492.

Ordnance survey 2006 (1:10 000 Scale Raster and 1:1000 Landranger) maps reproduced with permission of The Controller of Her Majesty’s Stationery Office, © Crown copyright CEH, Lancaster Environment Centre, Library Avenue, Bailrigg, Lancaster, LA1 4AP. Agreement number 100017897.

Marsden, O.J.; Abrahamsen, L.; Bryan, N. D.; Day, P.; Fifield, L. K.; Gent, C.; Goodall, P. S.; Morris, K.; Livens, F. R. Transport and accumulation of actinide elements in near-shore environment: field and modelling studies. *Sedimentology* **2006**, *53,* 237-248.

Morris, K.; Butterworth, J. C.; Livens, F. R. Evidence of remobilization of Sellafield waste radionuclides in an intertidal saltmarsh, West Cumbria, U.K. *Estuar. Coast Shelf Sci.* **2000**, *51,* 613-625.

Oh, J. S. The migration and accumulation of radionuclides in the Ravenglass saltmarsh, Cumbria, UK. PhD thesis, Faculty of science, Southampton Oceanography Centre, **1999**.

Kershaw, P. J.; Denoon, D. C.; Woodhead, D. S. Observations on the redistribution of plutonium and americium in the Irish Sea sediments, 1978 to 1999: concentrations and inventories. *J. Envir. Radioact.* **1999,** *44*, 191-121.

Mitchell, P. I.; Condren, O. M.; León Vintró, L.; McMahon, C. A. Trends in plutonium, americium and radiocaesium accumulation and long-term bioavailability in the Western Irish Sea mud basin. *J. Envir. Radioact.* **1999**, *44,* 223-251.

Sanchez, A. L.; Horrill, A. D.; Howard, B. J.; Singleton, D.; Mondon, K. Anthropogenic radionuclides in tide-washed pastures bordering the Irish Sea coast of England and Wales. *Wat. Air Soil Pollut.* **1997**, *106*, 403-424.

Chapman, V. J. Studeis in saltmarsh ecology. *Journal of Ecology*. **1941**, 29, 69-82.

Carr, A.P; Blackley, M. W. L. Implications of Sedimentological and hydrological processes on the distribution of radionuclides. The example of a salt marsh near Ravenglass – Cumbira. *Limnol. Oceanogr.,* **1986**. 3 l(2), 266-276

Friddlington, M. A.; Allen, J. A. L.; McDonald, P.; Rae, J. E. Radionuclide depositional history in the Solway Firth. *Radioprotection – Colloques*; **1997,** *32* (C2), 293-298.

MacKenzie, A. B.; Cook, G. T.; McDonald, P. Radionuclide distributions and particle size associations in Irish Sea surface sediments: implications for actinide dispersion. *J. Envir. Radioact.* **1999**, *44*, 275-296.

Stanners, D. A; Aston, S. R. An improved method of determining sedimentation rates by the use of artificial radionuclides. *Estuarine, Coastal and Shelf Science.* **1981a.** 13, 101-106.

Livens, F. R.; Baxter, M. S. Chemical associations of artificial radionuclides in Cumbrian soils. *J. Envir. Radioact.* **1988**, *7*, 75-86.

Horrill, A. D. Radionuclide levels and distribution in grazed saltmarsh in West Cumbria. *Environmental Pollution Series B, Chemical and Physical*, **1984,** *8* (4), 265-280.

Livens, F.R., Baxter, M.S., Chemical Associations of Artificial Radionuclides in Cumbrian Soils. *Journal of Environmental Radioactivity*, **1988,** *7*, 75-86.

International Atomic Energy Authority (IAEA). Sediment distribution coefficients and concentration factors for biota in the marine environment. Technical report series No. 422. IAEA, Vienna, **2004**.

Baxter, M.S; McKinley, I.G; MacKenzie, A.B; Jack, Windscale Radiocesium in the Cylde Sea area. *Marine Pollution Bulletin*. **1979**. *10*, 116-120.

Pulford, I.D; Allan, R.L; Cook G.T; MacKenzie, A.B. Geochemical associations of Sellafield-derived radionuclides in saltmarsh deposits of the Solway Firth. *Environmental Geochemistry and Health*, **1998**, *20*, 95-101.

Kelly M, Emptage, M. Radiological assessment of the Esk estuary. UK DoE Report, DOE/HMIP/RR/015. DoE, London, **1992**.

Bradley, S. B.; Clapham, P. Contemporary flux of radionuclides to contaminated saltmarshes in the Esk estuary, Cumbria. *Wat. Air Soil Pollut.* **1998,** *107*, 175-184.

Tyler, A. N. Monitoring anthropogenic radioactivity in salt marsh environments through in situ gamma-ray spectrometry. *J. Envir. Radioact*. **1999**, *45*, 235-252.

Choppin, G. R, Actinide speciation in aquatic systems. *Marine Chem,* **2006,** 99 (1-4), 83-92.

Choppin, G. R, Wang, P. J, The Chemistry of Actinide Behavior in Marine Systems. *Aquatic Geochemistry*. **1998,** *4 (1)*. 77-101.

Day, J. P, Cross, J. E, $^{241}$Am from the decay of $^{241}$Pu in the Irish Sea *Nature* **1981**, 292, 43 – 45.

Hetherington, J. A. The uptake of plutonium nuclides by marine sediments. *Marine Science Communications*. **1978.** 4, 239-274.

McDonald, P.; Vives i Batlle, J.; Bousher, A.; Whittal, A.; Chambers, N. The availability of plutonium and americium in Irish Sea sediments for re-dissolution. *Sci. tot. environ.* **2001**, *267,* 109-123.

Nelson, D.M.; Lovett, M. B. Oxidation state of plutonium in the Irish Sea. *Nature* **1978**, *276,* 599-601.

Livens, F. R.; Horrill, A. D.; Singleton, D. L. Plutonium in estuarine sediments and associated interstitial waters. *Estuar. Coast. Shelf. Sci.* **1994**, *38,* 479-489.

Aston, S. R; Stanners, D. A. The determination of estuarine sedimentation rates by $^{134}$Co/$^{137}$Co and other artificial radionuclide profiles . *Estuarine and Coastal Marine Science.* **1979**, 9, 529-541.

Aston, S. R; Stanners, D. A. Plutonium transport to and deposition and immobility in Irish Sea intertidal sediments. *Nature.* **1981**, 289, 581-582

Clifton, R. J; Hamilton, E. I. The application of radioisotopes in the study of estuarine sedimentary processes. *Estuarine, Coastal and Shelf Science*. **1982**, 14, 433-466

Brown, J. E; McDonald, P; Parker, A; Rae, J. E. The vertical distribution of radionuclides in a Ribble Estuary saltmarsh, transport and deposition of radionuclides. *J. of Env. Rad.* **1999**. 43, 259-275.

Harvey, M. M; Hanson, J. D; MacKenzie, A. B. Constraints on the use of anthropogenic radionuclides derived chronologies for saltmarsh sediments. *J. of Env. Rad*. **2007**. 95, 126-148.

MacKenzie, A. B; Scott, R. D. Radiocaesium and plutonium in intertidal sediments from southern Scotland. *Nature.* **1982.** 299, 613-616.