UNIVERSITY OF SOUTHAMPTON

FACULTY OF NATURAL AND ENVIRONMENTAL SCIENCES

Ocean and Earth Sciences

Migration and distribution of ^{237}Np in saltmarsh sediments

by

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Thesis for the degree of Doctor of Philosophy

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ABSTRACT

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Neptunium is present in the environment from a number of nuclear related sources and due to its presence in High, Intermediate and Low Level wastes, long half-life ($t½ = 2.13 \times 10^6$ y), availability, high radiotoxicity and secondary source from ingrowth of ^{241}Am ($t½ = 432.6$ y, α) and ^{241}Pu ($t½ = 14.33$ y, β^-) is a major component of the dose commitment to the public. It is highly mobile in the environment and readily absorbed by man therefore radiologically significant especially for longer term waste management and safety case assessments.

Due to difficulties with analysis there have been limited studies of the behaviour of neptunium in the environment required to understand the impact of its mobility and distribution; important when considering the burial and storage of nuclear waste. A review of cited methods showed most were based on the analysis of ^{237}Np in a specific sample matrix. As the nuclear industry in the UK moves towards decommissioning phase, there is an increased demand for the analysis of more complex and varied samples types. In this study a method of the determination of ^{237}Np was developed which was capable of analysing a wide variety of sample matrices. During the development phase, the lack of reference materials, especially for ^{237}Np in solid matrices, became evident and to overcome a novel approach was developed using experimental design with the method scope based on elemental composition rather than sample type, increasing the flexibility of the method.

Since 1952 authorised releases of many fission products and transuranic radioisotopes, including ^{237}Np, have been discharged into the Irish Sea from the Sellafield nuclear site. The radionuclides become attached, dependent on particle reactivity, to sedimentary particles and incorporated by sedimentary deposition and suspension processes into intertidal and estuarine environments resulting in the contamination of the surrounding environment. Parallel to the coastline is an area of fine-grain size dominated sediments commonly known as the ‘mud patch’ where sedimentary particles, with associated radionuclides, accumulate as a result of tidal movement and currents in the shallow Western Irish Sea basin. Particulates are redistributed and deposited onto the saltmarsh as a result of tidal processes and storm events.

Ravenglass saltmarsh is a highly dynamic ecosystem situated in the mouth of the River Esk, 5 km from Sellafield site. Like other saltmarsh environments, sediment both rapidly accumulates and degrades due to perturbations in sea level and storm events retaining a chronological profile of radionuclide discharge history. Research has shown that the Ravenglass saltmarsh is one of the most radioactively contaminated areas within the Irish Sea due to the significant levels of radionuclides, accumulated during tidal processes. The developed method was used to analyse surface scrape samples taken over a twenty five year period and an intertidal marsh sediment core from Ravenglass saltmarsh to gain a greater understanding of the behaviour, distribution and mobility of ^{237}Np in the environment. Surface scrape samples provide a pragmatic method of measuring sediment contamination over large areas. The approach is used by most routine environmental monitoring programs, with the results used to calculate dose transfer factors and ascertain risk of exposure to the general public. The samples indicate recent contamination and are used in this study to identify temporal and spatial distribution across the saltmarsh. Samples from across the saltmarsh were analysed for a range of radionuclides (^{106}Ru, ^{137}Cs, Pu alpha, ^{237}Np and ^{241}Am) at four time points over the twenty five years. The greatest rate of change was reported for ^{106}Ru, ^{137}Cs and ^{237}Np followed by Pu alpha and ^{241}Am with a number of factors influencing the rate of reduction with time such as radiological half-lives, decreasing discharges and remobilisation. Considerable spatial variation for the different radionuclides across the saltmarsh was also 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. The variation shows the importance of sampling from the exact same location for long term studies to ensure any changes in data are not an artefact of spatial variation but reflect temporal trends.

The radionuclide profile of ^{237}Np was determined in a sediment core taken from the saltmarsh which had a distinct geochemical redox profile. The core had been previously analysed for other radionuclides (^{137}Cs, ^{241}Am and Pu α) showed a chronological profile which had a strong correlation with published Sellafield discharge records indicating that the sediment was largely undisturbed. The highest activities of ^{237}Np were in the upper sections of the profile with the presence of two minor peaks further down and activities decreasing to below the limit of detection at a depth of 21.5 cm. The profile was partially reconciled with the Sellafield effluent discharges however less defined than for other radionuclides. The lack of correlation was due to limited discharge data, increased ^{237}Np activities in the upper sections and a differing profile distribution compared to the other transuranic nuclides possibly indicating redistribution of Np within the core. The distribution profile was consistent with other cores sampled at the Ravenglass saltmarsh which did not show redox zonation indicating ^{237}Np is not redox sensitive in this environment.

Comparison of nuclide ratios in the surface scrape and core concluded ^{237}Np exhibited conservative behaviour, similar to ^{137}Cs, and activities closely reflecting Sellafield discharges due to the lower affinity for inorganic particles. This was in contrast to Pu alpha which exhibited a higher affinity for inorganic particles becoming strongly associated with the fine grained sediment and exhibiting non-conservative behaviour with input sources originating from discharge and the mud patch with results reflecting both current and historic contamination. Such information is essential in assessing the long-term behaviour of ^{237}Np in the environment, importance in radiological dose assessment and mobility and distribution in long term storage options such as geological disposal.

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DECLARATION OF AUTHORSHIP

I, JANE ADELE CABORN, declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

MIGRATION AND DISTRIBUTION OF ^{237}Np IN SALTMARSH SEDIMENTS

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;

2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;

3. Where I have consulted the published work of others, this is always clearly attributed;

4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;

5. I have acknowledged all main sources of help;

6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;

7. Parts of this work have been published as:

Caborn, J.A.; Howard, B. J.; Blowers, P.; Wright, S. M. Spatial trends on an ungrazed West Cumbrian saltmarsh of surface contamination by selected radionuclides over a 25 year period, *Journal of Environmental Radioactivity*, **2016**, 151, 94-104.

Signed:

Date:

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I dedicate this thesis to the three people in my life who have given me the most amazing support during my studies. To my Dad who without his support and belief in me throughout my life I would never have had the chance to undertake this study or many other opportunities. To John, my husband, for putting up with me as I have spent many an hour at my laptop, the supply of tea and most importantly the amazing encouragement. And lastly to my daughter Evie Mary who arrived in the middle of my studies and has been my inspiration to complete.

1 Introduction

Neptunium was the first synthetic transuranium element to be discovered in 1940 by Edwin McMillan and Philip H. Abelson at Berkeley Radiation Laboratory of the University of California. It was synthesised by bombarding ^{238}U with neutrons to produce ^{239}Np. In 1942, Neptunium-237 was discovered by A. C. Wahl and Glenn T. Seaborg also using neutron bombardment of ^{238}U, but this time with fast neutrons in the Berkeley cyclotron produced by the following reaction:

$$^{238}_{92}U\ (n\ ,2n)^{237}_{92}U\ \xrightarrow[\beta-,\ \ 6.75d]{}\ ^{237}_{93}Np$$

Neptunium is the fifth member of the actinide series and has 24 isotopes ranging from ^{225}Np to ^{244}Np. It exists in five oxidation states (from +III to +VII) with the IV, V and VI the most common. Np-237 is the most radiologically significant isotope, an alpha emitter with a long half-life ($t_{½}$= 2.1 x 10^6 y), high radiotoxicity and significant presence in the environment. It is an alpha decay product of ^{241}Am and heads the neptunium (4n+1) decay sequence ending with ^{209}Bi.

There are several anthropogenic sources of ^{237}Np in the environment:

- Nuclear weapons' fallout, with the total world integrated deposition of ^{237}Np from nuclear weapons' tests carried out between 1945 and 1963 estimated at 2,500kg (Holm et al., 1987). As a result of underground weapons testing at the Nevada Test Site and French Polynesia, the radionuclide inventory for ^{237}Np is 1.8 TBq and 0.25 TBq respectively (Hu et al., 2010).
- Np-237 is formed from ^{235}U and ^{238}U by neutron capture in thermal reactors with 760 g of Np being produced per ton of irradiated fuel (Germian et al., 1987).
- High level nuclear waste containing ^{237}Np is produced in large quantities as a result of the use of enriched uranium (^{235}U, ^{236}U) fuel rods used in nuclear reactor operations. The UK national inventory stated in 2013 the activity of ^{237}Np in high level waste, not already disposed of, was at 36 TBq increasing to 43 TBq by 2050 (NDA, 2013). The increasing activities mean that, after a few hundred thousand years, ^{237}Np will be the prevailing transuranic element in used nuclear fuel, by activity.
- Discharges from nuclear installations, including fuel reprocessing operations at Sellafield, have contributed 6.87 TBq of ^{237}Np to the environmental inventory between 1978 and 2014.
- In-situ decay of previously discharged ^{241}Am.

1.1 Problem definition

Why do we need to study ^{237}Np distribution and mobility?

Neptunium is present in the environment from a number of nuclear related sources and due to its presence in High, Intermediate and Low Level wastes, long half-life, availability and high radiotoxicity (Cohen, 1982; Hill et al., 1982) is a major component of the dose commitment to the public. It is highly mobile in the environment and readily absorbed by Man leading ^{237}Np to be classed as one of the thirty-seven priority radionuclides for Radioactive Waste Management's (RWM's) safety cases (NDA, 2014) and predicted to be the "most hazardous material in high-level nuclear waste in geological repositories from 10,000 to 30,000,000 years after disposal" (Thompson, 1982).

Often referred to as the "neglected actinide" (Thompson, 1982) due to difficulties with analysis there have been limited studies of the behaviour of neptunium in the environment especially regarding the factors which effect its mobility and distribution; important when considering the burial and storage of nuclear waste.

In Sellafield liquid discharges, ^{237}Np is present at lower activity concentrations compared to other transuranics however the levels do not decrease as rapidly and will increase over time due to ingrowth from ^{241}Am, raising the radiological importance of the radionuclide as shown in *Figure 1*. The most likely pathway for marine discharges of radioactive waste to land and into the human food chain via terrestrial pathways is through incorporation into sediments, particularly in tide washed pastures and grazed salt-marshes (Sanchez et al. 1999).

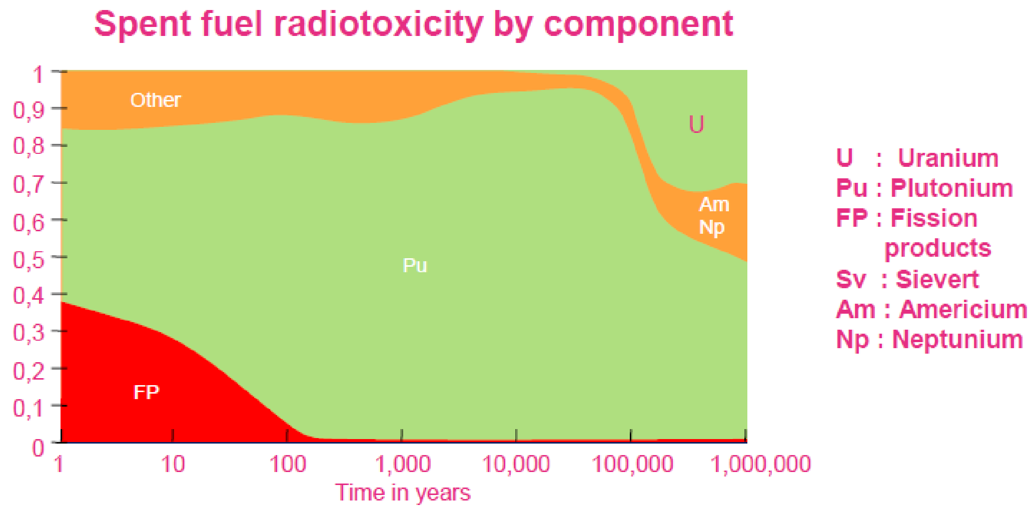

Figure 1 Spent fuel radiotoxic inventory versus time (Greneche, 2010)

Why is there a need to develop another method for the determination for ^{237}Np?

Presently, most existing methods focus on the analysis of a specific sample matrix and final measurement technique, for example determination of ^{237}Np soil and sediment samples by alpha spectrometry. As the nuclear industry moves towards decommissioning phase, there is a greater emphasis on the analysis of more complex and varied samples types. There is a need to develop flexible methods capable of analysing a wider scope of environmental and decommissioning matrices to support:

- Routine environmental monitoring of nuclear sites for public reassurance, to meet regulatory requirements and in case of an accidental release;
- Calculation of dose assessments to the public through analysis of foodstuffs;
- Characterisation of nuclear waste and facilities and subsequent clean-up operations;
- Characterisation of waste to enable treatment and/or categorisation for disposal;
- Research into the mobility and distribution of ^{237}Np in long term storage option such as geological disposal.

Development of a method which is robust, capable of determinations in a wide range of sample matrices and utilises with more than one final measurement technique would provide the flexibility laboratories require to achieve the analysis scope required.

How can you validate a method without reference materials?

The nuclear industry is a highly-regulated sector and is facing the challenges of decommissioning with an increased requirement for the analysis of a wide range of α, β and γ emitting radionuclides in diverse sample types. Radiochemical separation methods need to be flexible without compromising quality, essential to underpinning public and environmental safety and often demonstrated by accreditation of the analytical procedure to ISO 17025. This challenge of method validation is exacerbated by a shortage of reference materials which poses a “particularly serious weakness in the validation process when new methods are being introduced” (Parry, 2012).

The issue surrounding the shortage of reference materials has long been discussed and ideally certified reference materials would be analysed. However due to the shortage of such material a new approach is proposed whereby the scope is based on elemental concentration ranges and not the specific sample type and uses experimental design.

Prior to analysis, for most radiochemical separations, samples are solubilised using a total dissolution technique or leached to quantitatively extract the radionuclide of interest from the sample matrix. The elemental composition of the digested sample is then the main factor which affects the efficiency of separation, the analyte recovery and final measurement of the analyte. Experimental design can then be used to assess the impact of matrix elements on ^{237}Np recovery over a range of concentrations at key stages in the separation procedure. The overall impact of matrix composition on the method can then be evaluated and the operational envelope of the method defined in terms of matrix elemental composition thus providing the evidence for method development and validation.

Why study radionuclide behaviour around the West Cumbrian coastline?

The presence of Sellafield on the west coast of Cumbria and the activities associated with the operations have had an impact on the environment. The site has been integral to the UK's nuclear programme with spent fuel reprocessing, associated waste management operations and nuclear electricity generation all occurring. The reprocessing facilities on site have released authorised low level waste into the Irish Sea since operations began in the early 1950s, until termination of the effluent discharge in 1992. The liquid effluent discharged was a combination of purge water used in waste storage ponds and process liquors that originate from spent fuel reprocessing. The effluent contains actinides and fission products, which have a radionuclide fingerprint that changes over time reflecting operations at the Sellafield site. As the radionuclides accumulate in the mud patches in the Irish Sea and become distributed in neighbouring estuaries, a chronological history is produced which enables the study of the mobility and distribution of key radionuclides in the environment. These characteristics can be used to develop strategies in other areas of the nuclear industry such as waste characterisation and management, and the development of long term storage options.

What are the key Sellafield operations and how have they influenced the activity levels of ^{237}Np in the Irish Sea?

Sellafield is the largest nuclear complex in the UK. Onsite operations have changed over the years from its initial use as a munitions site to the current focus on waste management, reprocessing, spent fuel receipt, and decommissioning (Figure 2). The site is one of the world's largest contributors of anthropogenic radionuclides to the environment via the nuclear fuel cycle (Figure 3).

Neptunium-237 is routinely produced in nuclear reactors as a result of the neutron irradiation of ^{235}U and ^{238}U, the two most common constituents of nuclear fuel. Also it is a decay product of ^{241}Am.

Its presence in the nuclear fuel cycle is an issue of concern due to its long half-life, presence in spent nuclear fuels and stability as the pentavalent neptunyl ion and associated mobility in the environment under certain conditions.

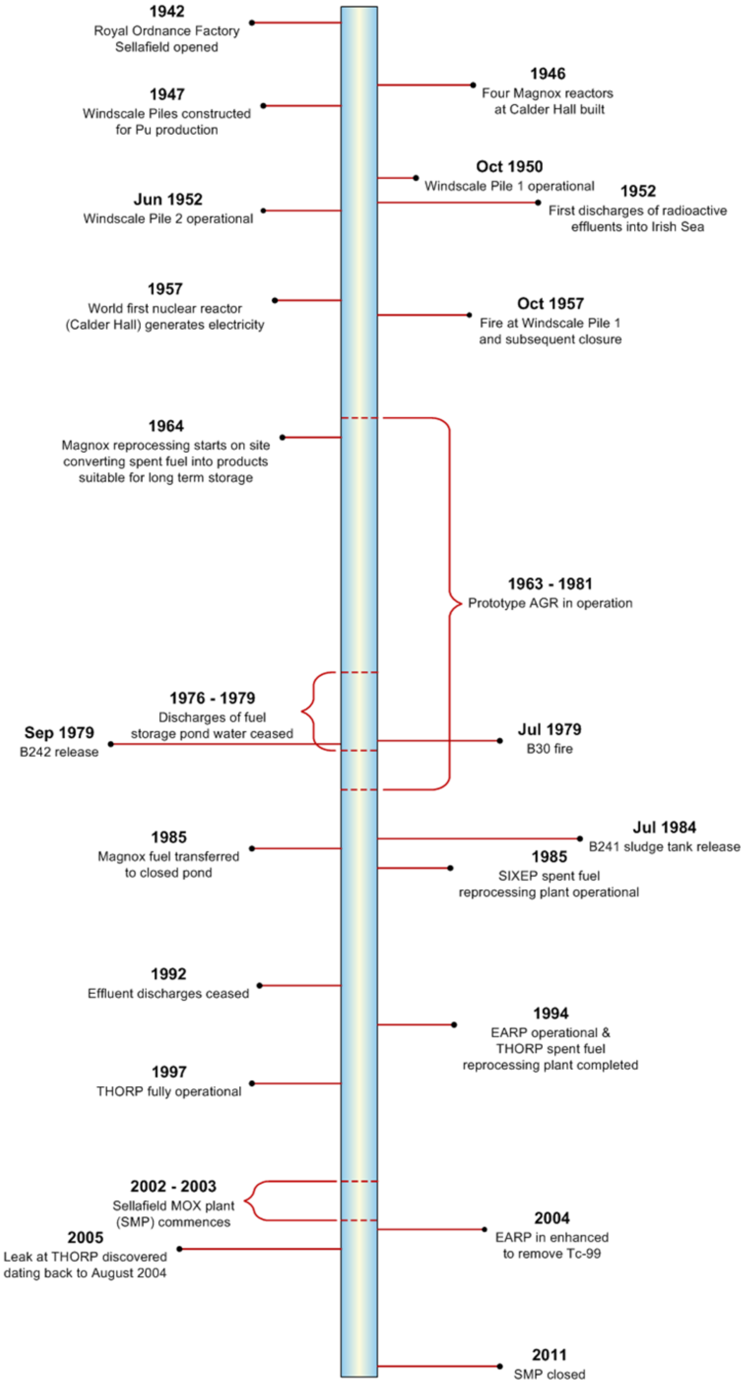

Figure 2 Timeline of operations and events at Sellafield Site, West Cumbria.

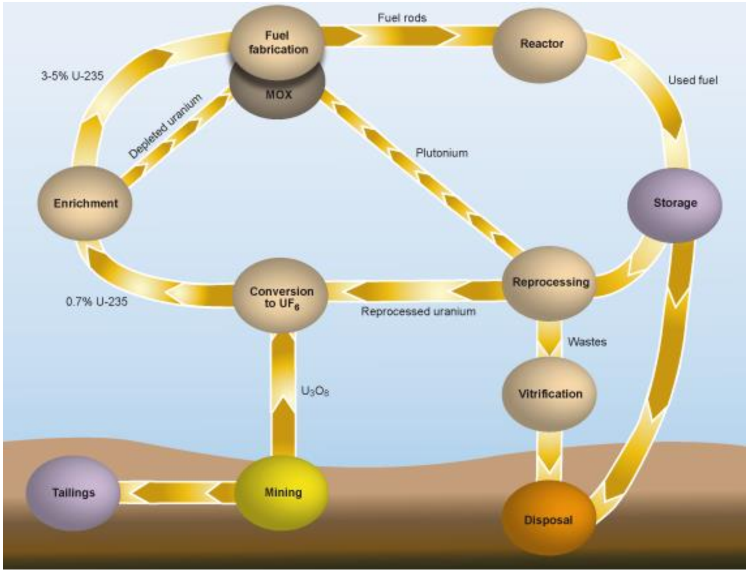

Figure 3 Nuclear Fuel Cycle (World Nuclear Organisation 2017).

Neptunium is treated as a waste during nuclear fuel reprocessing with the uranium and plutonium products separated and purified from it. It is then routed as high level waste for vitrification.

These outputs have originated from:

- Waste streams associated with the generation of nuclear power;
- Accidental releases of radioactivity;
- Authorised effluent discharges into the Irish Sea from 1952-1992.

At Sellafield ^{237}Np is present from a number of sources:

- Used nuclear fuel (UNF): After a few hundred thousand years ^{237}Np will be the prevailing transuranic element in UNF.
- Radioactive Decay: The levels of ^{237}Np in stored wastes and nuclear fuel is increasing as formed by the alpha decay of ^{241}Am.
- Discharges and releases due to reprocessing operations.

Np-237 was first reported in Sellafield's annual discharge inventory in 1979 when the activities of most of the radionuclides had started to decline. As a consequence, it is difficult to collate the activities with the changing events which have occurred on site (Figure 4) prior to the mid 1980's.

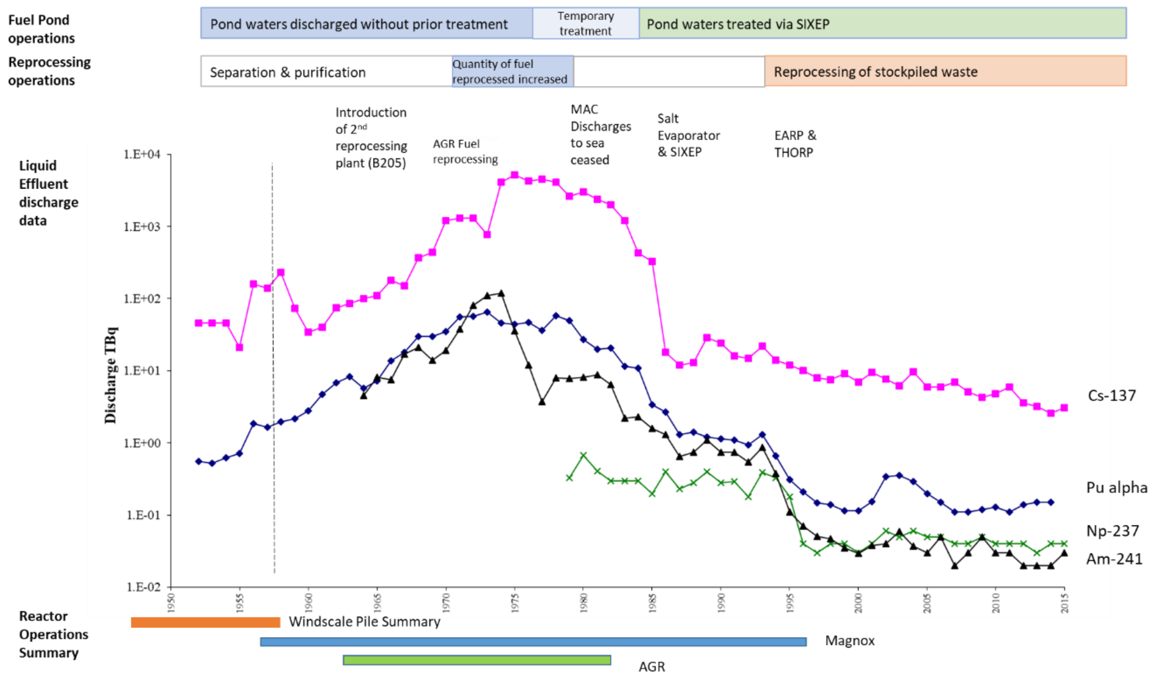

Figure 4 Radionuclide activities in liquid effluent discharges in comparison to key events at Sellafield site.

The activities of ^{237}Np are seen to decline which aligns with the commissioning of the Site Ion Exchange Effluent Plant (SIXEP) facility and Enhanced Actinide Removal Plant (EARP) on site. SIXEP is an effluent plant, commissioned in 1985, which treats liquid effluents from several plants across the site to reduce the radioactivity content. The plant settles out and filters solids using a carbonation process to neutralise the alkaline pond water. Ion Exchange, using Clinoptilolite, then removes the radionuclides. The plant was designed to remove the major contributors to soluble activity (predominantly ^{137}Cs and ^{90}Sr) and alpha emitting particulate material from pond effluents before sea discharge.

The Ion Exchange process will not significantly reduce the ^{237}Np content of the effluent, however the initial filtration will remove any ^{237}Np which is associated with particulates. EARP was commissioned in 1994 removing the radioactive components from liquid waste streams that originated from the plants which supported Thorp and Magnox reprocessing. The ^{237}Np activities around this time showed a step reduction and have since become relatively constant. The EARP process is primarily focused on the removal of actinides from processing effluents by a reaction with an iron oxyhydroxide floc. The mechanism for removal of other radionuclides, including ^{237}Np, during floc formation under processing conditions is not fully understood.

Why study the accumulation of ^{237}Np in saltmarsh sediments?

The definition of a saltmarsh is “an area of coastal grassland that is regularly flooded by seawater” (Oxford English Dictionary) with an estimated 44,370 ha of active saltmarsh around the UK (Allen and Pye, 1992). They are ecosystems in the upper coastal intertidal zone between land and open salt water where frequent tidal inundation occurs. Salt tolerant vegetation are present which are essential to the stability of the salt marsh, trapping and binding sediments. Deposition and accretion of sediments occurs in the dynamic environment followed by degradation as a result of perturbations such as sea level rise or storm events (Dyer et al., 2002). Relatively high sedimentation rates, stabilisation of sediment by vegetation and low sediment mixing rates result in the generation of chronologies of pollution history.

The saltmarshes in the vicinity of Sellafield act as sinks for radioactivity discharged from the Sellafield site. Scrape samples indicate recent contamination and provide a spatial and temporal source of data to study the effect of physical processes on radionuclide distribution. The saltmarsh has high and low energy areas impacting on radionuclide distribution and allowing the factors affecting the distribution regime of ^{237}Np to be studied. Surface scrape samples are routinely taken for environmental monitoring programs with the results used to calculate dose transfer factors (e.g. the pathways from crops to sheep or inhalation). Varying distribution across the saltmarsh may impact on long term data assessments and impact on environmental monitoring if samples are not taken from the exact same location.

A sediment core was also analysed from the saltmarsh. As the discharge profiles from Sellafield are retained, a chronological record of radionuclide activities formed as the sediment accumulates over time is preserved. This enables the activity profile to be related back to the discharges and geochemistry to evaluate radionuclide behaviour.

1.2 Summary and aims of the study

There is a requirement for the development of an analytical method which is capable of analysing ^{237}Np in a range of sample matrices to increase the capability of laboratories and to meet the future challenges of the nuclear industry. The method will then be used to analyse sediment samples from an ungrazed West Cumbrian saltmarsh to understand, including the factors which effect, the distribution and mobility of ^{237}Np. This will include comparing the findings to other radionuclides, elemental data and Sellafield discharge histories.

The aims of this study were three-fold:

1. To develop and validate a method for the determination of ^{237}Np in low-level wastes and environmental samples;

2. To determine the activities of ^{237}Np, and other key radionuclides, in surface scrape and sediment core samples;

3. To interpret the above results in terms of the behaviour of ^{237}Np, and other key radionuclides, in the saltmarsh environment.

1.3 Research approach

The study of the behaviour of ^{237}Np in saltmarsh samples requires the development of an analytical method which is robust with a high level of precision to ascertain the chemical behaviour of ^{237}Np in the sediments. An inventory of ^{237}Np in a saltmarsh should be made and compared to other radionuclides and elemental composition to determine the temporal and spatial distribution and the factors that influence its distribution, mobility and behaviour.

Chapter 2 is dedicated to a review of the chemistry of ^{237}Np and the current methods presented in the literature. This paper reviews the literature for techniques associated with the separation and quantitative determination of ^{237}Np in environmental samples. It identifies the key aspects that effect analysis in several separation techniques, from initial sample preparation to final determination, along with the associated chemistries. Published analytical methods are also presented in more detail as a summary table (Table , Appendix A).

Chapter 3. Many analytical methods have been developed for the determination of ^{237}Np in environmental and nuclear decommissioning samples, however generally focus on the analysis of a specific sample matrix and final measurement technique. As the nuclear industry moves further into decommissioning there is a need to develop a method which has a more flexible scope. This chapter details the optimisation of a method for the analysis of ^{237}Np in a wide variety of sample matrices and includes two different final measurement techniques. Each stage has been optimised to allow for flexibility and considers the knowledge gaps identified in literature reviews (Thakur, 2012).

Chapter 4 outlines the development and validation of a method for the determination of ^{237}Np using a novel approach employing experimental design. The statistical, experimental design, approach was used to determine which elements, at what concentrations, affected the recovery of ^{237}Np at different separation stages. The impact of matrix elements on ^{237}Np recovery was evaluated for the entire method and the potential to interfere with final measurement. This allowed for the development of an operational envelope for the method defined in terms of sample elemental concentrations instead of the traditional approach of by sample matrix.

Chapter 5. 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. By measuring the variations in radionuclide activity in surface scrape samples in a contaminated ungrazed saltmarsh near Ravenglass, Cumbria at four time period the long term spatial and temporal were determined. This chapter details the determination of the rates of change and spatial variation of key radionuclides (^{106}Ru, ^{137}Cs, Pu alpha and ^{241}Am) over the saltmarsh and identification of the contributory factors. The use of surface scrape samples does not allow for interpretation of the effect of variation in sedimentation rates. It also proposes a method for calculating indicative sedimentation rates across the saltmarsh using surface scrape data.

Chapter 6. Following on from the previous chapter, ^{237}Np was determined in the same sediment scrape samples to determine long term spatial and temporal variations over a twenty five year period and the contributing factors which impact on its distribution and mobility. Comparison of the Np, Pu and Cs isotopic compositions was also carried out to identify the oxidation state chemistry of ^{237}Np in the saltmarsh environment.

Chapter 7 describes the activity depth profile of ^{237}Np in a sediment cores taken from the Ravenglass saltmarsh. It outlines the distribution profile in the sediment core and correlation with cores previously analysed from the Ravenglass saltmarsh and Sellafield effluent discharges. Further comparison of distribution profile of ^{237}Np with the cores geochemical redox profile and spatial variation enabled identification of the factors which influence the inventory.

1.4 Notes on the presentation of papers

In several instances, the research has been prepared for publication or published in papers in peer-reviewed journals. These papers have been presented in their entirety as discrete sections within

Chapters in the thesis. Where this is the case, the journal and status of submission is clearly stated at the start of each Chapter. Referencing is in the style consistent with the style required by the respective journal with the lists of references that are specific to the paper are given at the end of each Chapter rather than at the end of the thesis.

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2 Review of Analytical Techniques for the Determination of Neptunium-237 in environmental samples

2.1 Abstract

As the nuclear industry moves further towards decommissioning there is more emphasis on the analysis of more varied samples types and less on the routine resulting in the development of methods which are flexible with varying purification, separation and/or determination stages. This paper reviews the literature for techniques associated with the separation and quantitative determination of ^{237}Np in environmental samples. The review identifies the key aspects that affect analysis in a number of separation techniques, from initial sample preparation to final determination, along with the associated separation chemistries. Published analytical methods are also presented in more detail as a summary table (Table).

2.1.1 Introduction

The majority of existing neptunium (Np) is a synthetic element and the fifth member of the actinide series with 20 stable and 4 meta stable isotopes ranging from ^{225}Np to ^{244}Np. The most radiologically significant isotope and the one discussed in this study is ^{237}Np, an alpha emitting radionuclide (4771.4 keV, 23.0% yield and 4788.0 keV, 47.64% yield) [1] with a half-life of 2.144 x 10^6 years. Neptunium-237 is an alpha decay product of ^{241}Am and heads the neptunium (4n+1) decay sequence ending with ^{208}Tl.

All primordial ^{237}Np has decayed so the nuclide is only found naturally in trace quantities in minerals containing uranium and thorium as a result of (α, n) and (γ, n) reactions within the mineral itself. The main sources of ^{237}Np in the environment are nuclear weapons' fallout, cooling water from fission reactors, industrial processing of ^{237}Np produced in fission reactors, presence in high level nuclear waste and from the in-situ decay of previously discharged ^{241}Am [2]. The total world integrated deposition of ^{237}Np from nuclear weapons' tests is estimated at 2500 kg [3]. Neptunium- 237 is formed from ^{235}U and ^{238}U by neutron capture in thermal reactions, by alpha decay from ^{241}Am (see Figure 5). In spent fuel from a Pressurised Water Reactor (PWR) approximately 13 GBq of ^{237}Np (equivalent to approximately 0.5 kg ^{237}Np) is contained in each tonne of spent nuclear fuel [3,4,5,6].

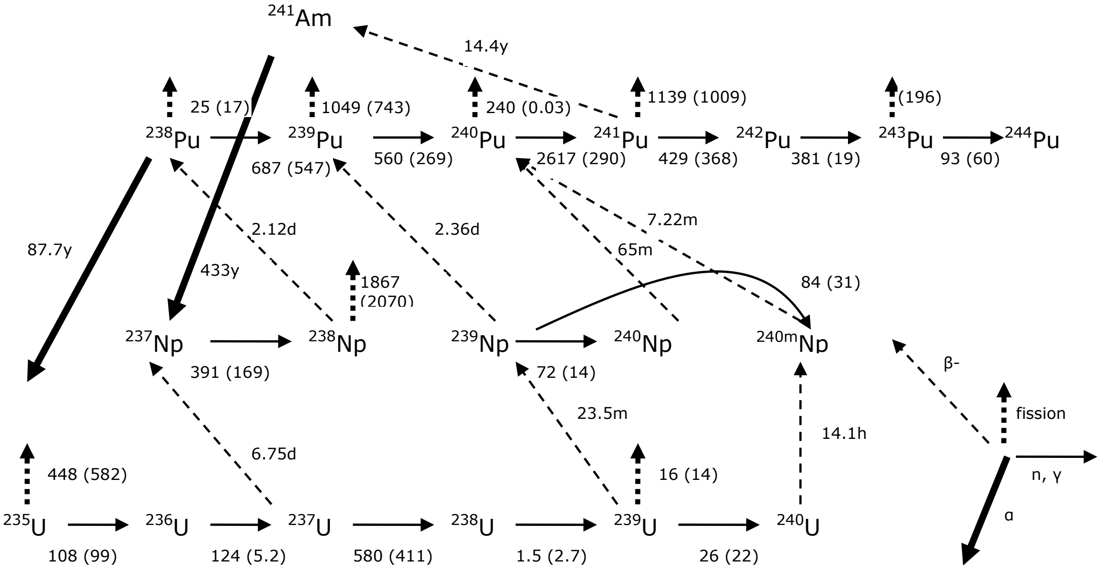

Figure 5: Production routes of neptunium-237. Figures along the arrows are half lives (indicated by units) or effective cross sections [5]

The chemistry of ^{237}Np is complex compared with other actinides leading the nuclide to be described as the 'neglected actinide' [7,8]. As an f block element, the 5f electron shell is unfilled ([Rn] $5f^4 6d^1 7s^2$). The 5f electrons have lower binding energies and less effective shielding than the 4f electrons allowing the formation of multiple oxidation states and complex species [9]. In solution Np has five ionic oxidation states, Np^{3+} (analogous to the rare-earth ion Pm^{3+}), Np^{4+}, NpO^{2+} and NpO_2^{2+}. The element forms tri- and tetra-halides and, like other actinides, a dioxide neptunyl core (NpO_2) [10]. Np(III) is stable in water, easily oxidised in air and is a powerful reductant with a standard potential of -1.856 volts [11]. $Np^{3+}_{(aq)}$ will precipitate as an insoluble hydroxide in alkaline solutions which do not form soluble hydroxyl anions with water [10]. Neptunium (IV) is a mild reductant and oxidises to NpO^{2+} in air with an electrode potential (E_O) of 0.749 volts [11]. In acid or neutral solutions Np(IV) hydrolyses to form colloidal hydroxyl compounds. In alkaline solutions, it precipitates as insoluble, metastable $Np(OH)_4$ which slowly changes to stable NpO_2.

Neptunium (IV) forms stable complexes with fluorides and sulphates but will only complex with chlorides and nitrates in the presence of concentrated acids [10]. Np is stable in the Np(V) state in acidic and basic solutions. In aqueous solution the ion is too acidic to exist and immediately reacts with water to form stable NpO^{2+}, present in acidic solution as $NpO^{2+}_{(aq)}$ and in alkaline solution as the soluble hydroxyl-anion, $NpO_2(OH)_2$. Neptunium (VI) is stable in both acidic and basic solutions but is only formed at high redox potentials. Like Np^{5+} the $Np^{6+}_{(aq)}$ is too acidic to exist in aqueous solutions and reacts immediately with water to form NpO_2^{2+}, present in alkaline solution as $NpO_2^{2+}{}_{(aq)}$. Neptunium (VII) is stable in alkaline solutions as $NpO_5^{3-}{}_{(aq)}$ or $NpO_2(OH)_6^{3-}{}_{(aq)}$ and is a strong oxidising agent in acid media [10].

Neptunium in the (III) and (VII) oxidation state is highly reactive and is unlikely to exist in the environment. Under moderately oxidising conditions in the environmental pH range (pH 4 to 10) Np in the pentavalent state as NpO_2^+ is the most commonly occurring species. The ion is soluble and therefore mobile in the environment. NpO_2^+ sorbs weakly onto colloids and in contrast irreversibly onto marine carbonate species [12]. Neptunium (V) is the predominant Np species (> 90%) in oxidised seawater except under strongly oxidising conditions when NpO_2^{2+} is formed [12,13]. In solutions with carbonate concentrations of $\leq 10^{-4}$M approximately 95% of the Neptunium is present as NpO_2^+. At higher CO_3^{2-} concentrations Np forms $NpO_2(CO_3)^-$, $NpO_2(CO_3)_2^{3-}$ and $NpO_2(CO_3)_3^{5-}$ [12]. The distribution coefficient of ^{237}Np between suspended particulate matter and seawater in the Irish Sea ranges from $2.4\text{x}10^{-3}$ to $3.3\text{x}10^{-4}$. The distribution coefficient (K_D) decreased with increasing distance away from the Sellafield pipeline which may be due to a change in oxidation state as Neptunium is discharged in the IV state and could be subsequently oxidised to Np(V). However other factors such as differing suspended particle size and mineralogical composition need to be considered [119].

In the terrestrial environment Np(V) sorption can occur directly or via reduction to the tetravalent state by surface reactions e.g. with Fe(II) bearing minerals. Adsorption of Np to soil constituents was not simply due to ion exchange and proceeds more slowly than for other actinides [12]. In the aquatic environment Np behaviour is similar to that in the terrestrial surroundings with Np(V) less associated with the sediment and particulate fractions. The sediment-water distribution coefficient in open ocean and ocean margins is $1\ \text{x}10^{-3}$ [14].

Neptunium-237 is present at low levels in the environment with global fallout levels of ^{237}Np are less than 10^3 Bq per kg of soil and per m^3 of seawater [15]. Elevated levels are detected as a result of nuclear operations as illustrated in Table 1.

Table 1 Np-237 concentration in the environment (Bq kg^{-1} dry weight for soils/sediments and fresh weight for biota unless stated).

Location	**Origin**	**Material**	**^{237}Np activity**	**Reference**
Ribble Estuary	Sellafield, UK	Shrimps	0.00035	[16]
St Bees		Winkles	0.020	[16]
Nethertown		Winkles	0.043	[16]
Sellafield coastal area		Crabs	0.058	[16]
Sellafield coastal area		Lobsters	0.016	[16]
Sellafield coastal area		Winkles	0.016	[16]
Sellafield Offshore area		Plaice	0.00060	[16]
Drigg		Winkles	0.019	[16]
Riveracre Brook,	Capenhurst, UK	Sediment	<1.0	[16]
Riveracre Brook		Freshwater	<0.10 Bq	[16]
40km NW Munich, Germany		Grassland soil	0.06 to 1.05	[17]
Stevens Hill, Pennsylannia, USA		Soil	1.81 - 2.20 atoms g^{-1}	[18]
Goury	La Hague, France	Seawater	0.00008	[6]
Goury		Fucus serratus	0.0036	[6]
Goury		Winkles	0.0057 (shell) 0.0020 (flesh)	[6]
North, Barents & Greenland seas		Surface water	0.00034 to 0.011	[3]
Fukui & Ishikawa Prefecture, Japan		Soil/sediment	0.0020 to 0.0031	[19]
Chernobyl, Russia	Chernobyl, Russia	Lichen	0.00008 to 0.0021	[20]

2.2 Methodology

Measurement of ^{237}Np in environmental samples is typically performed by either alpha spectrometry or, given its low specific activity of 26 MBq g^{-1}, mass spectrometry. For detection of ^{237}Np at the mBq kg^{-1} level, the analyte must be preconcentrated and separated from matrix elements that may interfere with the final determination. For alpha spectroscopy measurement, the presence of matrix elements in the final fraction may result in thick sources which significantly decrease the counting efficiency and alpha peak resolution. The presence of ^{234}U and ^{230}Th will interfer with ^{237}Np due to the similar decay energies when measured by alpha spectroscopy. As with all ICP-MS measurements care is needed to limit dissolved solids present in the sample solution prior to measurement otherwise blocking of cones will decrease the intensity of signal and interferences from other radionuclides with similar mass characteristics should ideally be removed. For example, the monoisotopic ^{237}Np peak will be masked by the presence of high concentrations of ^{238}U in a sample for ICP-MS determination.

2.2.1 Chemical yield monitors

Ideally the yield monitor and analyte should be chemically identical, where possible using isotopes of the same element. The tracer and analyte should be in the same oxidation state, usually achieved by a reduction and/or oxidation cycle in the initial stages of the analysis. Any daughter products formed should not interfere with the final measurement and ideally the tracer should not contain any of the determinand or be present in the samples. For alpha spectrometry, the tracer should ideally emit alpha particles to permit simultaneous determination of the tracer and ^{237}Np. The half-life should be long enough to avoid the use of higher activity levels to compensate for decay. Based on these criteria, no ideal tracer exists for ^{237}Np analysis.

Neptunium-235 has a half-life of 396 days and is measured by gamma spectrometry (13.6 keV with 0.00164% yield) [21]. The presence of the ^{237}Np daughter, ^{233}Pa, though usually separated from Np during chemical separation, can lead to an overestimation of the method recovery as it is indistinguishable from ^{235}Np by gamma spectrometry. The yield monitor is free of ^{239}Pu interferences permitting sequential Pu and Np analysis by alpha spectroscopy [22]. However, determination of ^{235}Np by alpha spectrometry is unreliable due to the low alpha emission probability (1.6 to 7 x 10^{-4} α emission probability). The production of the tracer requires an accelerator to produce ^{235}Np via a ^{235}U(d, 2n)^{235}Np or ^{238}U(p, 4n)^{235}Np reaction [22]. Np-235 has a high specific activity of 5.19 x 10^{13} Bq g^{-1} and short half-life. A concentration of 1 ppb ^{235}Np is equivalent to 5.2 x 10^{4} Bq ml^{-1} making detection by mass spectrometry unachievable due to the radiological hazard.

Neptunium-236 has a half-life of 1.55 x 10^{5} years with beta and electron capture emissions. The nuclide is prepared via ^{238}U(d, 4n)^{236}Np and decays 87.8% by electron capture to ^{236}U, 12% by beta minus emission to ^{236}Pu and 0.16% by alpha emission to ^{233}Pa. The source of production limits its availability [23]. Np-237 impurities have been identified in the tracer using mass spectroscopy [24].

Neptunium-239 is a short lived (half-life 2.356 days) β-γ emitter, emitting principally gamma photons of 106.1, 228.2 and 277.6 keV with yields of 25.9%, 11.32% and 14.4% respectively [25]. The ingrowth of ^{239}Pu from ^{239}Np decay (100 Bq of ^{239}Np decays to 2.67 x 10^{-5}Bq ^{239}Pu over a year) and tracer impurities if produced from ^{243}Am prevent the sequential analysis of Np and Pu or Am respectively. The nuclide can be produced by irradiating uranium with high intensity neutron sources (flux of 2×10^{12} n cm^{-2} s^{-1} for 20 hours) followed by complex separation [26], or isolating from a pure ^{243}Am source using a pre-clean up stage [27]. The uranium irradiation method has limited availability as it requires an accelerator and any uranium present in samples can generate a ^{237}Np interference via ^{238}U (n, 2n) ^{237}U and subsequent β- decay to ^{237}Np or from ^{235}U by successive neutron capture. Methods for the isolation of ^{239}Np from ^{243}Am use ammonium iodide to ensure the Np is present in the tetravalent state [28] followed by separation of Am/Np by anion exchange chromatography [3,29,30] or solvent extraction [27]. The short half-life of ^{239}Np becomes an advantage as one half of the equilibrium activity will grow back into the parent in 2.35 days allowing for an almost continuous tracer supply. Am-243 is readily available and ^{239}Np is easily determined by gamma spectroscopy or gas flow proportional counting (GFPC) but analysis time is restricted due to its half-life. A typical limit of detection for ^{239}Np based on measurement in a well detector for a count time of 59000 seconds is 0.03 Bq/sample.

Plutonium-242 has been used as a yield monitor for the simultaneous analysis of ^{237}Np and $^{238,\ 239+240}$Pu by alpha or mass spectroscopy. It is assumed the plutonium and neptunium chemistries are similar [31,32,33,34,35]. This approach was validated by measuring IAEA 135 and IAEA 381 reference soil and seawater samples for Pu-238, 239+240 and 242 isotopes along with ^{237}Np on several occasions and comparing with the measured concentrations and nuclide ratios [32]. The results showed good agreement. Re-validation would be necessary for each new method as the co-separation of Pu and Np is dependent on the chosen separation procedure.

Standard addition of ^{237}Np to a duplicate sample has been used [36,37,38]. None of the issues of chemically compatibility needs to be considered and the recovery can be determined using the same final measurement technique. However, this approach assumes that the two samples will behave identically and there will be no differential losses during the procedure. The requirement to analyse a spiked and unspiked fraction of each sample also decreases the possible sample throughput. Batch yield can be used i.e. addition of ^{237}Np to one sample analysed in duplicate or QC material and the recovery determined is applied to all the samples analysed in the batch. This increases the number of samples that can be analysed, but relies on the assumption that all samples are chemically identical.

2.2.2 Sample preparation

For aqueous samples, Np must be pre-concentrated from large volume water samples to achieve sufficiently low limits of detection. Across the methods reviewed, all the studies, employed the same basic approach regardless of total dissolved solid content e.g. for pore, river and sea waters. Samples were evaporated then filtered to remove any suspended particulate matter [31,39]. To preserve the sample and minimise losses to container walls during the evaporation stages samples were acidified using concentrated nitric or hydrochloric acids. Acidification approaches differs from the addition of nitric acid to achieve a final concentration of 0.15 M [40], to the adjustment of the samples pH to <1 [41] and pH 2 [28]. Where evaporation was not practical, i.e. due to large sample size (200 to 750 litres) and sampling conditions (such as on board research vessels), co-precipitation using a number of reagents was used:

- Iron hydroxide [32,37,43],
- Manganese dioxide [44],
- Mixed hydroxide and carbonates of calcium and magnesium [3].

Solid samples such as biota, vegetation, sediment and soils, are pre-treated to reduce sample masses, remove organic matter and homogenise the material. Generally, biota samples such as molluscs, crustacea and fish, were washed to remove residual sediment, and then dried and ashed at 500ºC [20,43,44,]. Sheep organs, such as liver, bones, lungs, were pre-treated by wet oxidation using 8M nitric acid [45]. Sediment and soil samples, ranging from 0.5 to 200g, were dried (60ºC to 110ºC), sieved to remove stones/roots, ground and homogenised [2,16,44,46,47,48]. To remove organic matter samples were ashed at temperatures ranging from 450 to 600ºC. No specific studies regarding the volatility of ^{237}Np have been reported although in a number of studies the tracers are added post ashing suggesting that loss of Np at temperatures up to 600ºC is not considered significant [20,30,37,49].

2.2.3 Solubilisation

Total dissolution or leaching techniques are used to quantitatively extract ^{237}Np from the sample matrix. The form of Np in samples can range from soluble species in effluent samples to refractory forms in fallout samples where the actinide can be present in an insoluble form fused with silicates. Compared with plutonium there is limited information into the extent of solubilisation needed.

Acid leaching relies on the high solubility of the determinand and is used for elements which are not tightly bound to or incorporated within the sample matrix. The following conditions have been used for Np extraction:

- Nitric and hydrochloric acids (1:1) [15,47],
- Aqua regia [8,9,30,32,35,50],
- Aqua regia and hydrogen peroxide [51],
- Concentrated hydrochloric acid [20,26,42,],
- 8M nitric acid [28,52],
- Concentrated nitric acid [34,53,54,55,56],
- Fuming nitric acid [6,44,57].

A number of studies suggest acid leaching only removes surface contamination and does not solubilise nuclides tightly bound in the inorganic matrix. Total dissolution completely breaks down the sample ensuring quantitative Np recovery by utilising fusion or extended treatments with mineral acids including perchloric and hydrofluoric acids. Total dissolution is required for samples from high impact event sites, such as the Nevada Test Site or the Chernobyl accident where refractory fission products become incorporated into fused silicates [58]. The acid type varies but all dissolve any refractory transuranic radioelements present through the addition HF to decompose any siliceous material.

- Hydrochloric and hydrofluoric acid [59],
- Nitric, hydrofluoric and perchloric acids [17,49],
- Nitric-hydrofluoric acid [45,60],
- Hydrofluoric acid and aqua regia [46,61],
- Hydrofluoric acid/aqua regia, concentrated hydrochloric, 30% hydrogen peroxide, concentrated nitric acid [24].

Highly refractory or intractable particles were solubilised by HF digestion, repeated fusions with potassium fluoride, sodium sulphate, barium sulphate and sodium carbonate followed by HF digestion [58]. Another effective fusion procedure with significant advantages is borate fusion which has significant safety advantages and is highly effective in solubilising virtually any material [62]. Microwave digestion with concentrated nitric and hydrochloric acids was also used [31].

2.2.4 Reduction

The reduction of Np(V) to Np(IV) is essential to ensure the yield monitor and analyte are in identical oxidation states, ensure effective sorption on to chromatographic columns (extraction and anion exchange) and achieve efficient co-precipitation. The following reducing agents have been used:

- Ascorbic acid ($C_6H_8O_6$) [54],
- 0.05 to 0.1M hydroiodic acid at 70-80˚C [30],
- 0.1M Ammonium iodide (NH_4I) [3,42],
- Hydroxylamine ($NH_2OH.HCl$) [24,50,55],
- 0.1M Hydroxylamine ($NH_2OH.HCl$) and 0.05M hydrazine sulphate [47],
- Hydrazine ($N_2H_4.H_2O$) [28].
- Hydrazine sulphate ($(N_2H_5)HSO_4$) [52],
- Hydrazine sulphate, iron (II) ammonium sulphate [6,44],
- Iron Chloride ($FeCl_2$) [20,40],
- Iron (II) ammonium sulphate $(NH_4)_2Fe(SO_4)2.6H_2O$[51],
- Iron sulphamate $Fe(H_2NO_3S)_2$ [15,24,43,46],
- Potassium metabisuphite ($K_2S_2O_5$) [35],
- Fe^{3+}/Fe^{2+} in 0.5M HCl [32,37],
- 3N nitric acid with 0.5N aluminium nitrate, 0.6N ferrous sulphamate and 0.1g ascorbic acid [39],
- 100mg Nd carrier and 10ml 1M hydrazine nitrate [43],

2.2.5 Co-precipitation

Co-precipitation is routinely used to concentrate the determinand and separate it from interferences such as matrix elements. The precipitation techniques are often non-specific carrying a range of nuclides. Actinides are concentrated from a range of matrices by co-precipitation onto ferric hydroxide by the addition of ammonia [2] or sodium hydroxide [37]. Co-precipitation of Pu, Am, Cm, Th and Np onto lanthanum and neodymium hydroxides and fluorides isolates the analyte from interferences including Pa, U(VI), and many fission and activation products [3,8,20,24,51,61,64]. Sequential co-precipitations of Np^{4+} onto neodymium fluoride followed by neodymium hydroxide have been reported [9,43].

The co-precipitation of Np(VI) and Np(V) with Fe(III) hydroxide is not efficient in solutions with an NaOH concentration of 1M or higher due to the formation of anionic complexes with the hydroxyl ions, e.g. $NpO_2(OH)^-_2$ and $NpO_2(OH)^{2-}_3$, which are not incorporated into the Fe(III) hydroxide precipitate or sorbed onto its surface [65].

The addition of $MnCl_2$ and $KMnO_4$ precipitates MnO_2 with Np, Pu, Am, Th and limited U co-precipitating [28, 44].

For the removal of residual iron, Np has been co-precipitated with YF_3 from a dilute nitric solution [61].

2.2.6 Solvent extraction

The solvent extraction methods are based on ion association or chelate extraction. In a chelating system, the reagent used must replace the hydration sphere surrounding the Np ion to form strong coordination complexes which are more soluble in non-polar organic solvents than in the aqueous phase. For example, compounds such as 2-thenoyltrifluoroacetone (TTA) form neutral chelate compounds, almost covalent in nature, that are soluble in organic compounds such as xylene.

TTA/xylene has been used to separate Np from alpha-emitting contaminants such as ^{234}U and Pu. Np is extracted in the tetravalent state from 1M hydrochloric acid in the presence of a reducing agent, with a high extraction coefficient of 10^4. Interfering ions such as Pu(III) and U(VI) have extraction coefficients of 10^{-6} and 3×10^{-5} respectively and are not extracted. Fe(III) and Zr(IV) will also be co extracted with the Np (extraction coefficients of 375 and 250 respectively). To complex any remaining fluoride ions originating from a previous neodymium fluoride precipitation, aluminium nitrate was added to the solution prior to TTA/xylene extraction [40,43]. $Al(NO_3)_3$ was also added to the aqueous phase to remove any phosphate ions present [15]. The Np was back extracted into either 8 M or 10 M nitric acid removing any Fe(III) and Zr(IV) present [18,64,66].

In ion association systems, uncharged, extractable compounds are produced due to the electrostatic attraction between oppositely charged ions. Trialkyl phosphates such as Di-(2-ethylhexyl)phosphoric acid (HDEHP) form organic soluble coordination complexes (any ion association) with the metal nitrate. The branching allyl chains increases the extractability of tri and tetra-valent actinides and reduces Th extraction. Np was extracted in 10% HDEHP in toluene from a nitric acid solution of pH 4.5 [61]. Interferences from rare earth elements, iron and Ca were removed in a 5N nitric acid wash. The organic phase, containing the Np and Pu, was washed with 1M oxalic acid to separate Np from Pu. Np was extracted from high uranic content samples in a sulphuric acid medium with a proprietary high-molecular weight tertiary amine [67].

For industrial scale processes tributyl phosphate (TBP) is used and forms an organic soluble coordination complex with the metal nitrate with extraction coefficients for Np(IV), Np(VI), Pu(III), Pu(IV), Pu(VI), U(IV) and U(VI) of 3.0, 12.0, 0.012, 16.6, 2.7, 10 and 23 respectively. Np(VI) is almost completely separated using a one stage extraction from Al(II), Am(III), Cr(III), Fe(II) and (III), Na(I), Zn(II) and other cations. To isolate Np from Pu and U, Np is oxidised to the Np(VI) for extraction and the Np(V) stripped [66].

Amine extractants such as tri-n-octylamine (TOA) react with acids to form an ion association complex that is soluble in the organic phase (e.g. xylene). Neptunium (IV), and UO_2^{2+} were converted to chloro- complexes $NpCl_6^{2+}$ and $UOCl_4^{2-}$ by the addition of 8 to 10M hydrochloric and extracted with TOA-Xylene. The trivalent species, Pu^{3+}, Am^{3+} and Cm^{3+}, are left in the aqueous phase along with Th(IV) which will not form chloro- complexes. To remove any uranium present Np was back extracted using a number of reagents; 2M HCl plus 2 drops 3M NaCl [37], 0.1M HF-1M HCl [30] and 4M HCl/0.02M HF [49].

Ketone's can also be used for extraction. Methylisobutylketone (MIBK) has a relatively low solubility (1.91 g in 100 ml water) so is suitable for liquid-liquid extraction. This extraction is based on the solvent forming adduct compounds with the covalent nitrates of the tetra-valent species present. MIBK was used to separate macro concentrations of iron from Np prior to extraction chromatography reducing the size of the column and decreasing the potential for iron interferences during final determination [26,50]. Residual iron (III) was removed by solvent extraction with isoproylether [8,18,30].

2.2.7 Ion Exchange

The tetravalent actinides, including Np(IV) are strongly retained on anion exchange resin forming chloro and nitro complexes in high concentrations of hydrochloric and nitric acid. The distribution coefficient (K_D) of Np(IV), Pu(IV) and Th(IV) are 4000, 8000 and 500 respectively in 8M nitric acid. U(VI) is retained to a lesser extent with a K_D of 20. Trivalent species, such as Am(III), Cm(III) and Fe(III) exhibit low distribution coefficients (<100) and pass through the column [3,28,37,40,43,47,57].

Plutonium (IV) is routinely reduced to Pu(III) using a mild reducing acid such as 12M hydrochloric acid containing iodine and eluted from the column. Neptunium^{4+}/Np^{3+} has a higher standard electrode potential of 0.155V (compared with 0.982V Pu^{4+}/Pu^{3+}) and is retained.

Th(IV), unlike Np, does not form chloro-complexes and can be removed by washing the column with 10 to 12M hydrochloric acid. By decreasing the nitric acid strength to 8M any U(VI) present is removed [8,30,37,40,47].

Neptunium is eluted by decreasing the hydrochloric acid concentration to 4.5M and reducing Np(IV) chloro complex formation resulting in a K_D to 2. Uranium(VI) chloro-complexes are also reduced to a lesser extent and some removal occurs [26,30,42,43,45,51,69]. By reducing Np from the IV to III state by the addition of hydroxylamine hydrochloride to the HCl elution the recovery increased from ~55% to almost 100% [32, 37]. Hydrofluoric acid (usually 0.1M) was added to the eluant to increase Np extraction whilst uranium was retained [3,28,44,47,51,52,55,57].

A second anion column in acetate form (4M) has been used for the removal of residual uranium. Uranium has a high distribution coefficient under these conditions effecting a separation from Np, which is not retained [8,30,47,55,56].

2.2.8 Extraction Chromatography

Extraction chromatography systems have three components, an inert support, stationary phase and the mobile phase. The inert support is usually porous silica or an organic polymer, the stationary phase a highly selective organic extractant and the mobile phase an acid solution. The resins used are similar to ion exchange but are more selective in nature.

2.2.8.1 TEVA

TEVA Spec® is a commercially-available resin (Triskem International, France) consisting of two aliphatic quaternary amines, trioctyl and tridecyl methyl ammonium chlorides (commercially available as Aliquat-336®) loaded onto an inert support. The resin's properties are similar to strong base anion exchange resins, but with greater flexibility to coordinate around target anions as the functional groups are in liquid form instead of being bound to the polymer's backbone.

TEVA Spec® is highly effective for the separation of actinides over a wide range of nitric acid concentrations (Figure 6) with distribution coefficients greater than those of anion exchange resin (K_D values for Np(IV) and Pu(IV) are 4000 and 2000 respectively). Like anion exchange resin tetravalent actinides are more strongly retained than tri-, penta- and hexavalent species, however this occurs at are much lower nitric acid molarities (i.e. maximum at 2 to 4M). To ensure Np was in the tetravalent state 1N aluminium nitrate, iron sulphamate and 4.2M sodium nitrate were added [24] or potassium disulphite [63]. As the nitric acid concentration increases the nitrate anions compete for the complexation sites on the resin and the distribution coefficient decreases. Th(IV) is adsorbed on TEVA along with Pu(IV) and Np(IV) whilst U(VI) and Am(III) are not effectively retained. Thorium will only form chloro-complexes at hydrochloric acid molarities above 9M so can be selectively eluted from tetravalent Pu and Np which are retained. The presence of thorium and uranium at concentrations above 0.05M reduces the retention of Np. Complexing agents, such as oxalic acid, reduce the Np sorption considerably by forming complexes with tetravalent actinides which are not retained by TEVA resin to elute Np [68]. By decreasing the nitric acid concentration and adding HF (0.1M HF-0.1M nitric acid) Np(IV) was eluted from the resin [28]. Pu and Np isotopes were eluted from the column using 0.1M hydoxylamine hydrochloride – 2M hydrochloric acid [63].

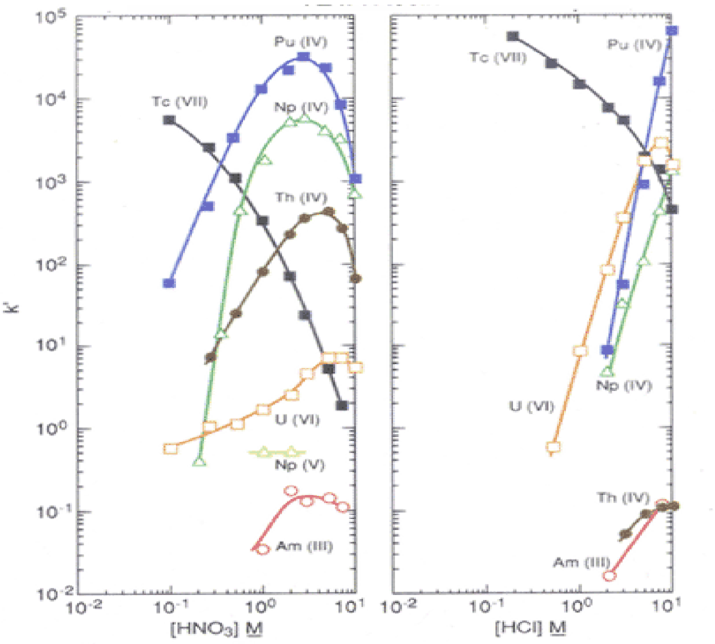

Figure 6: Acid dependency of capacity factor (k') in nitric and hydrochloric acid media for TEVA Spec® [68].

2.2.8.2 Eichrom TRU spec®

This extraction chromatography product (Eichrom, USA) has a stationary phase consists of a mixture of carbamoylmethylphosphine oxide derivative (CMPO) and tri-n-butyl phosphate (TBP) loaded onto an inert support. Like ion exchange systems Np(IV) is strongly retained from HNO_3 solutions with a K_D of 1 x 10^5 in 0.01M nitric acid increasing to 2 x 10^6 in 5M nitric acid. The combination of CMPO-TBP increases significantly the uptake of tri-, tetra- and hexavalent actinides extracting as their nitrato complexes. In nitric acid, the adsorption characteristics of the tetravalent actinides have similar profiles and high distribution coefficients (

Figure 7) preventing sequential separations. In hydrochloric acid, the order of extractability of Pu(IV), Np(V), Th(V), U(VI) and Am(III) is the same but there is greater separation with a sharp decrease in retention as the acid concentration reduces to 7 to 8M and continues to decline with lowering molarities. Uranium, is retained at low HCl concentrations (e.g. 0.7M HCl) unlike Np(IV) allowing for separation of the two elements. Removal of Am(III) can be affected by washing with 4M hydrochloric acid as the distribution coefficient for Am does not exceed 30 at any HCl molarity. The presence of Fe(III) can seriously affect the Np uptake efficiency and needs to be removed or reduced to Fe(II) prior to sample loading. Commonly occurring matrix elements, such as Cs, Sr, V, Tl, Co, Ni, Cd, Cu, Zn, In, Ru, P, Y and other heavy rare earth elements, exhibit little or no retention and are removed in the load or initial wash fractions.

Iron is initially reduced to Fe(II) and Np to the Np(III+IV) states using ascorbic acid prior to loading the sample onto the TRU-Spec® column in 2M nitric acid [30]. The column was converted to the chloride form using 9M HCl and washed with 4M HCl, 4M HCl-0.1M hydroquinine and 1.5M HCl to elute the Am, Pu and Th respectively. Neptunium was eluted in 1M HCl- 0.03M oxalic acid with the U retained on the resin.

Neptunium has been extracted on line using TRU-Spec® coupled with a sequential injection ICP-MS system. The sample was injected onto the column, washed with 2M HNO_3, 2M HNO_3/0.1M $NaNO_2$ and 2M HCl (remove the trivalent actinides) then Np eluted directly into the ICP-MS with 1M HCl/0.07M $H_2C_2O_4$. [38].

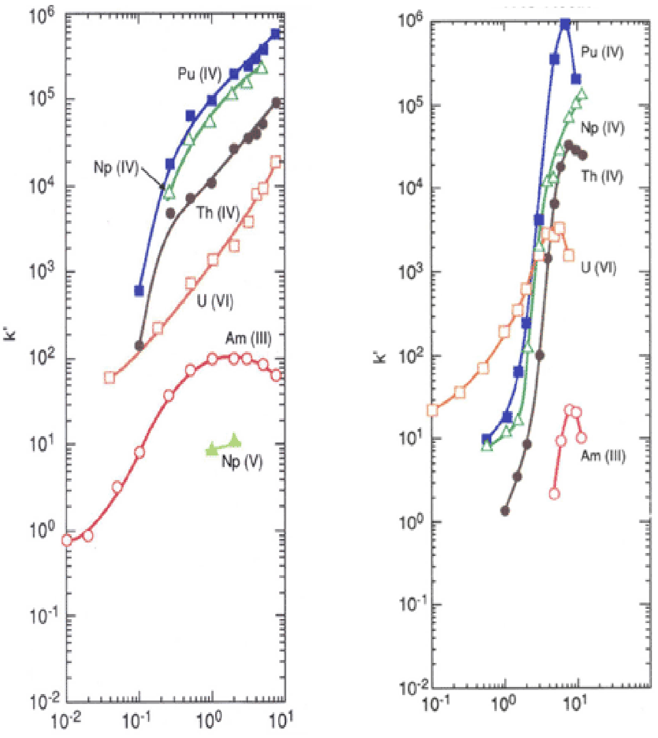

Figure 7: Acid dependency of k' in nitric (left) and hydrochloric (right) acid media for TRU Spec® [68].

2.2.8.3 EichroM UTEVA Spec®

UTEVA Spec® resin contains diamyl amylphosphonate (DAAP) as the stationary phase. Like ion exchange systems tetravalent actinides are retained but with a lower distribution coefficient compared to TRU Spec® resin (maximum ^{237}Np k' is ~1000 and ~10000 in nitric and hydrochloric acid respectively). DAAP, like TRU Spec®, extracts tetravalent actinides and U(VI) as nitrato complexes. Distribution coefficients increase with increasing HNO_3 concentration (Figure 8). As with TRU Spec® in nitric acid, the adsorption characteristics of Pu(IV), Np(V), Th(V), U(VI) and Am(III) have similar profiles and high distribution coefficients but in hydrochloric acid medium the order of extractability is the same but with greater separation (see Figure 8). In low nitric acid concentrations (e.g. <1M) uranium can be extracted unlike Np(IV) allowing for separation. As trivalent actinides are not retained Pu can be removed with Am by reducing to Pu(III). Neptunium, along with Th is eluted in 5N HCl/oxalic acid. The oxalic acid acts as a complexing agent decreasing the distribution coefficient of Np by 100-fold whilst the uranium sorption is unaffected allowing for separation [39,68].

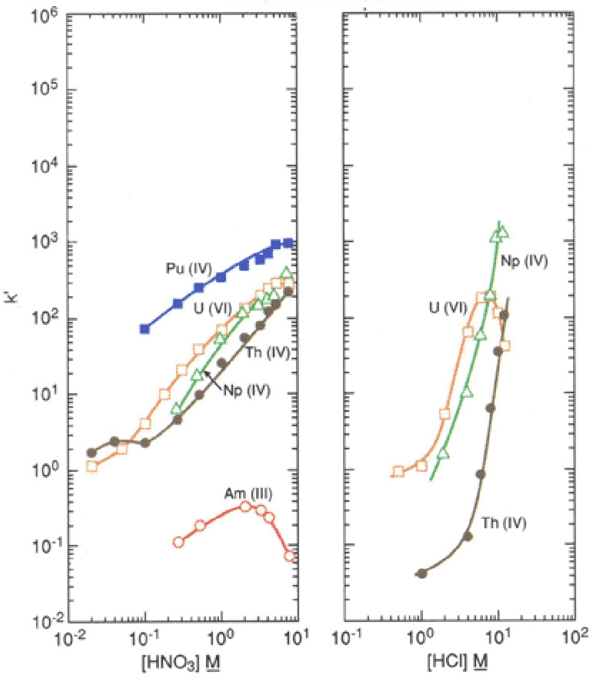

Figure 8: Acid dependency of k' in Nitric (left) and Hydrochloric (right) acid media for UTEVA Spec® [68].

Column extraction chromatography has also been used based on the reducing properties of hydroquinones and extracting properties of tri-*n*-octylphosphine oxide (TOPO) [71]. The hydroquinine 1,5-Dichloroanthrahydroquinone (DPHQ) was selected as the reducing agent as it exhibited good retention onto the inert support. Np(V) is not retained on the column. By washing the column with 6M HCl Np (VI) and (V) are completely reduced to the tetra valent state and Pu(IV) and Pu(VI) to Pu(III) with a reducing effect inversely proportional to the flow rate. The redox extraction chromatography is capable of separating Pu (III)-Np(IV) and Am(III)- Np(IV).

2.3 Final measurement

Published measurement techniques include the use of well-established radioanalytical techniques (e.g. alpha and gamma spectroscopy) and mass spectrometry. All have differing methods of source preparation, levels of sensitivity and precision and associated interferences.

2.3.1 Radiometric techniques

2.3.1.1 Alpha Liquid Scintillation Counting

Alpha liquid scintillation counting with the rejection of the β-γ emitters (PERALS spectrometer) provides high counting efficiency, relatively low background, pulse shape discrimination for photon/electron/beta-particle rejection and moderate energy resolution in the order of 10%. Prior to measurement the sample is extracted into a proprietary organic phase such as tri-n-octylphosphine oxide (TOPO) or bis-(2-diethylhexyl) phosphoric acid (HDEHP). Np-237 alpha decay has a fine structure with 85.5% of the total alpha emission associated with 5 alpha emissions in the 4766 keV to 4817 keV E_α range. The spectrum is complicated by a number of interferences; ^{237}Np peak at 4640 keV produces a shoulder, peaks from ^{238}Pu and ^{239}Pu impurities in the ^{237}Np standard and high energy interference from electron conversion of the ^{233}Pa gamma rays and alpha pulse (311.90 keV with yield of 38.3% [71]. Detection limits of 0.01 to 0.1 Bq have been achieved using this technique [39,72]. If Pu-242 is present due to incomplete separation during sequential analysis it gives an alpha emission at 4598.5 keV causing an interference with the ^{237}Np peak. A second method for determination of the yield monitor is required due to the lack of an alpha-emitting yield tracer.

2.3.1.2 Alpha spectrometry

This well-established technique uses high-resolution detectors with an energy range of 2.5-8MeV. Limits of detection of sub mBq have been achieved. The presence of ^{234}U and ^{230}Th in samples can cause interferences as the similar decay energies (^{234}U peak E = 4.72 MeV, 4.77 MeV, ^{230}Th peak Eα = 4.688 MeV to 4.721 MeV) overlap the ^{237}Np peak (Eα = 4.77 MeV, 4.79 MeV). Like Photon-Electron

Rejecting Alpha Liquid Scintillation (PEARLS) a second method for determination of the yield monitor is required.

Prior to measurement the sample is electrodeposited onto a stainless steel, or less commonly, platinum disc producing robust sources, which do not degrade over time. The electrolyte and conditions for deposition varies considerably (Table 2). For count times and detection limits see Table , Appendix A.

Table 2: Electrolyte used for the electrodeposition of ^{237}Np.

Electrolyte	**Conditions**	**Recoveries**	**Reference**
Ammonium chloride	Not stated	Not stated	[8]
	1.2A 1 hour	50-85%	[30]
Ammonia sulphate medium	pH 2.1 to 2.4		[42]
	pH 1.95	60-90%.	[58]
Ammonium oxalate/HCl mixture	1A cm^{-2} ,2 hours pH 2-3		[40]
Sulphuric acid-ammonia media	pH 2.4; 1A 1.5 hour		[52]
Sulphuric acid-ammonium media	1A 1.5 hours		[28]
Sulphuric acid (0.05M) / ammonia (25%)	4-5 hours 0.7 A/cm^2	92.6 ± 3.8%	[32,37]
Sulphuric acid (0.18M)	300 mA 6 hours		[49]
Sulphuric acid (0.2M)	pH 1.9 to 2.1; 1A, 2 hours		[3]
Sulphuric-Sodium sulphate	1A 1 hour	14-91%.	[28]
Sodium bisulphate/Sodium sulphate			[50]
Potassium sulphate/ ammonium oxalate		50-80%	[43]

Co-precipitation of Np with NdF_3 prior to alpha spectrometry removes the need for electrodeposition and is more rapid. The sources have a greater mass which can result in a decrease in the resolution of the alpha energy spectrum [56].

2.3.1.3 Gamma spectroscopy

The main advantage of gamma spectrometry is that minimal sample preparation or chemical separation is required. Np-237 is measured via its daughter ^{233}Pa (t½ = 27.01 days) using the 311.904 keV photon emission (38.3%) assuming that secular equilibrium has been achieved, obtaining a limit of detection of 0.014 Bq g^{-1} [73].

2.3.2 Neutron activation analysis (NAA)

The elemental analysis measurement is based on the production of radionuclides with shorter half-lives than those of the parent. The daughter nuclides have a higher specific activity which improves the detection limit. For ^{237}Np, the improvement was estimated to be a factor of 3.5 x10^{5} [74].

Limited sample preparation is required but the removal of uranium is essential to prevent spectral overlap. Neutron irradiation produces ^{238}Np (t½ = 2.1 days) from ^{237}Np which is measured by gamma spectrometry. The presence of sodium, bromine, chlorine, and fissionable elements results in the generation of activation products including ^{22}Na, ^{87}Br, ^{188}Au, during neutron irradiation. These interferences produce a high Compton continuum that interferes with the ^{238}Np gamma spectrum. To purify ^{238}Np post irradiation a UTEVA® column or extraction into thenoyltrifluoracetone (TTA) was used [26,53].

Following purification, the activity of the yield monitor ^{239}Np was measured to calculate recovery. The ^{238}Np activity is determined by gamma spectroscopy (984.5 keV peak) with chemical yields of between 90-95% and limits of detection of 0.1 to 0.5 mBq [26]. Recoveries greater than 100% were reported using a similar technique due to incomplete removal of ^{238}U at the purification stage producing ^{239}Np via (n,γ) reaction [50].

2.3.3 Mass spectrometric techniques

Inorganic mass spectrometric methods provide a very sensitive multi-element determination of long-lived radionuclides elements at the trace and ultratrace levels. A number of mass spectrometry techniques have been used with differing levels of precision, sample introduction methods and interferences to be considered.

2.3.3.1 Accelerator Mass spectrometry (AMS)

AMS is a highly selective and ultrasensitive mass spectrometry technique achieving high abundance sensitivity (10^{-16}) and the elimination of isotopic, isobaric and molecular interferences. Limits of detection at the µBq level have been achieved [42]. The instrumentation is highly specialised, expensive and not widely available. Negative NpO^- ions are produced by sputtering the sample with a Cs+ beam in an ion source. The ions are then accelerated to 130 keV prior to magnetic mass analysis, set at mass 253 ($^{237}NpO^-$). The selected ions enter the accelerator and the electrons are stripped from the ions in a long canal containing oxygen gas. The high-energy charge-changing collisions with the stripper gas destroy any molecular interference present in the beams. The positively charged atomic ions are then accelerated back to ground potential where a large analysing magnet selects the ^{237}Np ions in the +7 charge state with energies of 40 MeV. The ions are identified and counted in a longitudinal field ionisation chamber. The energy resolution of AMS for 40 MeV ^{237}Np is 2.8% which is sufficient to resolve the $^{237}Np^{7+}$ from any other molecular fragments in lower charge states.

For the analysis of Np in aqueous samples, Np was preconcentrated and purified using iron hydroxide co precipitation and ion exchange prior to final measurement. The sources were prepared by adding ^{242}Pu (internal tracer) and iron, ashing and mixing an aliquot of the resulting sample with Al powder. Reproducibility of 1.2% was reported [41]. The technique was in good agreement with ICP-MS measurements (9%) [33].

2.3.3.2 dc Glow Discharge Mass Spectrometry (dc-GCMS)

Solid samples were analysed directly using dc-GDMS, avoiding extensive sample preparation. Pellets were prepared by compacting dried, homogeneous sample into a disc using a hydraulic press. Tantalum was used as the secondary cathode to produce a stable discharge and good sensitivity in relation to the silicon ion intensity. The silicon ion yield indicates the efficiency of the ionisation and atomisation of the sample. Although there are no isobaric interferences, there is a polyatomic interference from $^{181}Ta^{40}Ar^{16}O+$ (mass 236.9069) which if the resolution is greater than 1700 will be distinguishable from ^{237}Np (mass 237.0482). Analytical precision was between 10-15% with a limit of detection of 80 pg g^{-1} (2 mBq g^{-1}) [73, 75].

2.3.3.3 Inductively coupled plasma mass spectrometry (ICP-MS)

This well-established technique has become more widely used for the determination of long-lived radionuclides including Np. Samples are introduced into the inductively coupled plasma in a range of dilute acid matrices, atomised and ionised. The positively charged ions are then extracted into the vacuum of the mass spectrometer and the ions separated based on their mass-to-charge ratio. The signal at the detector is proportional to the ion's concentration. The limits of detection achieved are at the ppb level. The presence of ^{238}U in the sample can interfere as the tail in the m/z=238 peak can overlap the mono-isotopic Np m/z=237 peak.

By altering the nebuliser type to ultrasonic or micromist the limits of detection can be improved to 0.186 ngL^{-1} (4.85 x 10^{-3} Bq kg^{-1}) and 0.257 ngL^{-1} (6.70 x 10^{-3} Bq kg^{-1}) respectively. The limits are further reduced by inserting a grounded platinum electrode between the quartz ICP torch and radio frequency load coil preventing capacitive coupling and eliminating secondary discharge between the sampling cone [76].

High Resolution (HR) ICP-MS uses a magnetic and electric sector to separate and focus the ions which coupled with an ultrasonic nebuliser increases the sensitivity as fewer photons and ions are scattered inside the device, produces a lower continuum background and clearer spectrum [45,78]. The overall effect is a 10% increase in sensitivity and a detection limit of 2 fg mL^{-1} for ^{237}Np [77].

Double focusing (DF) ICP-MS using direct liquid sample introduction (DIHEN – direct injection high efficiency nebuliser) produces the highest oxide formation (^{237}Np^{16}O^{+}) which is directly injected into the ICP, replacing the injector torch, eliminating waste and reducing sample sizes. The DF-ICP-MS has a low instrumental background, high sensitivity in low-mass operation mode and the ability to separate many isobaric interferences of the molecular ions from atomic ions of analytes in higher-mass resolution [79,80].

Sequential injection (SI) and extraction chromatography, using TRU resin, have been coupled with ICP-MS detection to address isobaric and spectral interferences for the analysis of the trivalent and tetravalent actinides. By utilising the TRU Spec® resin the ^{238}U peak tailing on the ^{237}Np was resolved [38]. The spectral interference was also removed by using Ion Chromatography (IC) coupled to ICP-MS. Differences in net charge of oxo-complexes are used to separate the Np (V), U (VI) and Pu (IV and VI) on cation exchange columns with DAP (2,3-diaminopropionic acid monohydronitrate redox agent). A detection limit of 6 pg mL^{-1} was achieved [36]. IC was also coupled with isotope dilution

ICP-MS using anionic/cationic mixed bed exchange columns to simultaneously determine fission products (lanthanides) and actinides (Np, U, Pu, Am and Cm). The technique achieved a detection limit of 0.45 ng mL^{-1} with a precision of better than 5% [81].

Sector field (SF) ICP-MS interfaced with a sample injection system and extraction chromatography was used for simultaneous determination of Np, Pu and Am. TRU-Spec and TEVA Spec resins were used achieving limits of detection in the femtogram range [34,54].

Laser Ablation (LA) ICP-MS is a sensitive, multi-element, mass spectrometry technique used for the direct analysis of solid samples at ultratrace concentration levels. A laser beam is focused at the sample in a laser ablation chamber and the ablated material is transported in argon into the ICP-MS. To overcome the issue of homogeneity samples are ground to powder form, mixed with lithium borate mixture and iron oxide (increases absorption of the laser photons during ablation) and fused. Detection limits of 0.05 ng g^{-1} have been achieved which can be reduced three-fold by coupling to a DF-CP-MS [82].

Thermal ionisation MS (TIMS) uses magnetic sector mass spectrometer to analyse ^{237}Np and ^{239}Pu. Following chemical separation, the sample present in micro volume was placed onto an anion exchange resin bead and transferred into rhenium filament. The sample is thermally ionized by applying a current to the filament. The ions are accelerated across an electrical potential gradient and focused into a beam via a series of slits and electrostatically charged plates. The ion beam passes through a magnetic field and the original ion beam is dispersed into separate beams based on their mass to charge ratio. These mass-resolved beams are then directed into collectors where the ion beam is converted into voltage [18,59,83].

2.3.3.4 Resonance ionisation mass spectroscopy

Resonance-ionisation mass spectrometry (RIMS) is a selective photoionisation method used mainly for studying the electronic structure of atoms. It has been used for quantitative measurements of ^{237}Np achieving detection limits at the femtogram level [84]. One or more lasers are tuned to the excitation wavelength of the target analyte producing highly selective ionisation. Samples are subjected to a source of evaporation e.g. thermal vaporisation from a Re filament, laser ablation or ion bombardment, creating an atomic beam. The laser beams interact with the atomic beam. The ionisation by multi step resonant laser excitation takes place in an electric field which accelerates the resulting ions in the spectrometer where they are mass selectively determined [85,86].

2.3.4 Luminescence determination

Luminescence determination has been used for measuring ^{237}Np concentrations to a detection limit of pico grams. The sample is mounted onto CaF_2 pellets and the luminescence intensity measured following a laser pulse and strobe time. The presence of Fe, Mg, Al and Si above the micro gram level can cause quenching of the Np luminescence. To minimise the effect a series of chemical separations, co-precipitation solvent extraction and extraction chromatography, were used [15].

2.4 Methodology discussion

A comparison of a number of techniques which have been published for the separation and purification of ^{237}Np from environmental samples is given in Table (Appendix A). The table gives the details of the yield monitor, sample preparation, chemical technique applied to the separation stage and final determination method. Typical recoveries and limits of detection are published.

Over half of the studies used ^{239}Np as the yield tracer due to its relative ease of preparation and final determination. Tracers are generally added at the beginning of the procedure. There are a few exceptions where the tracer is added post ashing indicating that Np is not considered to be volatile but studies are limited and worthy of further consideration. The majority of the methods incorporate a reduction stage to convert all Np to its tetravalent state.

Pre-concentration of Np from large volumes of water is usually achieved by acidification to preserve and minimise losses followed by co-precipitation using a variety of complexing agents with iron hydroxide the most commonly used. This stage is not specific for Np with the precipitate carrying other transuranics and matrix elements.

There is divided opinion in the literature as to whether acid leaching of the solid samples is sufficient to ensure that the total ^{237}Np content of the sample is measured. For samples where there is a possibility the ^{237}Np may be bound within the sample matrix, present as oxides or fused with silicates, total dissolution was recommended. Unlike Pu chemistry there is no definitive study of this aspect, possibly due to the lack of reference materials.

Reduction of Np to the tetravalent state appears to be critical for further separation techniques including co-precipitation, ion exchange and solvent extraction and achieving good recoveries. Over ten reducing agents are cited. Np(VI) and Np(VII) reduction and Np(III) oxidation are less well discussed as these are less dominant species.

Most of the methods use a co-precipitation stage to separate Np from any matrix elements present in the samples. A number of reagents are used but generally iron hydroxide precipitation is the favoured and well established approach for actinide determination.

The most common procedure for the separation of ^{237}Np from interfering ions and matrix elements is solvent extraction and used in approximately half of the methods. Prior to ion exchange this stage is used to remove fluoride ions from the co-precipitation stage or rare earth elements, iron and calcium that may affect the retention characteristics. Following the ion exchange stage solvent extraction is reapplied; this technique is used to remove any remaining impurities, such as uranium, which may interfere with the final measurement. This combination of chemical separation procedures is similarly adopted for the determination of Pu and other actinides.

Anion exchange is the most commonly used separation technique. Tetravalent Np is strongly retained and the chemistry well characterised for the isolation from other transuranics present, allowing for sequential separations. A number of methods suggest using a second anion column in acetate column to remove uranium interferences. Extraction chromatography is used by less than 10% of the papers reviewed indicating the effectiveness of the ion exchange procedures

For the final determination of ^{237}Np twenty one different techniques have been reported of which twelve were based on mass spectroscopy with limits of detection ranging from nBq to mBq levels. The techniques ranged from the highly specialised (AMS and NAA) to instrumentation generally available in many laboratories (alpha and gamma spectroscopy). Most commonly alpha spectroscopy was used with limits of detection achieved 0.02 Bq kg^{-1} and 100 µBq L^{-1} based on a 10 g soil and 150 L water samples respectively. Gamma spectroscopy is used mainly for the determination of the ^{239}Np tracer. Typically, reported recoveries were in excess of 50%.

2.5 Acknowledgements

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3 Optimisation of a method for the determination of Neptunium-237

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3.1 Keywords

^{237}Np, optimisation, determination, ICP-MS, alpha spectroscopy, separation, decontamination.

3.2 Abstract

A number of analytical methods have been developed for the determination of neptunium-237 in environmental and nuclear decommissioning samples. Each method, generally, focussed on the analysis of a specific sample matrix and final measurement technique. As the nuclear industry moves further into decommissioning there is a need to develop a method which has a more flexible scope including different methods for measurement. This paper details the optimisation of a method for the analysis of ^{237}Np in a wide variety of sample matrices including the production of a suitable yield tracer. Each stage has been optimised to allow for flexibility and considers the knowledge gaps identified in literature reviews.

3.3 Introduction

Neptunium-237 is a radioactive, long-lived ($t_{½}$= 2.1 x 10^6 years), alpha emitting radionuclide which is only found naturally at ultra-trace quantities in minerals as all primordial ^{237}Np has decayed. The main sources of ^{237}Np in the environment are nuclear weapons' fallout, fission reactor cooling water, processing of spent fuel, presence in high level nuclear waste and from the in-situ decay of previously discharged ^{241}Am (Assinder, 1999). The total world integrated deposition of ^{237}Np from nuclear weapons' tests is estimated at 2500 kg (Holm et al., 1987) with global fallout levels at less than 10^{-3} Bq per kg of soil and per m^3 of seawater (Alexsandruk, 1991). Presently this isotope has less environmental significance than other transuranic radionuclides, such as plutonium and americium. However, in the future, due to its long half-life and ingrowth from ^{241}Am, ^{237}Np will become more significant. It has been estimated that in 2013, the activity of ^{237}Np present in High, Intermediate and Low Level waste in the UK was 36, 78 and 0.0081 TBq respectively with levels increasing to 43, 110 and 0.021 TBq by 2150 (RWM, 2015). Due to its high radiotoxicity, being a long-lived alpha emitter which is readily concentrated in the liver and/or bones, ^{237}Np has been demonstrated to be of potential significance in preliminary radiological safety assessment calculations for human intrusion and coastal erosion scenarios for future waste disposal. As such ^{237}Np is one of the thirty-seven radionuclides classed as a priority that are, or potentially will be, significant for RWM's safety cases (NDA, 2014). Despite this, ^{237}Np is frequently described as the 'neglected actinide' due to the lack of research compared with other transuranics (Thompson, 1982).

As the nuclear industry moves further towards decommissioning there is greater emphasis on the analysis of more varied samples types resulting in the need to develop more generally applicable methods. Typically most methods isolate the radionuclide of interest using a combination of sample preparation, pre-treatment, solubilisation, separation from interferences and purification, source preparation and measurement. The presence of matrix elements can reduce the efficiency of the separation chemistry, reducing recovery and increasing detection limits. For alpha spectroscopy measurement, the presence of matrix elements in the final fraction can result in thick sources which significantly decreases the counting efficiency and alpha peak resolution. The presence of dissolved solids has a similar effect for ICP-MS final measurement, reducing the ionisation efficiency of the analyte, leading to a decrease in signal intensity and potentially blocking the sample introduction system. Radiometric interferences include ^{234}U and ^{230}Th which have similar decay energies to ^{237}Np and are difficult to deconvolve by alpha spectroscopy. For ICPMS measurements high concentrations of ^{238}U can tail into the m/z=237 mass region, interfering with the determination of the monoisotopic ^{237}Np. Such interferences must be separated during the chemical separation stages dependant on the final measurement technique used. Turnaround times are often critical to decommissioning programs with a desire to achieve quicker, more accurate results. For this study we have utilised ICP-MS where samples can be analysed in minutes compared to hours or days count times needed for alpha spectrometry measurements.

This study aimed to develop a robust method for the determination of ^{237}Np in a variety of environmental and decommissioning sample types and which were applicable to ICPMS measurement of ^{237}Np. The study considered the key stages within a radiochemical method to isolate the radionuclide of interest (sample preparation, pre-treatment, separation from interferences and purification, source preparation and measurement) and optimise each of these stages.

Specifically, the study aimed to:

a) Identify and develop a method to produce an efficient, continuous and easily obtainable yield tracer for ^{237}Np analysis as presently there is no ideal tracer for the determination of ^{237}Np considering issues of half-life, tracer availability and need for specialised equipment.

b) Evaluate potential loss of ^{237}Np during sample ignition as it is common practise to destroy organic and inorganic matrices using either wet or dry ashing.

c) Investigate the optimum procedure to achieve quantitative extraction of ^{237}Np from a range of sample matrices.

d) Identify a suitable redox reagent to control Np oxidation state.

e) Investigate the effectiveness of co-precipitation techniques to pre concentrate the ^{237}Np and acts as a preliminary separation stage.

f) Develop a method capable of separating and purifying ^{237}Np from high levels of elemental interferences and produces good determinand recoveries.

g) Develop a separation scheme that is suitable for final measurement by ICP-MS.

Using the findings, an optimised method for the determination of ^{237}Np in a wide variety of sample matrices is outlined. Analysis was carried out on 122 sediment samples originating from an ungrazed saltmarsh in the River Esk estuary, Cumbria using the procedure with measurement using the new Agilent 8800 Series Triple Quadrupole ICP-MS. |The method was validated by analysing three NPL Intercomparison materials and comparing the results obtained by direct gamma measurement and the expected values listed by NPL.

3.4 Methodology

3.4.1 Equipment and reagents

Traceable ^{237}Np and ^{243}Am tracers were supplied by AEA Technology, Harwell, UK and NPL, Teddington, UK.

The following equipment was used during the experiments:

- Total alpha measurements were performed on the Wallac 1220 Quantulus Liquid Scintillation counter (LSC).
- Neptunium-237, Pu alpha and elemental measurements were performed on a Perkin Elmer Elan DRC-e® ICP-MS.
- Neptunium-237 measurements were performed on an Agilent 8800 Series Triple Quadrupole® LC/MS.
- Elemental measurements were performed on an Agilent 725 ICP-OES.
- Neptunium-237 alpha measurements were performed on an EG&G Octete-PC alpha – particle spectrometer fitted with 450mm^2 ruggedised low-background ion-implanted detectors.
- Neptunium-239 determinations were performed on EG&G Gamma spectrometers.
- All resins (TRU, TEVA Spec and Dowex 1 x 8) were supplied by Triskem, France. Goldstar Liquid scintillation cocktail was supplied by Meridian Technologies, UK. Certiprep elemental standards were supplied by Fisher Scientific, UK. All other reagents were supplied by Fisher Scientific, UK and are at least analytical grade unless otherwise stated.

3.5 Yield monitor production

3.5.1 Introduction

The yield tracer is critical to the analysis and ideally should be chemically identical to the analyte, preferably a different isotope of the same element. The tracer and analyte should be in the same oxidation state, usually achieved by a reduction and/or oxidation cycle in the initial stages of the analysis and any daughter products formed should not interfere with the final measurement. The tracer should not contain any of the determinand or be present in the samples and preferably the yield tracer and determinand can be measured by the same technique simultaneously. The half-life should also be long enough to avoid the use of higher activity levels to compensate for decay. For ^{237}Np analysis no ideal tracer exists. The advantages and disadvantages of each approach is discussed in this study along with a proposed method to produce ^{239}Np by milking a sample of ^{243}Am, an approach which does not require specialised facilities and removes an availability issues. This tracer is not ideal for the measurement by alpha spectrometry and this study uses both ^{239}Np and ^{242}Pu to calculate the separation and then deposition and counting recoveries respectively.

3.5.2 Methodology

Neptunium-239 was prepared by in-growth from an ^{243}Am parent solution. Aliquots of traceable ^{243}Am tracer (44 Bq) were added to either 2 M nitric acid (10 ml) or 0.5 M nitric acid/5% hydrogen peroxide (10 ml). The samples were loaded onto pre-packed, 2 ml, 100-150 µm TRU spec columns, pre-conditioned with the same reagent as the samples, and then washed with 10 ml of the same solution. The initial elution fraction from the load fraction was combined with the wash and measured by gamma spectrometry to determine the ^{239}Np activity for between 10 and 60 minutes, with count times dependent on the activity levels. ^{243}Am was removed from the column with 20 ml 4 M HCl. An aliquot of the eluant was combined with Goldstar cocktail and measured by LSC to determine the alpha activity present.

3.5.3 Results

Isotopes commonly used to analyse ^{237}Np include ^{235}Np, ^{236}Np, ^{239}Np, ^{242}Pu and standard addition to duplicate samples of ^{237}Np. They all have a sufficient half-life to allow for analysis but if ^{239}Np ($t_{½}$= 2.356 days) is used the analysis time needs to be considered. Simultaneous determination of the tracer and analyte is possible using mass spectrometry techniques (^{236}Np, ^{242}Pu and standard addition) or alpha spectrometry (^{242}Pu and standard addition) whilst ^{235}Np and ^{239}Np are measured by gamma spectrometry. Most neptunium isotopes require specialised production using accelerators, limiting the availability. However ^{239}Np can be isolated from a pure ^{243}Am source using a pre clean up stage which utilises the short half-life as one half of the equilibrium activity will grow back into the parent in 2.35 days allowing for an almost continuous tracer supply. Interferences also must be considered to minimise the risk of method recovery overestimation against the level of precision and accuracy needed for the determination. For example,^{235}Np is indistinguishable from ^{233}Pa (^{237}Np daughter product). Np-239 decays to ^{239}Pu (100 Bq of ^{239}Np decays to 2.67x 10^{-5} Bq ^{239}Pu over a year) and needs to be corrected for if sequential analysis of Pu and Am is required and also present as a tracer impurity if ^{239}Np is produced from a ^{243}Am source. The use of ^{242}Pu assumes the chemistries of plutonium and neptunium are the same throughout the separation chemistry whilst the standard addition approach relies on the sample and duplicate behaving identically with no differential losses during the procedure.

Considering all the advantages and disadvantages a method was developed to produce ^{239}Np by milking a sample of ^{243}Am, an approach which does not require specialised facilities and removes availability issues. The main disadvantage to this approach is that alpha spectrometry measurement is not possible as the tracer is measured by gamma spectrometry prior to electrodeposition. To overcome this ^{239}Np is used to calculate the recovery of the chemical separation technique and the gamma activity measurement in the sample post column chemistry. Prior to source preparation ^{242}Pu is added and measured simultaneously with ^{237}Np allowing the electrodeposition recovery and counting efficiency to be calculated. This also allows for the samples to be counted for longer periods of time without having to consider the decay of the ^{239}Np tracer.

TRU Spec® resin has a stationary phase which consists of a mixture of carbamoylmethylphosphine oxide derivative (CMPO) and tri-n-butyl phosphate (TBP) loaded onto an inert support. Np(IV) is strongly retained from HNO_3 solutions with a k_D of 1 x 10^5 in 0.01 M nitric acid increasing to 2 x 10^6 in 5 M nitric acid (Figure 9). Across the same molarity range Am(III) is also retained with a k_D of between 10^1 and 10^2. The combination of CMPO-TBP increases significantly the uptake of tri-, tetra- and hexavalent actinides extracting as their nitrato complexes. Less data is available for the retention of Np(V), however the distribution coefficients in 1 to 2 M nitric acid are lower allowing for separation of the two elements. Removal of Am(III) can be effected by washing with 4 M hydrochloric acid as the distribution coefficient for Am does not exceed 30 at any HCl molarity.

To minimise the preparation, especially due to the short half-life of the tracer, a method has been developed which allows for the ^{243}Am to be loaded and retained onto a TRU Spec® resin column whilst the ^{239}Np is eluted, but it is critical that Np is present in the pentavalent state. It is known that Np(V) undergoes appreciable disproportionation in high acid concentrations to form Np^{4+} + NpO_2^{2+} (Burney and Harbour (1974) and therefore the ^{239}Np present in the ^{243}Am is likely to not be present solely in the V state. Burney and Harbour (1974) stated that redox reactions that involved forming or rupturing of the neptunium-oxygen bond e.g. Np^{4+}/NpO_2^{+} and Np^{4+}/NpO_2^{2+} would have a slower rate of reaction.

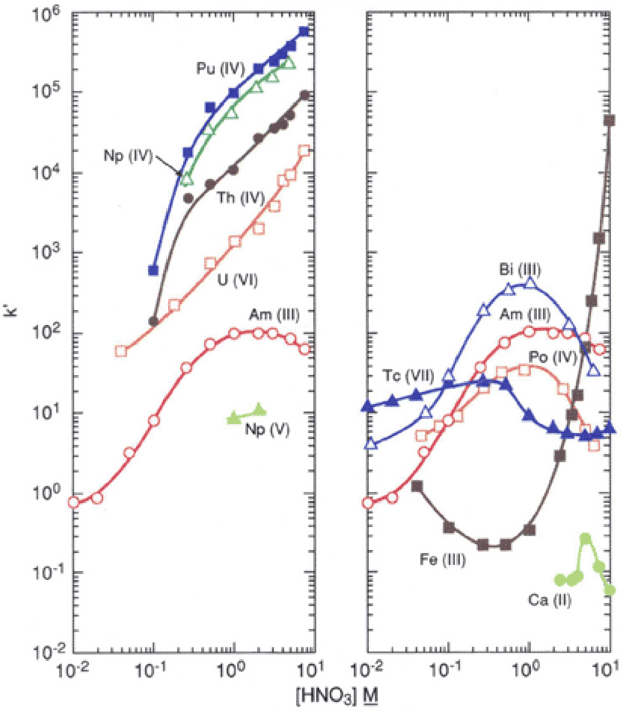

Figure 9 Acid dependency of k' for various ions at 23-25°C on TRU Spec® resin

Loading the ^{243}Am onto a TRU Spec® column in 2M HNO_3 yielded between 33 and 36% ^{239}Np however by altering the reagent to 0.5M HNO_3/5% H_2O_2 the recovery increased to 81% in the initial load solution with a further 18% eluting in the subsequent 0.5 M HNO_3/5% H_2O_2 wash (Figure 10). The result confirmed Burney and Harbour's findings (Burney and Harbour's 1974) which classed the rate of reaction for Np(IV) to Np(V) as slow when NO_3^- was added but increased to immediate for NO_3^- with H_2O_2 at 25°C. Post elution the column is sealed, stored at room conditions and left for at least one week to allow for ingrowth then milked again using 0.5M HNO_3/5% H_2O_2. Almost all of the ^{243}Am (99.8%,Figure 10**Error! Reference source not found.**) was then removed by eluting in 4M HCl.

The method, as detailed in Figure 11, is capable of producing within a short time period (approximately 2 hours) a readily available source of ^{239}Np by milking a sample of ^{243}Am that regenerates allowing for multiple elutions.

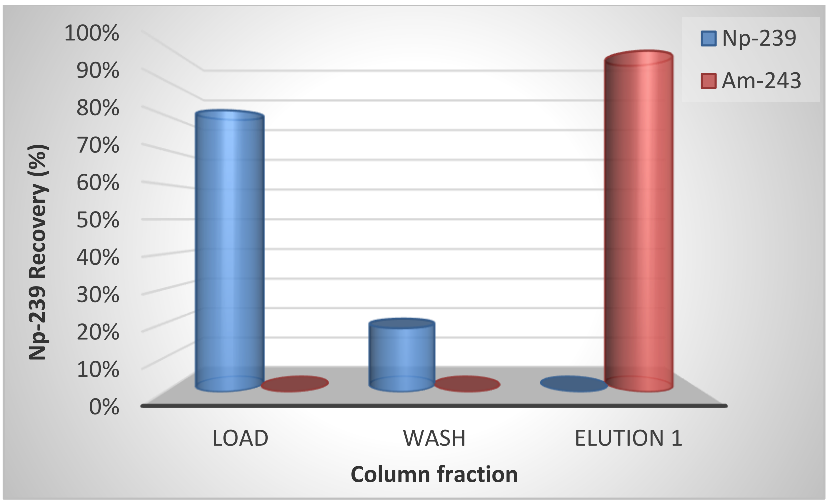

Figure 10 Np-239 elution profile

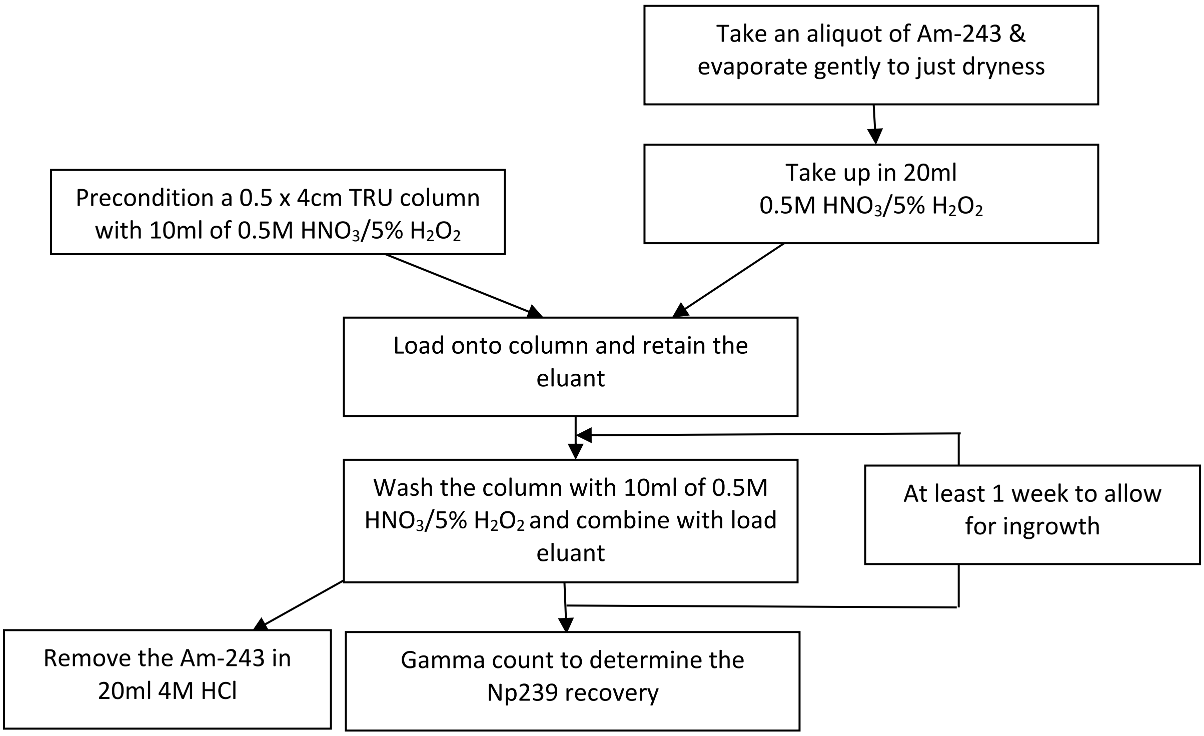

Figure 11 Np-239 tracer production methodology.

3.6 Sample preparation - Volatility

3.6.1 Introduction

Solid samples, both environmental and decommissioning, are generally dried then ashed at temperatures ranging from 450 to 600°C to reduce sample mass and remove organic matter. However, there are no specific volatility studies to investigate the effect of temperature on ^{237}Np with the literature showing the addition of the yield tracer pre and post ashing (Lindahl, Roos et al., 2004, Chen, Dahlgaard et al., 2001; Schulz, Wink et al., 1981 and Yamamoto, Chatani et al., 1989).

3.6.2 Methodology

The potential for loss of ^{237}Np during ignition was assessed through a series of ignition tests over a range of temperatures. Five ashless filter papers were spiked with a certified ^{237}Np tracer (91 Bq) and heated to 450°C, 600°C, 800°C, 900°C and 1000°C in platinum crucibles. At each temperature point a crucible was removed, allowed to cool and nitric acid added to solubilise the ^{237}Np. The samples were prepared and measured by ICP-MS and the percentage ^{237}Np recovered was calculated.

3.6.3 Results

The chemistry of Np-237 does not suggest that upon exposure to high temperatures losses will occur but there is little evidence of a definitive study. Increasingly sample dissolution techniques involve the use of fusion and the use of high temperatures therefore the volatility was assessed. Taking into account the measurement uncertainties which are estimated at 10% and those associated with the solubilisation efficiency, neptunium is not lost at temperatures up to 1000 °C (Figure 12). As a result, the tracer can be added pre or post ashing.

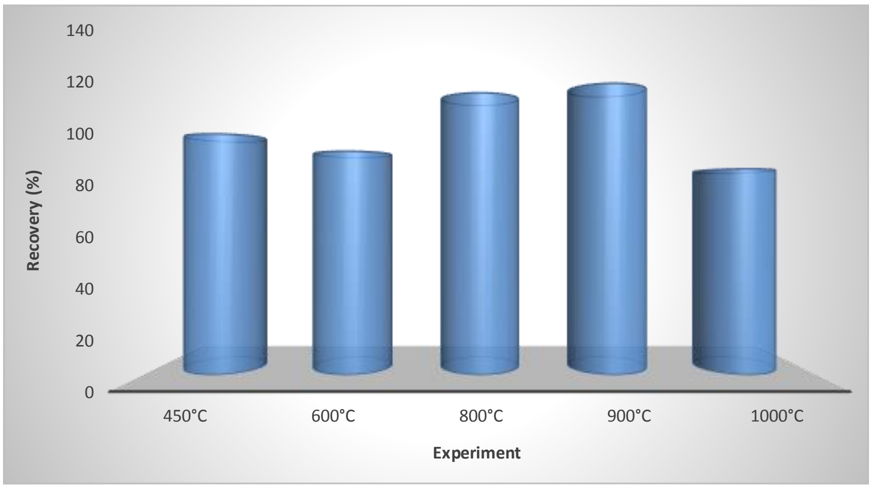

Figure 12 Volatility of Np-237 over a range of temperatures.

3.7 Extraction of ^{237}Np

Presently there are no solid reference materials for ^{237}Np and therefore a sequential leaching experiment could not be carried out. However evidence from other radionuclides should be considered when extracting Np particularly Pu. If refractory material is likely to be present or if the composition is unknown it is advisable to carry out total dissolution whilst for environmental samples a comprehensive and aggressive acid leach is likely to be sufficient.

3.8 Oxidation state control

3.8.1 Introduction

Controlling the oxidation state of Np is critical throughout the analytical procedure for example for yield tracer production Np-239 must be present in the pentavalent state to ensure elution from the TRU spec column. During the separation chemistry, the tracer and analyte need to be reduced to the four state for effective sorption on to chromatographic columns (extraction and anion exchange) and achieve efficient co-precipitation. Neptunium exists in several oxidation states and a wide variety of reducing agents have been used for the adjustment of the oxidation state including ammonium species (NH_4I [Holm et al., 1987; Duniec et al., 1984], $NH_2OH.HCl$ [Kenna, 2002; Sumiya et al., 1994, Hursthouse et al., 1992]), iron compounds ($FeCl_2$ [Lindahl et al., 2004; Harvey and Thurston, 1998], Iron (II) ammonium sulphate [Holm and Nilsson, 1980], iron sulphamate [Alexsandruk et al., 1991; Kenna, 2002; Pentreath and Harvey, 1981; Ji et al., 2001]), hydrazine sulphate [Michel et al., 1999] and Mohr's salt [$(NH_4)_2Fe(II)(SO_4)_2.6H_2O$] [La Rosa at al., 2005]. This paper considers the use of ferrous sulphamate and demonstrates its effectiveness.

3.8.2 Methodology

The effectiveness of the reducing agents at controlling Np oxidation state, and the effect of other reagents and evaporation stages on Np oxidation state was evaluated.

Two ^{237}Np standards were used in the study: (i) certified ^{237}Np tracer (Np present as Np(IV) and Np(V) and (ii) ^{237}Np tracer with Np adjusted to the (V) state. To convert to Np(V) a known amount (2 Bq) of the standard was evaporated to near dryness, re dissolved in 5 ml 0.5 M HNO_3/5% H_2O_2

and left for at least 12 hours. To verify the oxidation state an aliquot was taken and the method detailed for ^{239}Np production followed (section 3.5).

The oxidation state of Np under a range of test conditions was determined by utilising the different K_D's for tetra and penta- valent Np (10^1 and 20^5 respectively) on anion exchange resin from 3 M HNO_3. Under the conditions used, any Np retained on the column would be present in the tetravalent state whilst any eluted in the initial load and wash fractions would be present as Np(V).

Aliquots of certified ^{237}Np tracer (0.5 Bq g^{-1}) were added to the following samples containing 50 ml of each reagent as detailed in *Table 3*.

Table 3 Preparation of samples for redox state study

Sample	Reagent	Np Oxidation State
A	3M Nitric acid	IV, V
B	3M Nitric acid, Fe sulphamate	IV, V
C	3M Nitric acid	V
D	3M Nitric acid, Fe sulphamate	V
E	3M Nitric acid, Fe sulphamate, Na nitrite,	V
F	Evaporated, redissolved in 3M Nitric acid + Fe sulphamate	V

The samples were loaded onto anion exchange resin, preconditioned with 50 ml of each reagent. The columns were washed with the sample reagent (30 ml), which was combined with the load fraction, and eluted with 30 ml 4.5 M HCl/0.1M HF. The load/wash and elution fractions were then diluted and measured by ICP-MS to determine the percentage of ^{237}Np recovered.

3.8.3 Results

For the unadjusted samples in 3 M nitric acid (A and B), Np was present predominately, but not exclusively in the IV state (Figure 12). In the absence of the reducing agent 87% was present as Np(IV) which increased to 100% when ferrous sulphamate added. The results for sample C, where the oxidation state was adjusted to Np(V), show that 3 M nitric acid alone does not convert the Np to the IV state with 83% present in the load and wash fractions therefore in the pentavalent form. On addition of ferrous sulphamate (sample D) the conversion is significant with all present as Np(IV) in the final elution fraction. Sodium nitrite is used to reduce Pu and may be added if simultaneous determination is required. The Np(IV) results showed a recovery of 92% however the losses occurred are not significant when the uncertainties on the measurement result and method are considered, with the addition of the addition redox agent having minimal impact on Np recovery. For the evaporated sample, less than 1% of the activity was present as Np(V) with 69% present as Np(IV) in the final elution and approximately 30% unaccounted for. It is unlikely that Np is lost due to evaporation as seen in section 3.6. The activity may have been retained on the column indicating Np is present in another oxidation state or not fully resolubilised indicating the need to add the yield tracer prior to any evaporation stages to account for losses.

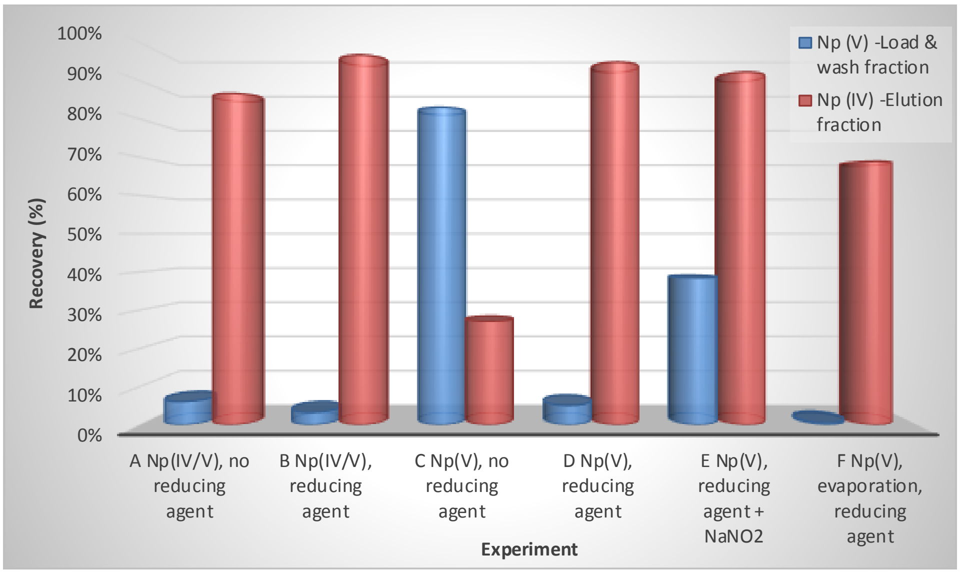

Figure 13 Effect of reagent on Np oxidation state

3.9 Pre-treatment, separation and purification of ^{237}Np

3.9.1 Introduction

The presence of elements in the sample solution and final measurement sample can reduce the efficiency of separation, impact on the recovery of ^{237}Np and interfere with the final determination. The effectiveness of separation techniques was assessed based on elemental concentrations found in environmental and decommissioning samples that could be analysed by laboratories. The maximum elemental concentrations of 130 samples were ascertained from characterised certified reference material data and samples analysed at NNL Preston laboratory (summarised in Table 4). The data set included the following range of sample matrices:

- Decommissioning – sludge, fuel element debris, tank supernate, hoover bags and walnuts, resin, aqueous slurry, oil and ash;
- Biota – algae, fish tissue, tuna;
- Soil and Sediment – marine, estuarine, clay, various compositions of soil, stream, channel, harbour, lake, river;
- Sludge- sewage, domestic, industrial;
- Vegetation – seaweed, lichen, plankton, grasses, wood, branches and leaves, cotton;
- Aqueous- ground water, rain water, waste water effluent, landfill leachate;
- Other – coal fly ash.

Twenty-three elements were selected (in italics) based on the following criteria to prepare mixed elemental standards:

a) At least one element from each group except 4, 17 and 18 analysed usually of the highest concentration e.g. in the group one elements, K and Na were selected.

b) From each group, at least one element at the higher concentration e.g. for the alkaline earth metals Mg, Ca and Sr.

c) Uranium and thorium to demonstrate the final measurement determination potential interferences.

d) Cerium was used as an analogue for plutonium.

e) The mixed elemental standards were prepared using, where possible, certified standards from Certiprep and if unavailable high purity chemical regents. The ^{237}Np activity added to all the standards was constant (180 Bq). To verify the ^{237}Np and elemental concentrations aliquots of each were taken and measured by ICP-MS and ICP-OES.

Table 4 Summary of elemental concentrations found in samples (μg g^{-1})

Maximum Concentration	**Element**
>100000	*Al, Fe, Mg, Na,* Mn*
10000-100000	*Cu, Ni, Ca, As, Si*
1000-10000	*Zn, Pb, S, K,* Cd, *Cr, P, Sr,* Ba
100-1000	Se*, Sn, V,* Li, Be, Sb, *B, U, Co, Mo*

10-100	*Ce,* Hg, Rb, Ag
1-10	Dy, *La, Th,* Cs

*The high level for this element is due to the presence of one ground water sample. If this outlier is removed the concentration decreases to between 1000 and 10000 µg g^{-1}.

3.9.2 Pre- treatment

3.9.2.1 Introduction

Co-precipitation is a well-established approach used in actinide determination methods to pre-concentrate and separate the analyte from any matrix elements present in the samples which can decrease significantly method recoveries and affect final counting source purity. The precipitation techniques are often non-specific, carrying a range of nuclides. A literature review highlighted three common co-precipitation methods (Chapter one) which this study compares to evaluate the effect on elemental behaviour.

3.9.2.2 Methodology

Three aliquots of each mixed elemental solution were taken (5 ml) and the following co-precipitation methods followed. All of the resulting filtrates were prepared and measured using ICP-MS and ICP-OES to determine the elemental and ^{237}Np concentrations.

Method A – Ferrous hydroxide co-precipitation **(Chen, Dahlgaard, Nielsen & Aarkrog, 2002)**

The samples were acidified to pH 2 using 12 M HCl and 0.5g L^{-1} $K_2S_2O_5$. The method states the addition of 1 mg/L $FeCl_3.6H_20$ but due to the high iron concentrations in the samples this reagent was omitted. The samples were warmed for one hour and the pH adjusted to 10 using 6 M NaOH (final concentration ~0.5-1 M NaOH) to form a precipitate ($Fe(OH)_2$- $Np(OH)_4$).

Method B – Manganese Dioxide co-precipitation **(Germian & Pinte 1990)**

To each sample 1mg L^{-1} potassium permanganate at pH 9-9.5 was added with the precipitate forming on standing.

Method C – Mixed carbonate/hydroxide precipitate **(Holm & Aarkrog, 1987)**

The samples were acidified to pH 1-2 using conc. HCl and then heated to boiling for an hour. The pH was then adjusted to pH to 9-10 using NaOH solution.

All the samples were left overnight to settle then filtered through a 0.2 µm filter. The resulting supernatant was made to a known volume prior to analysis.

The average concentration for each element present in the supernatant was calculated after separation. To calculate a recovery for each element the concentration in the standard was divided by the average concentration in the final solution post separation.

3.9.2.3 Results

To understand the efficiency of separation of Np from the matrix elements the decontamination factors achieved for three co-precipitation techniques and two resin separation methods were determined.

Apart from two samples there was a greater than 99% uptake of ^{237}Np on all three precipitates (iron hydroxide, manganese dioxide and mixed carbonate/hydroxide) for all thirty five multi element standards. In the two samples with lower recoveries, the Np recovery was reduced to 78% and 83% following manganese dioxide co-precipitation. The boundary between the aqueous and solid layers for some of the samples was difficult to define and therefore the reason for the decrease could be due to the difficulty separating the two phases or interaction of ^{237}Np with other elements.

Decontamination factors for each element at each method stage were calculated (ratio between initial and final radioactivity that results from a separation process). The behaviour of some of the elements did not significantly vary with co-precipitation technique (Table 5) for example the alkaline metal, K, did not co-precipitate with Np for any of the methods producing decontamination factors of between 1.0 x 10^{+02} and 2.0 x 10^{+02}. The alkaline earth metals behaved similarly across the three approaches with between 70 and 90% of the Ca and Mg co-precipitating with Np whilst over 70% of the Sr remained in solution. For phosphorus, polyatomic non-metal, the three methods were similar with between 68% and 82% of P remaining in solution producing decontamination factors ranging from 7.4 x 10^{+02} to 3.9 x 10^{+03} and for the lanthanides (La and Ce) less than 1% remained in solution. Ce is often used as a non-active analogue for Pu which will co-precipitate with

Np. The actinides (Th and U) followed the same trend with the majority (~91% and ~73% respectively) following Np with decontamination factors of 1.4 x10^{+01} and 7.10 x $10E^{+02}$ respectively.

The results for aluminium and lead were consistent across the three methods with contrasting trends. Almost all the Al was present in solution (DF of 1.1 x 10^{+01}) whilst over 90% of the Pb co-precipitated with Np. For tin the uptake was method dependant with approximately 50% remaining in solution for the iron and mixed carbonate/hydroxide precipitate methods whilst the Mn precipitation method completely separated the element from Np.

Table 5 Comparison of the decontamination factors following co-precipitation

Decontamination factor			
1.0E+07		La	
1.0E+06	Co, La	Cu	Cu, La
1.0E+05	Ce, Fe, Co	Ce, Sr, Fe, Co	Ce, Sr, Fe, Co, Sn, Si
1.0E+04	Cr, P	Sn, Si, Cr, As	Cr, As, Th, B
1.0E+03	Zn, Sn, U, Ni, Sr, Ca, Mg, K, V	Th, B, Zn, U, P, Ni	Zn, U, P, Ni, V, Ca, K
1.0E+02	Pb, As, Th, Al	V, Ca, K	Pb, Mg, Al
1.0E+01	Si, B, Mo	Pb, Mg, Al, Mo	Mo
1.0E+00	**Fe hydroxide**	**Manganese dioxide**	**Mixed carbonate/hydroxide**

Co-precipitation method

The mixed carbonate/hydroxide precipitation for the metalloids, As and B, produced decontamination factors which were significantly higher than for the other two methods. Almost complete uptake of B onto the mixed co-precipitate was observed whilst all the element remained in solution for the Fe and Mn methods. For As the difference was less significant and although the decontamination factors showed significant variation, over 80% of the element did not co precipitate with Np and remained in solution regardless of the method.

The transition elements also had contrasting behaviours. Co and Fe co-precipitated entirely with Np regardless of the method with Cu and Ni exhibiting a similar trend for Cu and Ni with an uptake greater than 90%. In contrast, Mo remained in solution (low decontamination factor of $1.2E^{+00}$) whilst approximately half of the V co-precipitated. The Cr results showed the greatest variation. The co-precipitation efficiency for the Manganese dioxide method was significantly lower (29% in solution, DF of $9.2E^{+02}$) than for the iron and mixed carbonate/hydroxide approaches (DF ~$4.2E^{+03}$) where the uptake onto the precipitation was greater than 95%.

For most of the elements the behaviour did not vary significantly with co-precipitation technique and effectively separated Al, As, K, Mo, P and Sn from Np with greater than 80% remaining in solution. Some elements (Ca, Ce, Co, Cu, Fe, La, Ni, Pb and Th) co-precipitated with Np significantly (<90%) whilst for As, B, Cr and Sn the efficiency of separation was method dependent.

3.9.3 Separation and purification

3.9.3.1 Introduction

For the separation and purification of Np two approaches are most commonly used; anion exchange (Germian and Pinte, 1990; Holm, Aakrog et al., 1987; Holm and Nilsson, 1981; Kim and Takaku, 1989; Michel et al., 1999; Sumiya et al., 1994) and TEVA (La Rosa et al., 2005 ; Kim and Kim, 2004; Qiao, 2010 ; Eichrom 2014). Both methods have been shown to separate ^{237}Np however the effect on recovery and degree of decontamination from interfering elements is less known. At high hydrochloric and nitric acid molarities tetravalent actinides, including Np(IV), strongly retain on anion exchange resin forming chloro and nitro complexes. Uranium is retained but to a lesser extent whilst the trivalent species, Am(III), Cm(III) and Fe(III) exhibit low distribution coefficients and pass through the column along with the majority of matrix elements which do not form anion complexes. The 9M HCl wash removes Th(IV) which, unlike Np, does not form chloro-complexes and the conc. HCl-NH_4I solution reduces Pu(IV) to Pu(III) which is not retained on the column allowing for elution and separation from Np. Decreasing the hydrochloric acid concentration to 4.5M reduces the Np(IV) chloro complex formation and the addition of hydrofluoric acid increases the extraction of Np.

TEVA Spec® is also highly effective for the separation of actinides over a wide range of nitric acid concentrations with distribution coefficients greater than those of anion exchange resin. Like anion exchange resin tetravalent actinides are more strongly retained than tri-, penta- and hexavalent species however the nitric acid molarities this occurs at are much lower (i.e. maximum at 2 to 4 M). As the nitric acid concentration increases the nitrate anions compete for the complexation sites on the resin and the distribution coefficient decreases. The nitric acid load and wash solutions allow for absorption of the Pu(IV), Np(IV) and Th(IV) onto the resin whilst U(VI) and Am(III) are not effectively retained. Thorium will be removed with 9 M HCl as this only forms chloro-complexes at molarities above 9 M. By decreasing the acid concentration further and adding HF Np(IV) is eluted.

3.9.3.2 Anion Exchange (Dowex 1x8) methodology

An aliquot of each mixed elemental solution was taken (2 ml), evaporated and taken up in 50 ml 8 M HNO_3. The samples were loaded onto a 1 x 5 cm Dowex 1 x 8 column (preconditioned with 50 ml 8 M HNO_3) and washed with 30 ml 8 M HNO_3 (30 ml), 30 ml 3 M HNO_3 and 40 ml 9 M HCl. A further 20 ml conc. HCl- 5 w/v % NH_4I solution wash was used to remove any Pu and the Np eluted in 30 ml 4.5 M HCl-0.1 M HF.

3.9.3.3 Extraction Chromatography (TEVA) methodology

A further aliquot of each mixed elemental solution was taken (2 ml), evaporated and taken up in 15 ml of 3 M HNO_3 + 1.5 M sulphamic acid. The samples were loaded onto the pre-packed columns in 3 M HNO_3 (preconditioned with 3 M HNO_3), washed twice with 10 ml HNO_3 followed by 20 ml 9 M HCl and the Np eluted in 20 ml 0.1M HCl/0.05 M HF.

For both separation methods, the resulting elution fractions were then evaporated to near dryness, in the presence of nitric acid, to decompose any organic material (e.g. fine resin particles), prepared in 2% high purity nitric acid and measured using by ICP-MS and ICP-OES to determine the elemental and ^{237}Np concentrations.

The average result for each element was calculated after separation i.e. in the final eluant following resin separation. The decontamination factor is defined as ‘the number of atoms in the initial or solution’ divided by ‘the number of atoms in the final solution’. Therefore, for each element the concentration in the standard was divided by the average concentration in the final solution post separation.

3.9.3.4 Results

Generally, the decontamination factors are higher and percentages of each element in the final elution fraction lower for the anion exchange separation method (Table 6, Figure 14) with As, B, Th and V being the only exceptions. Both U and Th are present in the samples at appreciable levels despite a significant concentration being decontaminated (16.5% and 3.78% of original concentration). If high levels are likely, in the range of 500 µg g^{-1} it would be advisable to extend the initial nitric and hydrochloric acid washes to ensure complete separation. The Np recoveries were typically between 50 and 100% (80% of the results) with a mean of 74%.

Table 6 Percentage of each element present in elution fraction following resin separation

Percentage present eluant	Element present	
	Anion Exchange column	TEVA column
<LoD	Ca	
0.05-0.1	Ce	
0.1-0.2%	La, Sr	La
0.2-0.5%	Mo, Sn	
0.5-1%		As, K
1-2%	Co	Sr
2-3%	Cu	Al, Ce
3-4%	Fe, Th	Ca, Sn
4-5%	Al	Th
5-10%		P
10-30%	As, Al, Cr, K, P, U	Co, Fe, V
30-60%		B, U
60-90%		Cr
>90%	V	Cu, Mo

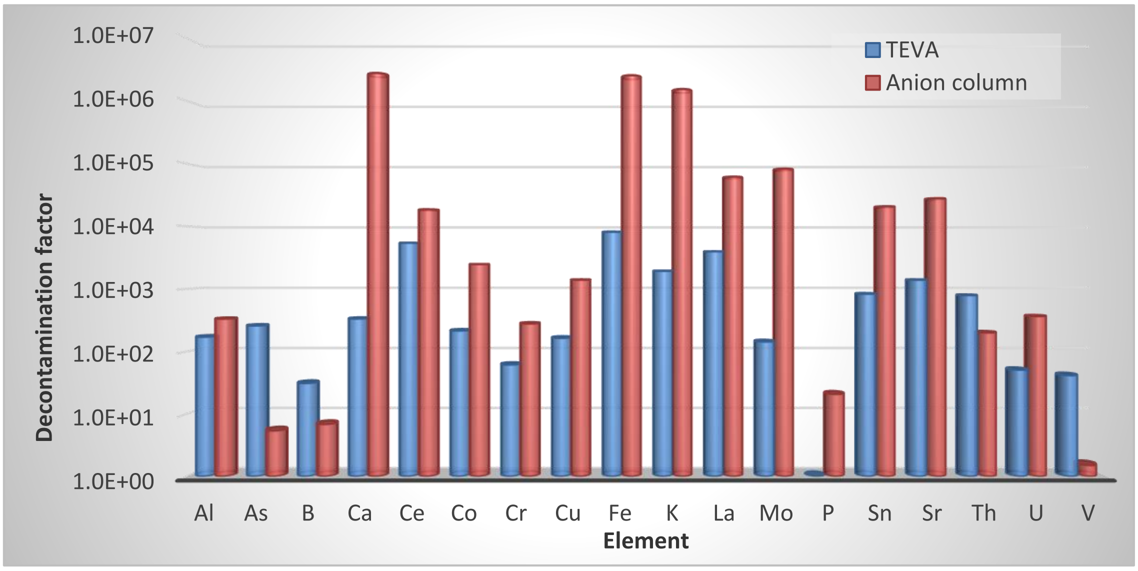

Figure 14 Decontamination factors of varying elements following resin separation

TEVA is a less robust resin and is unable to decontaminate the high elemental concentrations to the same degree which was reflected in the practical issues experienced (Figure 15). However, for analysis of samples with a lower elemental concentration the decontamination factors and degree of separation would probably increase.

The ^{237}Np recoveries reflected this tendency with lower results obtained for the analysis of the 35 elemental standards using the TEVA resin compared to the anion exchange approach (Figure 15). Typical chemical recoveries for the TEVA method were more variable and significantly lower; between 7.6% and 51% with a mean of 34% under the experimental condition tested. The variation was dependent on the differing sample matrix, with the higher recoveries generally observed for the samples with a lower elemental concentration. The extension of the wash volumes and/or dilution of the sample prior to analysis may increase the recoveries obtained but this would need further consideration.

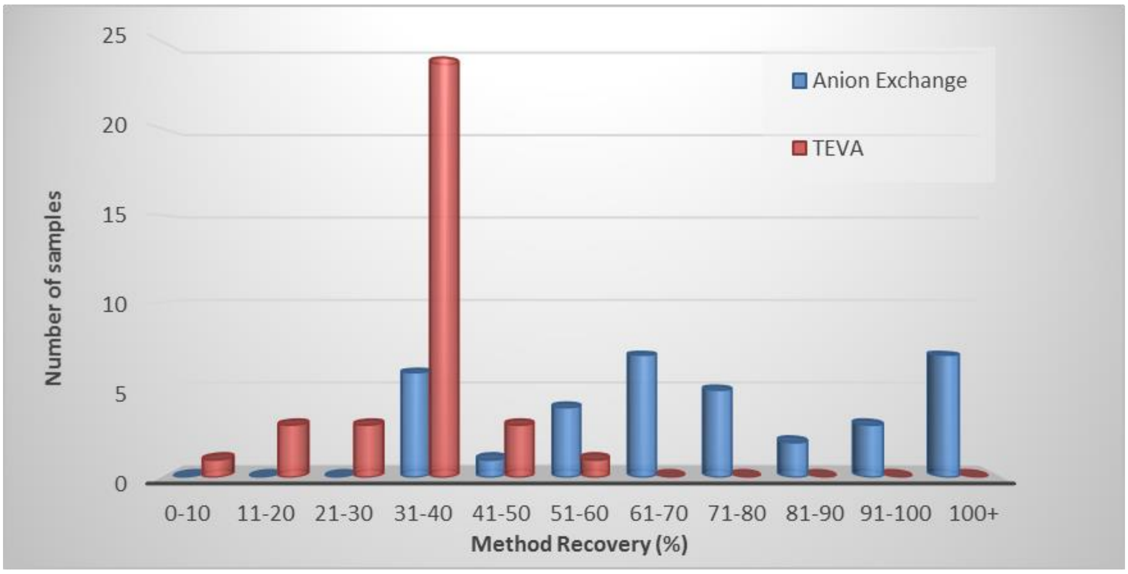

Figure 15 Np-237 recoveries following resin separation

Vanadium was not removed by the anion exchange separation. It is likely in 8M nitric acid tetra valent vanadium will be present which will be retained onto the resin column. The acidic matrix of the final elution oxidises Np(IV) to Np(V) and alters the oxidation state of V so co-eluted. However, Vanadium is not an interference for any of the final measurement techniques and does not affect the recoveries of ^{237}Np. The concentration of this element and others still present in appreciable amounts, can be removed prior to column chemistry by co-precipitation therefore if the samples have a high elemental concentration it would be beneficial to combine the two separation methods. The lower nitric acid conditions used for the TEVA resin separation decrease the retention of V and therefore a lower concentration is co-eluted with Np.

The elution profile of the column separation stage was assessed (Figure 16) and shows Am, U and Th were removed from the anion exchange column in the load, nitric acid and hydrochloric acid washes. The final elution fraction was analysed for Am, U, Th and Pu and none were present in measurable quantities indicating complete separation and purification of the ^{237}Np.

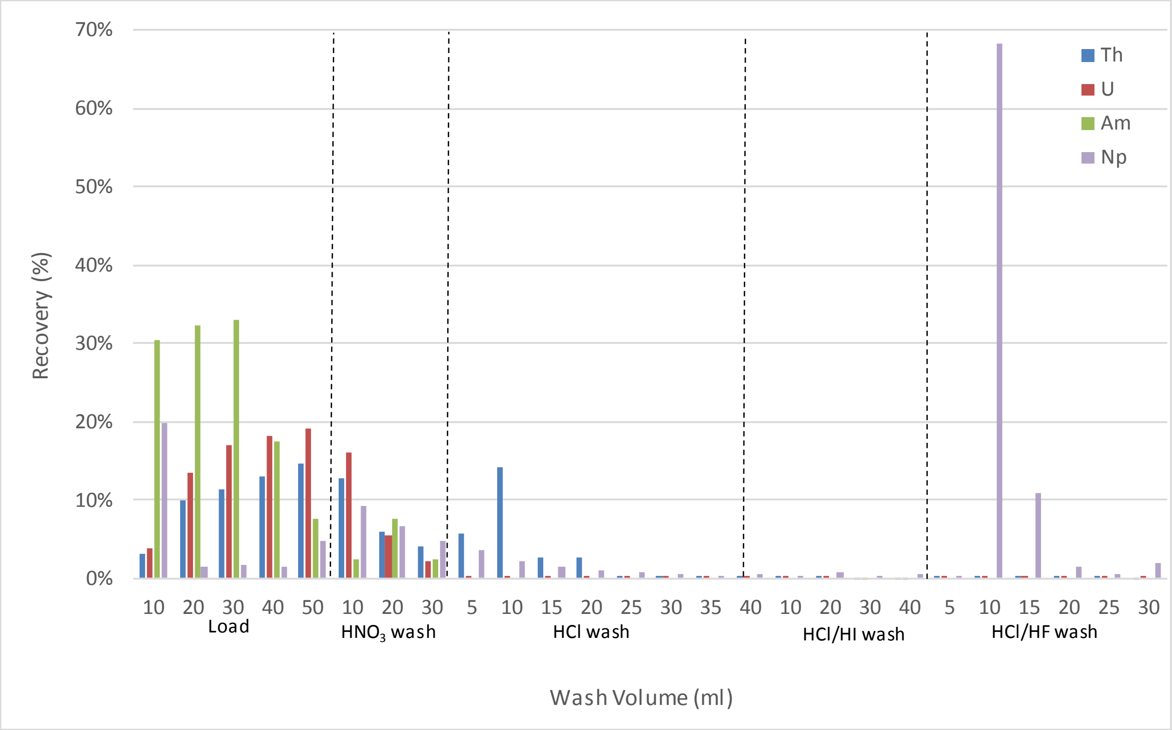

Figure 16 Elution profile for ^{237}Np methodology and separation from interferences

3.10 Final measurement of ^{237}Np

3.10.1 Introduction

The literature search showed that alpha spectrometry was the most common technique used for the determination of ^{237}Np in environmental sample. However increasingly due to advances in technology, ICP-MS is becoming the preferred approach due to the potential for higher sample throughput.

3.10.2 Methodology

Following analysis according to the optimised procedure (Figure 18), samples were analysed by ICP-MS. The final elution fraction (20 ml 4.5 M HCl/0.1M HF) was evaporated to near dryness with conc. nitric acid (~ 2 ml) added to remove any residual iodine present. The samples were re-dissolved in 2% nitric acid and the ^{239}Np activity measured by gamma spectrometry to calculate the ^{237}Np recovery to this point. An aliquot of the sample (50 µL) was removed for ICP-MS analysis.

Mass spectrometric measurements of ^{237}Np were performed using an Agilent 8800 ICP-QQQ mass spectrometer fitted with Ni cones and Micromist nebuliser. Instrument set up parameters are summarised in Table 7. All samples and standards were introduced in 2% HNO_3. The instrument was used in MS-MS mode with both mass spectrometers set to m/z = 237 to minimise ^{238}U tailing into the m/z = 237 region.

Table 7: ICP-QQQ set up parameters.

Component	Parameter	Setting
ICP	RF	1550 W
Mode	MS/MS	
	Q1-Q2	237 -> 237
	Dilution gas flow rate	0 ml/min
	Option gas flow rate	0 ml/min
Extraction lens	Extraction 1	0.0 V
	Extraction 2	-200.0 V
	Omega	6.8 V
	Omega bias	-100 V
	Q1 bias	-1.0 V
Cell	Cell gas	No Gas
	Cell gas flow rate	0.0 ml/min
	Octupole bias	-8.0 V
	KED	5.0 V
Quadrupole	Mass resolution	131, 127, 1.0006, 0.02
	Q2 pressure	
Sample introduction	Nebuliser	MicroMist (glass)
	Spray chamber temperature	2 ^{o}C
	Carrier gas flow rate	1.05 L/min
	Solution uptake	40 secs at 0.30 RPS & 30 secs stabilisation
	Sweep Ar gas flow rate	

3.10.3 Results

Screening of ^{235}U confirmed that U concentrations in the purified fraction were < 10 ppb and that tailing of ^{238}U was not significant. No significant isobaric / polyatomic interferences were identified. The ICP-MS was calibrated prior to measurement of unknowns against a set of solution standards ranging from 0 to 4 ppb. A good linear response was observed over the calibration range, with a sensitivity of 105 cps / ppb and background count rate of < 10 cps. Instrument stability and matrix suppression were corrected through the use of an internal In/Re spike although no significant matrix suppression was observed for the unknown samples. The estimated limit of detection for ^{237}Np is 0.1 ppt in solution.

3.11 Optimised method

From the results, an optimised method was derived (**Error! Reference source not found.**16) for the d etermination of ^{237}Np in environmental and decommissioning samples. The method was used, without the iron hydroxide co-precipitation stage, for the analysis of 122 sediment samples originating from an ungrazed saltmarsh in the River Esk estuary, Cumbria. Typical chemical recoveries for the method vary between 60% and 100% (96% of the results) with a mean of 86% (Figure 185).

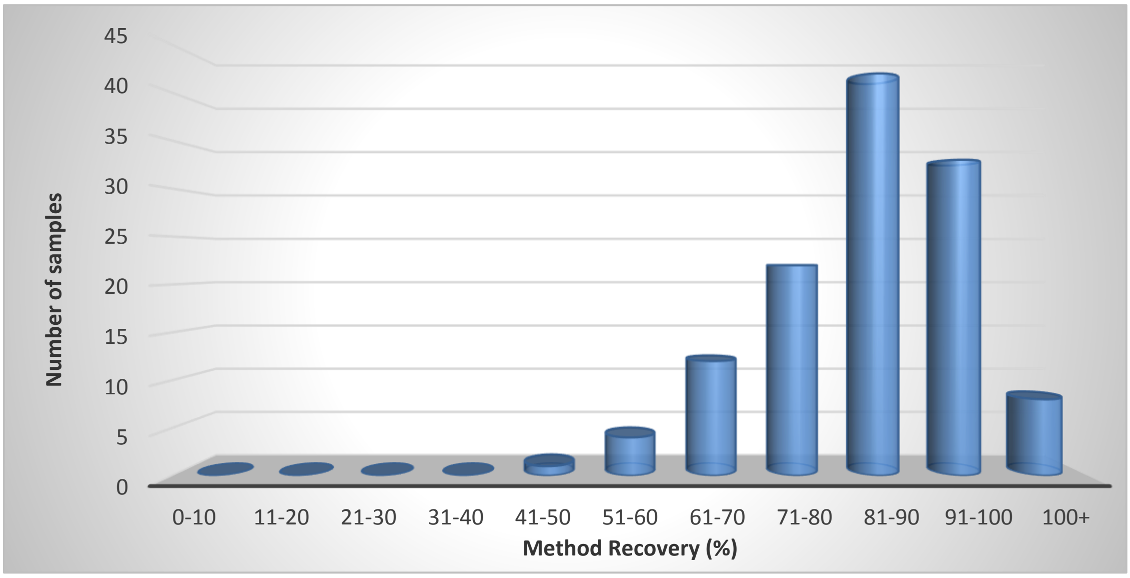

Figure 17 Histogram of method recoveries for the analysis of sediment samples

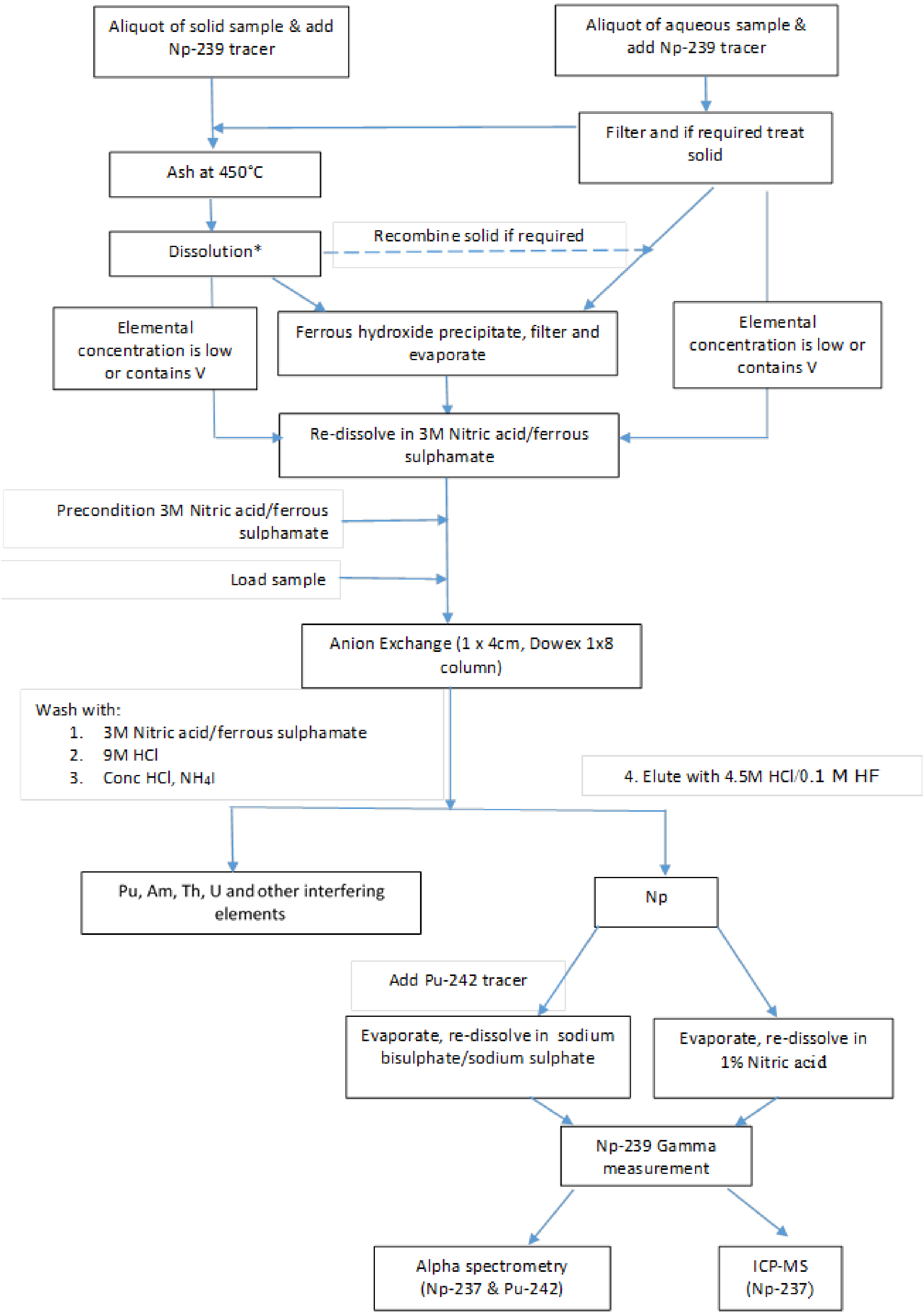

Figure 18 Separation procedure for the determination of Np-237

As no international reference materials exist for Np, therefore to validate the method a NPL Intercomparison exercise sample from the 2011 and 2013 exercises were measured using the method outlined in Figure 18 and by gamma spectrometry directly (Table 9). For the QC NPL AH2013 there was excellent agreement between the three data sets. The gamma spectrometry and results obtained from the full separation method for NPL AH2011 were also in good agreement however showed a high bias when compared to the expected value. The average of all the participants' values was calculated to be 11.6 Bq $g^{-1}$with results ranging from 10.6 Bq g^{-1} to 22.2 Bq g^{-1}. Uncertainties are based on total method uncertainties at the 95% confidence limit level.

Table 8 NPL Intercomparison sample analysis for Np-237

	Np-237 Activity (Bq g^{-1})		
	Gamma Spectrometry	Developed method	NPL Expected value
NPL AH2011	13.9 ± 0.97	14.0 ± 1.1	10.94 ± 0.44
NPL AH2013	15.9 ± 1.2	15.9 ± 1.3	15.12 ± 0.32

3.12 Conclusions

A method has been developed for the analysis of ^{237}Np in samples which have a high elemental concentration and final measurement using ICP-MS.

- A method capable of producing a readily available and regenerating source of ^{239}Np by milking a sample of ^{234}Am within a short period of time (approximately 2 hours) has been developed.
- The experiments showed no losses of ^{237}Np occurred at temperatures up to 1000°C.
- The addition of ferrous sulphamate to 3M HNO_3 converts Np(IV) to Np(V). The addition of sodium nitrite has little impact on the conversion.
- Complete co-precipitation of ^{237}Np occurs for either of the three methods (Fe hydroxide, Mn dioxide or mixed carbonate/hydroxide). For the majority of the elements the behaviour does not significantly vary with co-precipitation technique and is most effective for the

removal of Al, As, K, Mo, P and Sn from Np with greater than 80% remaining in solution. However, the efficiency of separation is method dependent for As, B, Cr and Sn.

- The ^{237}Np recoveries and decontamination factors achieved for the anion exchange method were higher than those obtained using the TEVA resin approach due to the impact of the sample matrix. For samples where the elemental concertation is high or unknown this method is recommended.

3.13 References

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Chapter Four

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4 Novel approach for the development and validation of radioanalytical methods using Neptunium-237 as a case study.

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4.1 Keywords

^{237}Np, matrix elements, experimental design, method development, validation, ISO 17025:2005.

4.2 Abstract

As the nuclear industry moves further towards decommissioning there is a greater emphasis on the analysis of more complex and varied samples types. Few laboratories in the UK use standard procedures and the development of flexible, in-house methods requires increased validation and subsequent demonstration of proficiency, especially if the laboratory is accredited to ISO17025:2005. Shortage of reference materials, for both environmental and decommissioning matrices, provides further challenges to such validation.

This paper outlines the development and validation of a method for the determination of neptunium-237 using a novel approach employing experimental design. The statistical, experimental design, approach was used to quantify the degree of interaction of each of a large number of matrix elements with the analyte at each stage of the separation, whilst keeping the number of experiments required at a practical level. The approach allows analysis and ultimately validation to ISO17025:2005 standards with a method scope based on generic elemental concentration ranges rather than specific sample type. In order to develop the method the behaviour of the matrix elements at each stage of the method were determined, allowing for

removal or mitigation of the potential interferences within the sequential extraction and identification of any inter-element interactions. An assessment of the tolerance of the procedure to a given element was then determined.

If validation only is required, the process can be simplified to assessment of the overall method performance rather than individual separation stages. Instead of revalidating for sample matrices not previously analysed, the elemental composition for a new matrix can be determined and assessed against the acceptance criteria to ensure that the procedure is appropriate or if additional testing is required. Using this approach, a method can be validated for a wide range of matrix compositions without the need for matrix-specific validation.

4.3 Introduction

The nuclear industry is a highly regulated sector which ensures the safe operations of nuclear installations, maintaining public safety and minimising environmental impact. The industry is facing the challenges of decommissioning with an increased requirement for the analysis of a wide range of alpha, beta and gamma emitting radionuclides in diverse sample types. Radiochemical separation methods need to be flexible without compromising quality which is essential to underpin public and environmental safety. Ideally the analytical methods used should be capable of analysing a wide variety of environmental and decommissioning sample types to ISO17025 accreditation standards. Such a wide range of sample types significantly increases the amount of development and validation, which dramatically increases the financial and resource requirements, especially if formal accreditation is required. This challenge is exacerbated by a shortage of reference materials. Parry (2012) concluded that the lack of reference materials posed a “particularly serious weakness in the validation process when new methods are being introduced.”

In the UK the Environment Agency’s monitoring emissions to air, land and water (MCERTS) standard recommends that for method validation a number of replicate analyses, usually seven, for each sample type is carried out with one measurement at the concentration level close to the limit of detection or at a value typical for the sample. Ideally certified reference materials would be analysed but if none exist materials can be spiked with known quantities of activity provided that the substrate has been established as analyte-free prior to measurement. If the method is modified then revalidation is required. For five sample types the validation exercise involves carrying out twenty five analyses at each concentration range plus measurement of the blank material to demonstrate background activity levels.

This paper outlines a more efficient approach to the development and validation of a method, using ^{237}Np as a case study, whereby the scope is based on elemental concentration ranges and not the specific sample type. Most radioanalytical methods have the same key stages of sampling/storage, sub-sampling, dissolution, separation and measurement. This paper focuses on the development and validation of the separation and measurement stages only. The storage, sub-sampling and dissolution stages would need to be assessed separately. Prior to analysis, for most radiochemical separations, samples are solubilised using a total dissolution technique or leached to quantitatively extract the radionuclide of interest from the sample matrix. The elemental composition of the digested sample is then the main factor which affects the efficiency of separation, the analyte recovery and final measurement of the analyte. Experimental design was used to assess the impact of matrix elements on ^{237}Np recovery over a range of concentrations at key stages in the separation procedure and then to evaluate the overall impact of matrix composition on the method and define the operational envelope of the method in terms of matrix elemental composition.

4.4 ^{237}Np determination background

The measurement of ^{237}Np is typically performed by either alpha spectrometry or, given its low specific activity of 26 MBq g^{-1}, mass spectrometry. For both approaches, chemical separation of the Np is required prior to measurement to remove matrix elements and potential radiometric/isobaric interferences. The majority of the methods used adopt co-precipitation and/or separation by chromatographic techniques (Thakur 2012) to decontaminate the ^{237}Np from any interferences which, if present, can affect the efficiency of the separation and impact on the final measurement. For alpha spectroscopy measurement, the presence of matrix elements in the final fraction can produce a thick source layer which will degrade the alpha spectrum decreasing the counting efficiency and alpha peak resolution. Alpha spectral interferences can arise from the presence of ^{234}U (4.768 MeV) and ^{230}Th (4.682 MeV) which have similar decay energies to ^{237}Np (4.781 MeV). For ICP-MS analysis the dissolved solids content of the measured fraction must be limited to maximise the intensity of signal and avoid nebuliser blockage. Although no isobaric interferences are likely for ^{237}Np the m/z=237 mass region can be impacted by polyatomic species or from tailing from more abundant ^{238}U. An optimum procedure is one that results in high percentage recovery of ^{237}Np in an interference free matrix, which is independent on the original elemental concentration and content.

The matrix elements may affect separation performance either through direct interaction / competition with the analyte or through complex inter-species interactions. Such interactions may not be fully evaluated using single element interference tests. Traditionally experiments are conducted by changing one parameter at a time until no further benefit is achieved (Change Only One Separate factor at a Time - COST approach) which is inefficient and interacting factors can be missed. Experimental Design (Design of Experiments, DOE) is a statistical technique which is able to produce empirical models that identify the most influential factors and their ranges using a set of carefully selected experiments in which all the relevant factors are varied simultaneously, but independently. Analysis of the acquired data identifies the optimum conditions and the key factors which influence the outcome, aiding the decision making process.

4.5 Mathematical principles

The design of experiments (DOE or experimental design) is the design of any task that aims to explain the variation of information under conditions that are hypothesized to reflect the variation. This approach is currently used in the pharmaceutical, chemical, natural and social sciences and engineering sectors. The benefit of Experimental Design (DOE) is to reduce the number of experiments that are required for a scientific study, where all the factors are systemically varied, whilst maximising the information gained (Umetri AB, 1998) Prior to the experiment the aim needs to be carefully defined. In this case study, the aim is to identify which elements affect the recovery of ^{237}Np and at what concentration ranges. It is then necessary to define the information that is known, that which is unknown and that which needs to be investigated. For example, it is known that the presence of elements can affect the recovery of ^{237}Np. It is unknown precisely which elements, at what concentrations and if the elements can interact to increase or decrease the effect. The experimental variables also need to be determined, in this case the presence of different elements over a range of concentrations and these can be changed independent of each other. For this study the response is defined as the elemental and ^{237}Np concentrations analytically determined. The objectives were as follows:

- Determine, using the statistical approach, which elements affect the recovery of ^{237}Np at different separation stages and at what concentrations (method development),

- Evaluate the impact of matrix elements on ^{237}Np recovery for the entire method (method validation),

- Using the concentration of elements in the final fraction assess which elements are present which can interfere with the final measurement of ^{237}Np,

- Determine the decontamination factor of each element in the final purified fraction arising from the separation procedure to support method validation and assess the potential impact of interferences on analyte measurement,

- Define the operational envelope of the method in terms of sample elemental concentrations.

The outcome of an experiment is dependent on the experimental conditions with the result described as a function based on the experimental variables. An empirical mathematical model is used where the process is not understood and the factors which influence the response are needed to be defined. DOE involves deriving a set of experiments which are repetitive with regards to a given question. For this study, a quadratic model is used to determine non-linear relationships between the experimental variables and responses.

An experiment is devised where the independent variables (in this case different elements) are laid out in a symmetrical fashion around a standard reference experiment or centre point in a cubic pattern as shown in Figure 19. For this study, the standard reference experiment is ^{237}Np recovery. Each variable is analysed at three different concentrations levels (low, medium and high) and the effect on the centre point i.e. ^{237}Np recovery determined for each of the model parameters using regression coefficients. This indicates how the independent variables influence the response. To carry out a full factorial model all the possible corners of the cube are analysed (Figure 19) and for nineteen elements this would equate to over 500,000 samples (2^{19}). The figure illustrates the analysis required where there are three elements. The “hypercube” becomes more complex as the number of elements increases and cannot be visually represented. Although the model allows all effects and interactions to be assessed it is not practical and is limited to the determination of linear influence of the variables. By using a fractional factorial model “confounded” higher order effects and interactions can be identified and the number of experiments for nineteen elements reduces to thirty five experiments. This approach provides a statistical model in which more than one element varies between each experiment, but overall, all elements vary independently.

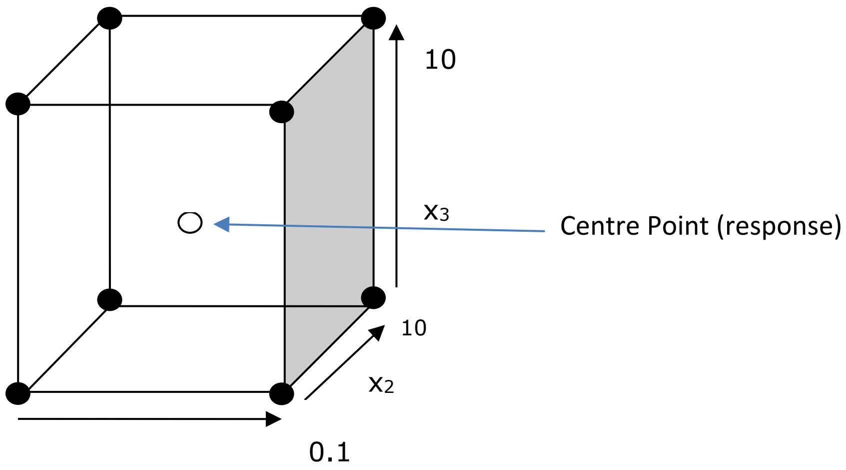

Figure 19 Example of full factorial experimental design model for three elements (2^3) showing 3 independent variables, 2 levels of each variable, 8 test conditions.

In all fractional factorials experimental designs all variables are normalised to vary between -1 and +1. The relative change of a variable is directly related to the size of its regression coefficient and therefore if the model parameters have either a large positive or negative value the corresponding variable has a large influence on the response(s). The ^{237}Np recovery data (response) from each of the experiments is analysed using a partial least squares regression model using a specified number of terms including a constant. The fit against the predictive model is then assessed allowing for identification of the elements which influence the recovery of ^{237}Np.

4.6 Methodology

4.6.1 Equipment and reagents

A certified ^{237}Np standard was supplied by NPL, Teddington, UK.

Elemental analyses were performed using either a Perkin Elmer Elan DRC-e® ICP-MS or Agilent 725 ICP-OES. All ^{237}Np measurements were performed using ICPMS.

Dowex 1 x 8 anion exchange resin was supplied by Triskem, France.

Goldstar liquid scintillation cocktail was supplied by Meridian Technologies, UK.

Certiprep elemental standards were supplied by Fisher Scientific, UK.

All other reagents were supplied by Fisher Scientific, UK and were at least analytical grade unless otherwise stated.

4.6.2 Preparation of Experimental Design elemental standards

Instead of developing methods based on sample type, elemental composition was considered as the accuracy and precision of the determination is affected by the presence of interfering sample matrix species which can decrease the method recovery and affect final counting source purity.

The matrix element concentration in environmental and decommissioning samples varies considerably. To evaluate the range of concentrations typically encountered, the composition of 78 certified environmental reference materials (CRM's) available from International Atomic Energy Authority (IAEA) and Laboratory of the Government Chemist (LGC) and 61 decommissioning waste samples characterised at NNL Preston laboratory were compiled. The data set included the following range of sample matrices:

- Decommissioning – sludge, fuel element debris, tank supernate, hoover bags, walnuts, resin, aqueous slurry, oil and ash;
- Biota – algae, fish tissue, tuna;
- Soil and sediment – marine, estuarine, clay, various compositions of soil, stream, channel, harbour, lake, river;
- Sludge- sewage, domestic, industrial;
- Vegetation – seaweed, lichen, plankton, grasses, wood, branches and leaves, cotton;
- Aqueous- ground water, rain water, waste water effluent, landfill leachate;
- Other – coal fly ash.

Table 9 summarises the maximum concentrations considered for each element representative of the range of sample types that have been routinely analysed. The range of concentrations was significant; for example, Al concentrations ranged over 6 orders of magnitude. The minimum, medium and maximum concentrations of thirty seven matrix elements in the range of matrices were determined.

Table 9 Summary of elemental concentrations found in samples (µg g^{-1})

Maximum Concentration	**Element**
>100000	Al, Fe, Mg, Na, Mn*
10000-100000	Cu, Ni, Ca, As, Si
1000-10000	Zn, Pb, S, K, Cd, Cr, P, Sr, Ba
100-1000	Se, Sn, V, Li, Be, Sb, B, U, Co, Mo
10-100	Ce, Hg, Rb, Ag
1-10	Dy, La, Th, Cs

*The high level for this element is due to one ground water sample. If this outlier is removed the concentration decreases to between 1000 and 10000 µg g^{-1}.

From the 37 elements stated above the list was reduced to 20 elements based on the following criteria:

- At least one element from each group except 4, 17 and 18 was assessed with the most abundant element typically chosen e.g. in the group one elements K was selected as the model element group 1.
- Uranium and thorium were included to assess decontamination of interferences
- Cerium was included as an analogue for plutonium.

The experimental design software (MODDE; Umetrics, Sweden) used the minimum, medium and maximum values for each element to produce the details of thirty five mixed element standards; thirty two solutions had differing minimum or maximum elemental concentrations with the remaining three solutions at the median range.

The mixed elemental standards were prepared using, where possible, certified standards from Certiprep and if unavailable high purity chemical reagents. The ^{237}Np activity added to all the standards was constant (180 Bq ^{237}Np). To verify the elemental and ^{237}Np concentrations in each of the prepared mixed elemental standard solutions aliquots were measured using ICP-MS and ICP-OES.

4.7 Method Development

Ideally when developing a method the impact of the matrix elements at each stage needs to be understood, including any possible elemental interactions, to identify those interactions that may impact on neptunium recovery. If any element(s) are found to have a detrimental effect on the method recovery then the separation and purification stages may need to be modified to remove the interference. Two key separation stages were assessed; pre-concentration (co-precipitation) and purification (anion exchange separation). Three co-precipitation techniques, previously reported for ^{237}Np pre-concentration, were evaluated to determine which approach was most efficient at separating interferences and recovering the ^{237}Np. The ^{237}Np recovery and the elemental separation efficiency were determined for the three co-precipitation options, for anion exchange separation and for the overall method (combining the co-precipitation and ion exchange separation) (Figure 20).

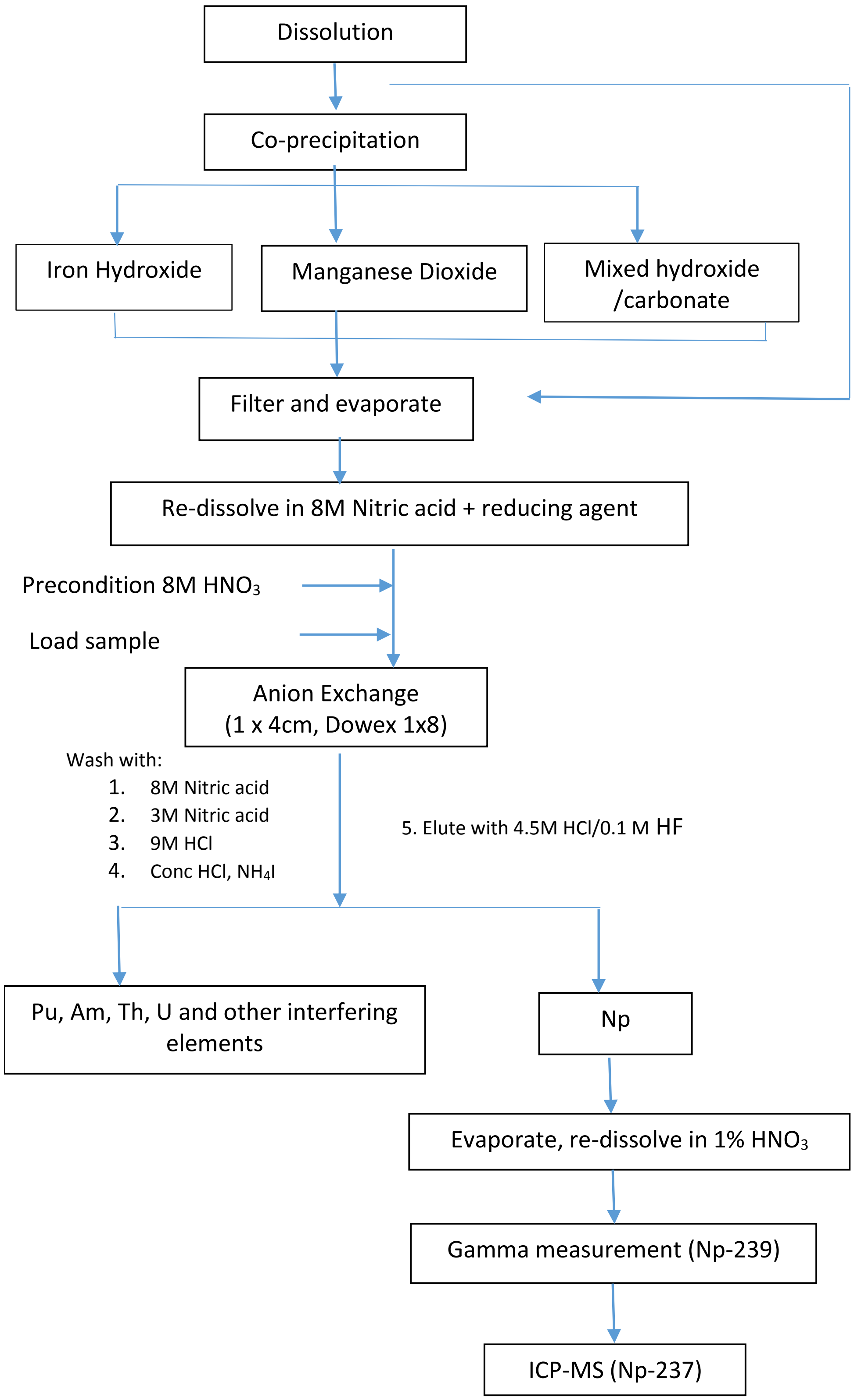

Figure 20 Schematic of methodology for the determination of ^{237}*Np*

4.7.1 Co-precipitation

The thirty-five mixed element standards were processed using the three co-precipitation methodologies to determine the extraction efficiency of ^{237}Np and separation from elemental interferences. Three 5ml aliquots of each mixed element solution were taken and one of the three co-precipitation methods followed. The elemental and ^{237}Np concentrations in the filtrate were measured using ICP-MS and ICP-OES. The concentration in the precipitate was determined by difference between the final and filtrate results.

Method A – Iron(II) hydroxide co-precipitation **(Chen et al., 2002)**

The samples were acidified to pH2 using 12M HCl and 0.5g/L $K_2S_2O_5$ added. The original method states the addition of 1mg/L $FeCl_3.6H_2O$ but due to the high iron concentrations in the samples this was omitted. The samples were warmed for one hour and the pH adjusted to 10 using 6M NaOH (final concentration ~0.5-1M NaOH) to precipitate ($Fe(OH)_2$- $Np(OH)_4$).

Method B – Manganese Dioxide co-precipitation **(Germian and Pinte, 1990)**

Potassium permanganate at pH 9-9.5 (1mg/L) was added to each sample and the sample left to stand. A black MnO_2 precipitate formed on standing.

Method C – Mixed carbonate/hydroxide precipitate **(Holm and Aarkrog, 1987)**

The samples were acidified to pH1-2 using conc. HCl and then the pH was adjusted to pH to 9-10 using 1M NaOH solution to precipitate the mixed hydroxide.

All the samples were left overnight to settle then filtered through a 0.2µm cellulose nitrate syringe filter. The resulting supernate was diluted to a known volume, acidified with high purity nitric acid to 2% and measured by ICP-OES and ICP-MS.

4.7.2 Separation using Anion Exchange resin (Dowex 1x8)

A 2ml aliquot of each mixed element solution was evaporated to dryness and redissolved in 50 ml 8M HNO_3. The samples were then loaded onto a 1x5 cm Dowex 1x8 column (preconditioned with 50 ml 8M HNO_3) and washed with 30 ml 8M HNO_3, 30 ml 3M HNO_3 (to complete the removal of U) and 40 ml 9M HCl (to elute Th). A further 20 ml conc. HCl-0.1M NH_4I solution wash was used to remove any Pu. Np was eluted in 30 ml 4.5M HCl-0.1M HF. The final elution fractions were then evaporated to near dryness, in the presence of nitric acid, to decompose any organic material (e.g.

fine resin particles), diluted and acidified with 2% high purity nitric acid then measured using ICP-MS and ICP-OES to determine the elemental and ^{237}Np concentrations.

4.7.3 Full Method validation

An aliquot (3 ml) of each of the mixed elemental solutions was taken and reduced by adding iron sulphamate and sodium sulphite, along with distilled water (10ml). The samples were warmed for one hour, transferred to a centrifuge tube and the pH adjusted to 10 using 6M NaOH (final concentration ~0.5-1M NaOH) to precipitate ($Fe(OH)_2$- $Np(OH)_4$). After one hour the samples were centrifuged and the supernate removed. Any residual moisture was removed by heating in a water bath until the sample was dry and then taken up in 70 ml 8M HNO_3. The samples were then loaded onto a 1x5 cm Dowex 1x8 column (preconditioned with 50 ml 8M HNO_3) and washed with 30 ml 8M HNO_3, 30 ml 3M HNO_3 and 40 ml 9M HCl. A further 20 ml conc. HCl-0.1M NH_4I solution wash was used to remove any Pu and the Np eluted in 30 ml 4.5M HCl-0.1M HF. The final elution fractions were then evaporated to near dryness, in the presence of nitric acid, to decompose any organic material, re-dissolved in 2% HNO_3 and measured using ICP-MS and ICP-OES to determine the element and ^{237}Np concentrations.

4.8 Data Analysis

The results obtained were corrected for any dilution factors associated with the volume of sample and ICP-MS measurement preparation. The percentage recovery for each element, including ^{237}Np, in each of the standard solutions was then calculated by dividing the concentration in the final fraction by the elemental concentration in the initial standard (also measured by ICP-MS). The percentage recovery results obtained for ^{237}Np were then used with the MODDE software to identify the significance of matrix elements on Np recovery. The Variable Importance (VIP) and coefficient plots (Figure 22, Figure 23, Figure 25 and Figure 26) were used to identify using a predictive model, the factor (elements) impacting on Np recovery. The data are displayed as bars with confidence intervals stated (error bars) at the 95% confidence limit level. Factors which have small piles within the boundaries of confidence intervals have no significance whilst factors with bigger piles are potentially influential e.g. affect the recovery of ^{237}Np to the greatest extent. The coefficient plots (Figure 23 and Figure 26) show the significance of the factors to the predictive model with the negative and positive piles reflecting the deviation from the actual versus predictive.

The VIP plots (Figure 22 and Figure 25) show the importance in terms of significance to prediction and explanation of factor variance. It is generally accepted that a VIP value greater than 1 indicates the variable has a significant effect on outcome and results below 0.5 are classed as insignificant. For values between 0.5 and 1 the associated confidence limits are considered and if greater than 50% of the result they have been classed as having a high level of uncertainty and therefore unlikely to have a significant impact on recovery.

4.9 Results

4.9.1 Co precipitation

Apart from two samples there was a >99% uptake of ^{237}Np for all three co-precipitation methodologies (iron (II) hydroxide, manganese dioxide and mixed carbonate/hydroxide) for all thirty five standards (Section 4.6.2). For two tests using the manganese dioxide method, the Np recovery decreased to ~80% with the lower recovery most likely due to incomplete filtration due to the fine-grained nature of the precipitate. As the ^{237}Np recoveries were largely unaffected the DOE analysis could not be used. The results of the three co-precipitation methods showed that none of the elements at any of the three concentrations tested affected the ^{237}Np recovery.

4.9.2 Anion exchange separation

4.9.2.1 Neptunium recovery

The chemical recoveries for the anion exchange method were generally good (Figure 21) considering the high elemental content of the samples with 85% of the results producing a yield greater than 40% with a mean value of 74%.

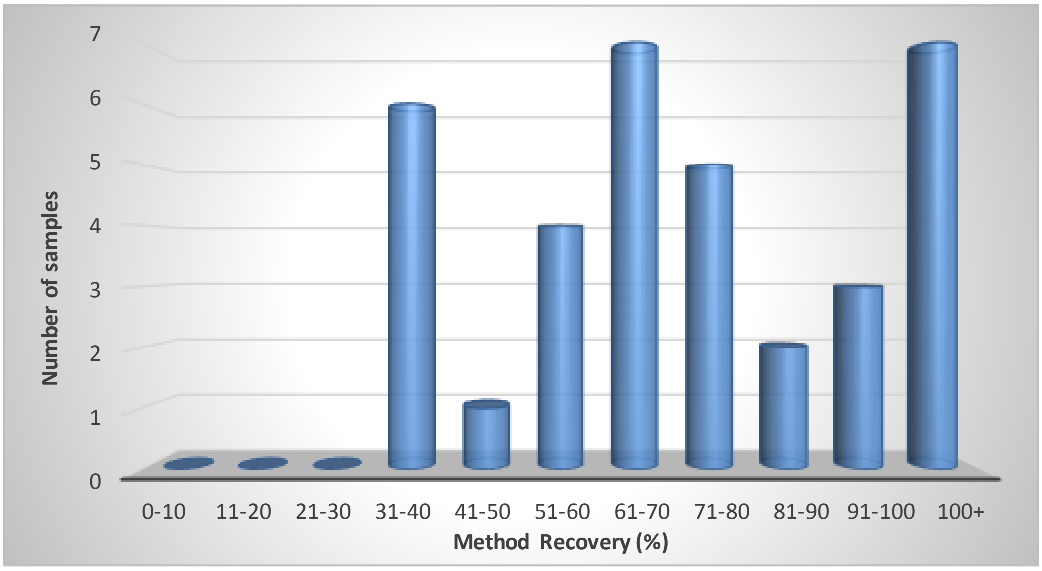

Figure 21 ^{237}Np recoveries for Anion Exchange method

4.9.2.2 Elemental effect on ^{237}Np recovery

For each approach (anion and full separation) the effect the elements have on ^{237}Np chemistry can be significant resulting in low and inconsistent recoveries (Figure 21). The statistical data allows us to evaluate this impact and identify the key elements.

The predictive model produces theoretical values for each element and the influence on Np recovery. For the anion exchange data the statistical data shows a reasonable agreement with the observed versus predicted or theoretical, results for the anion exchange method producing an r^2 value of 0.4075 which reflects the significant variation in the results across the 35 standards, also indicated by the error bars.

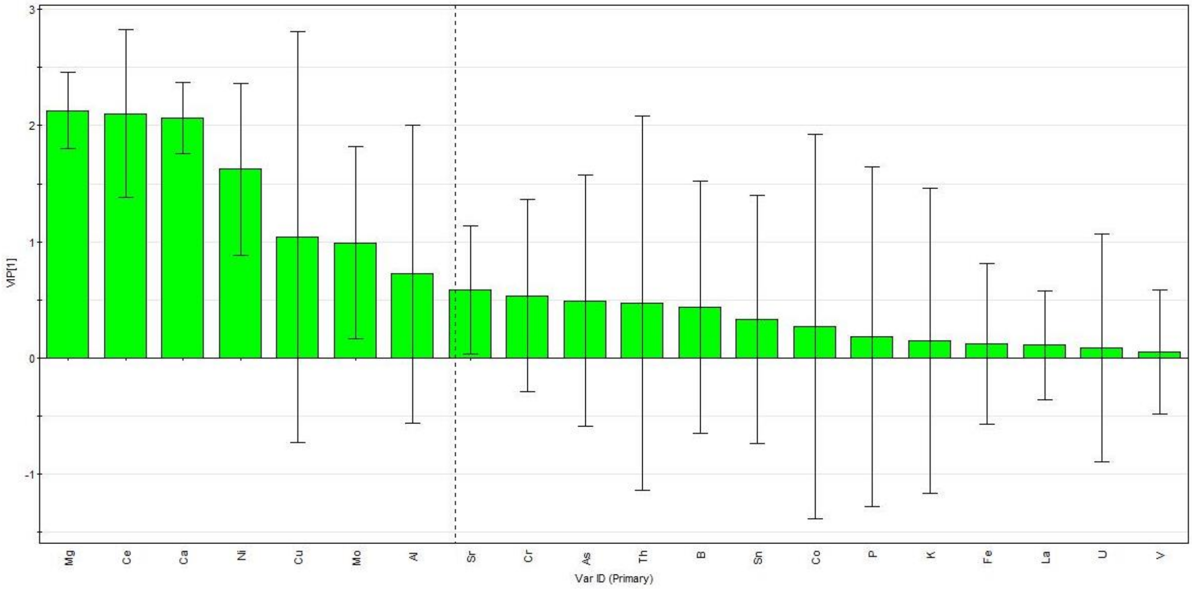

Figure 22 Variable Importance Plot for the elemental effect on ^{237}Np recovery using Anion Exchange separation

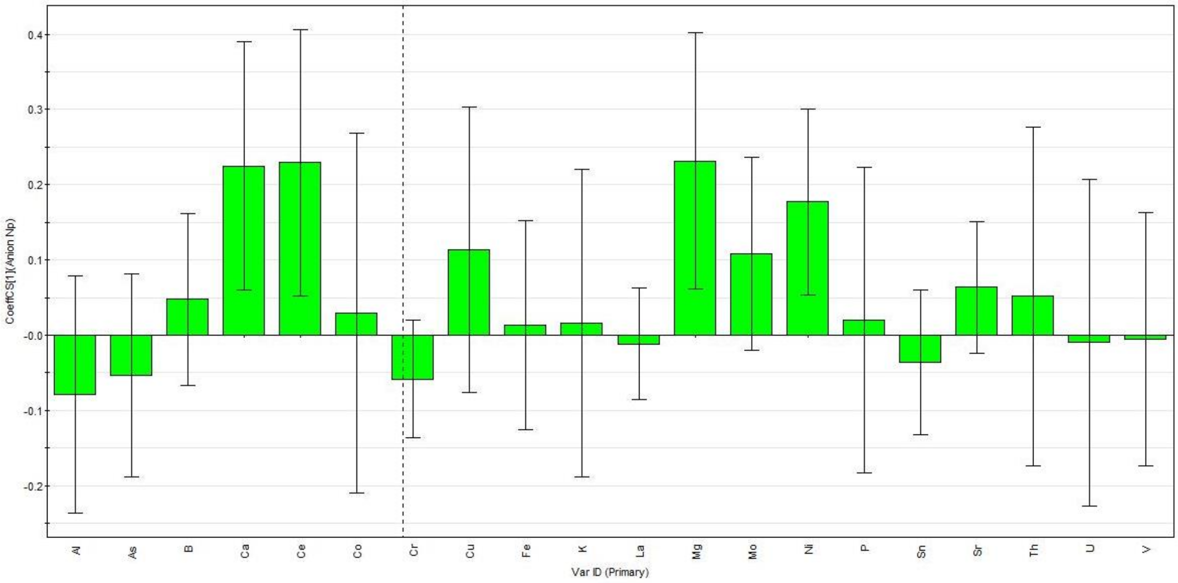

Figure 23 Plot of scaled and centred coefficients for the elemental effect on ^{237}Np recovery using Anion Exchange separation

Alkaline metal (K)

Potassium produced VIP results (Figure 22 and Figure 23) with a high associated uncertainty and below 0.5 for the anion method indicating it has an insignificant effect on the Np separation chemistry across the concentration range analysed (270 to 8280 ppm).

Alkaline earth (Ca, Mg, Sr)

Divalent cations have a high selectivity coefficient (ratios of ions in solution vs. ions on the resin) compared to monovalent species such as K^+ and therefore if higher levels of these total dissolved solids are present the column separation efficiencies decrease. This is reflected in the statistical analysis which showed the alkaline earth metals Mg and Ca had a significant effect on the Np recovery for the anion method across the concentration range (12.6 to 15,000 ppm). Mg and Ca were the first and third most influential elements respectively with low uncertainties (Figure 22 and Figure 23). Strontium was present in the samples at lower concentrations (up to 160 ppm) at a level which did not impact on separation efficiencies and had minimal impact on ^{237}Np recovery with the anion method result producing a result slightly greater than 0.5 with a significant associated confidence level.

Polyatomic non metal (P)

Phosphorus, present in the samples at concentrations up to 340 ppm, produced a VIP value below 0.5 (Figure 22 and Figure 23) with a high associated uncertainty and therefore has no significant impact on Np recovery.

Metalloid (As and B)

Arsenic and boron produced VIP values at or below 0.5 with significant associated uncertainties (Figure 22 and Figure 23) indicating the presence of these metalloids had little impact on Np recovery at concentrations of 88 ppm and 450 ppm respectively.

Lanthanides (La and Ce)

The statistical data found Ce to be the second most influential element for the anion exchange method and present in the samples at concentrations up to 218 ppm. The concentrations of La were lower (up to 17 ppm) with the element having an insignificant impact on Np recovery with a VIP value below 0.5(Figure 22 and Figure 23) .

Other metallic elements, group 3A and 4A (Al and Sn)

For the anion exchange method Al and Sn had VIP values of ~0.75 and less than 0.5 respectively with a higher level of uncertainty associated (Figure 22 and Figure 23) with both results indicating their presence had little adverse impact on Np recovery at concentrations of 4700ppm and 91 ppm respectively.

Transition (Co, Cr, Cu, Fe, Mo, Ni, V)

The statistical analysis showed Ni, Cu and Mo for anion exchange procedure were in the top 5 most influential elements having a detrimental effect on Np recovery. Vanadium, cobalt and iron were however shown to have an insignificant impact on Np recovery for the anion method even though cobalt and iron were present at higher concentrations (37 and 15000 ppm respectively). The impact of Cr was minimal due to the high uncertainty associated with the VIP results produced which ranged between 0.5 and 1 for both methods (Figure 22 and Figure 23).

Actinides (Th and U)

The methods are developed to separate U and Th from Np with the statistical analysis confirming that both of these elements had no significant effect on Np recovery. The results obtained were below the level of significance (VIP value of 0.5) with considerable errors.

4.9.3 Full Separation Method - Co-precipitation followed by Anion exchange separation

4.9.3.1 Neptunium recovery

The addition of the co-precipitation stage reduced the method efficiency (Figure 24) with the recovery falling below 40% for over half of the results (62%). Although the co-precipitation stage may increase the decontamination factors achieved it also has a significant and detrimental impact on the ^{237}Np recovery. The co-precipitation results showed almost complete uptake of ^{237}Np (greater than 99%) and therefore it is likely that the addition of the extra stages including precipitate washing, evaporation and re-dissolution caused the lower recoveries due to transfer losses and inconsistent removal of supernate.

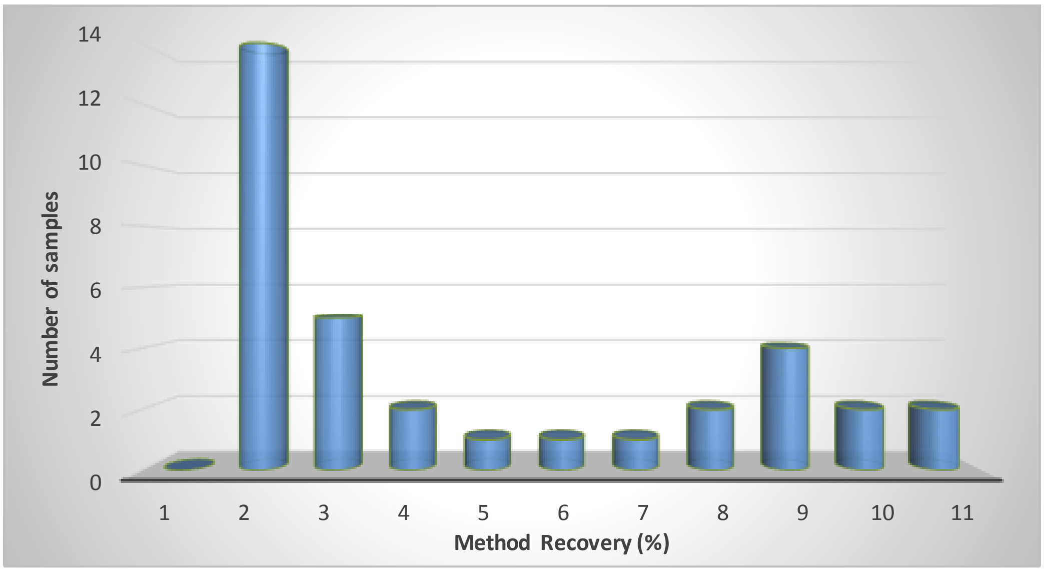

Figure 24 ^{237}Np recoveries for Full separation method

4.9.4 Elemental effect on ^{237}Np recovery

The predictive model produces theoretical values for each element and illustrates the influence on Np recovery (Figure 25 and Figure 26). The results obtained for the full separation method showed better agreement ($r^2 = 0.606$) than the anion exchange method, with evidence of non-linearity due to elemental interactions but again with high associated confidence level values.

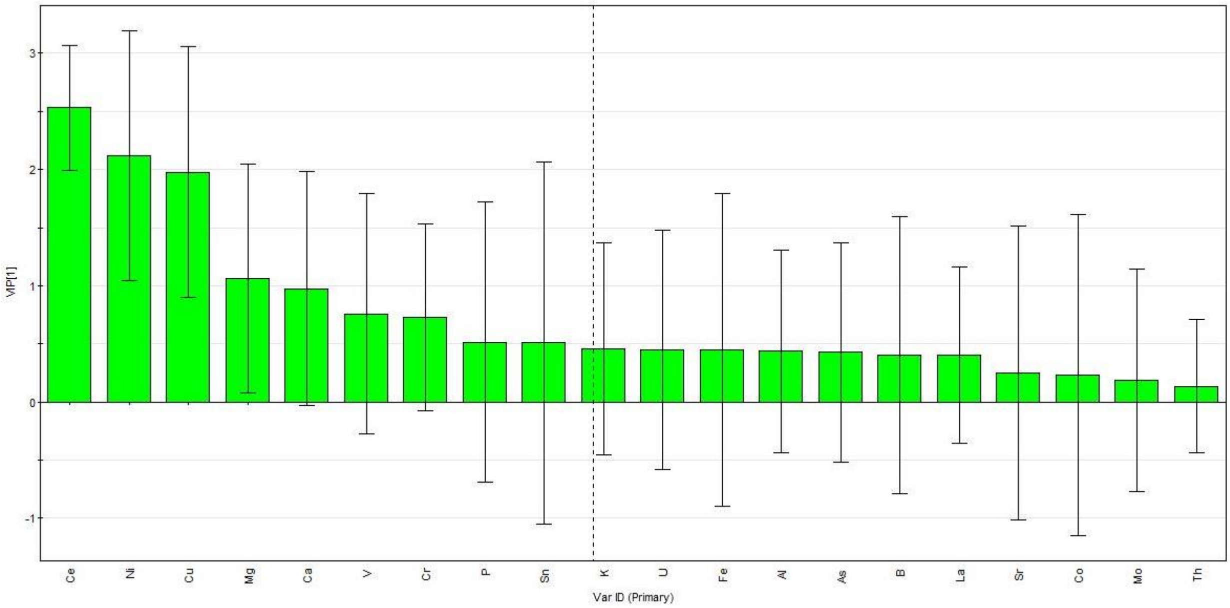

Figure 25 Variable Importance Plot for the elemental effect on ^{237}Np recovery using full separation method

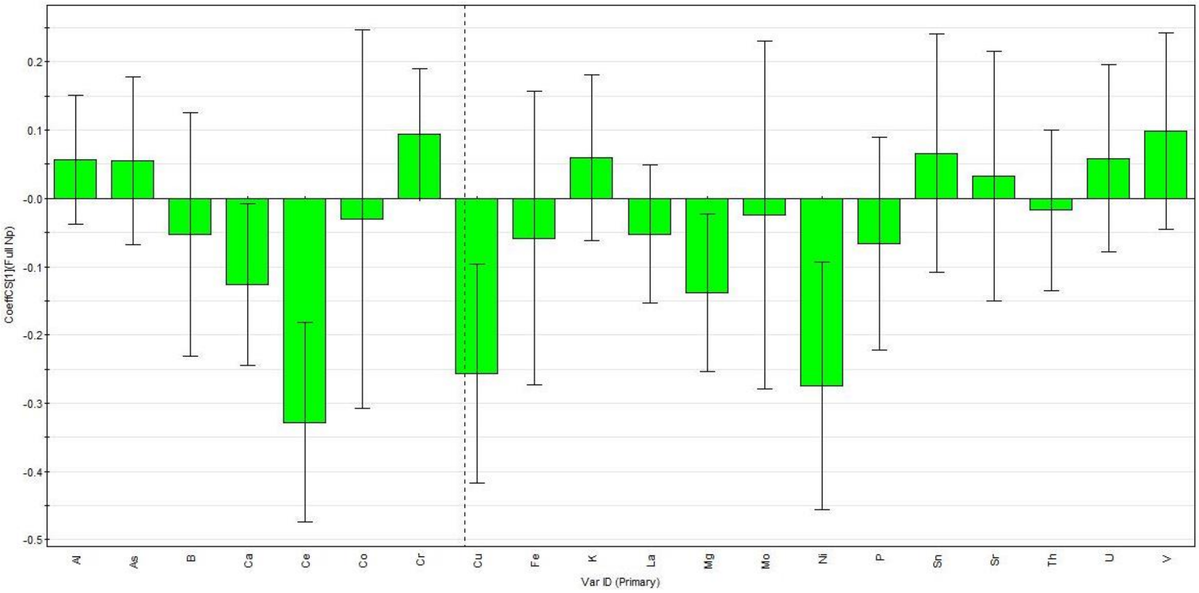

Figure 26 Centred and scaled coefficients for the elemental effect on ^{237}Np recovery using full separation method

Alkaline metal (K)

Similarly to the anion exchange method, potassium was present 504ppm, and had an insignificant effect on Np recovery reflected in the VIP value less than 0.5 with a high associated uncertainty (Figure 25 and Figure 26). Potassium does not co-precipitate with Np (Chapter 3) and has a low selectivity coefficient for anion exchange.

Alkaline earth (Ca, Mg, Sr)

The addition of the co-precipitation stage decreased the influence of Ca and Mg on Np recovery to the fourth and fifth most influential elements with the VIP values reducing by almost 50% (Figure 25 and Figure 26). The co-precipitation stage removed between 10% and 30% of the elemental concentration prior to column separation. The VIP value for strontium was classed as insignificant with reduction, compared to the anion exchange method, reflecting the decontamination obtained by addition of the co-precipitation stage (70% removed).

Polyatomic non metal (P)

For the full separation method a VIP value of 0.5 was obtained with considerable and significant associated uncertainty (Figure 25 and Figure 26). Although statistically insignificant it is worth noting the VIP order showed phosphorus had a greater influence on recovery when the additional co-precipitation stage was incorporated into the method which is surprising as between 68% and 82% remained in the supernate. It is likely that the influence increases in relation to that of the other elements and the higher concentrations in the sample (anion method at 8300 ppm, Full separation at 12000 ppm).

Metalloid (As and B)

Similarly to the anion exchange method arsenic and boron produced VIP values below 0.5 with significant associated uncertainties indicating the presence of these metalloids had little impact on Np recovery (Figure 25 and Figure 26).

Lanthanides (La and Ce)

For the full separation method Ce was shown to have the greatest impact on Np recovery if present whilst La had an insignificant influence.

Other metallic elements, group 3A and 4A (Al and Sn)

Aluminium and tin produced VIP values for the full method were below 0.5 indicating the presence of p block elements have little impact on neptunium recovery (Figure 25 and Figure 26). The addition of the co-precipitation stage decreased the impact of Al on recovery with over 90% of the element remaining in solution, not following Np.

Transition (Co, Cr, Cu, Fe, Mo, Ni, V)

As with the anion exchange method the presence of Ni and Cu had a significant impact on Np recovery (second and third most influential, Figure 25 and Figure 26). However the Mo had little impact with a VIP value of less than 0.5 due to the addition of the co-precipitation stage as the element does not follow Np and is completely removed prior to column separation. The impact of the presence of vanadium also decreased. Similarly to the anion exchange method Co, Fe and Cr also had an insignificant impact on Np recovery chemistry.

Actinides (Th and U)

The VIP values for uranium and thorium were below the level of significance (VIP value of 0.5) with considerable errors again indicating the presence of these elements had no detrimental impact on Np recovery (Figure 25 and Figure 26).

4.10 Decontamination factors

The statistical approach has shown that at the recovery of neptunium is affected by the presence of certain elements and the concentrations present in the sample. To ascertain the operational limits for the method for each element there needs to be a number of considerations.

1. The influence each element has on Np recovery using the statistical approach and identifying the concentration any detrimental effect occurs identifying the maximum permittable concentration.

2. The presence of interfering elements in the final elution fraction (4.5M HCl/0.1M HF) can decrease the final measurement efficiency of ^{237}Np. For alpha spectroscopy measurement the presence of matrix elements in the final fraction can produce a thick electrodeposited source resulting in a degraded alpha spectrum with reduced counting efficiency and alpha peak resolution. A high dissolved solid content can also result in blockage of ICP-MS cones and suppression of analyte signal. It is important therefore to identify which elements have not been fully removed by the separation procedure and quantify the degree of decontamination. To ensure free aspiration and low suppression, the total dissolved solid content in the sample solution should be lower than 0.1% and ideally less than 0.01%.

3. Radiometric interferences from the presence of ^{234}U, ^{230}Th and ^{242}Pu also affect the alpha spectrometry measurement as have similar decay energies to ^{237}Np causing spectral overlap. High concentrations of ^{238}U in samples measured by ICP-MS interfere with measurement due to peak tailing. The levels of these radiometric interferences in the final measurement solution should be at less than 0.1 mBq for both measurement techniques.

Alkaline metal (K)

Less than 0.5% of the original potassium content was present in the final fractions for the anion and full method at concentrations up to 8280 ppm and 6460 ppm respectively, achieving decontamination factors (DF) of approximately 700. Over 90% of the potassium was removed from the anion column in the load and 8M nitric acid washes and the remainder in the subsequent 3M nitric and 9M hydrochloric acid washes. At concentrations ranging from 6460 ppm and 12400 ppm, following the full separation method, the DF decreased to 21 with a significant amount (35%) present in the final fraction indicating that the separation was concentration dependent and should not exceed the mid standard value.

Alkaline earth (Ca, Mg, Sr)

The total concentration of alkaline metals (Ca, Mg and Sr) present in the final fraction is less than 0.25% of the original content, achieving decontamination values up to 280000, 60000 and 33000 respectively with the majority (>95%) eluted in load and 8M nitric acid wash. The decontamination values, similar to potassium, were reduced in the higher concentration samples following full separation (DF = 2000) however only 2% of the Sr was present in the final HCl/HF fraction indicating an operational envelope. Taking into account the decontamination and statistical analysis the operational envelope for the alkaline earth elements has been set at concentrations up to 250 ppm for strontium.

Non-metal (P)

The majority of P was removed in the load and 8M nitric acid wash however for concentrations ranging between 273 ppm and 336 ppm tailing occurred into the elution fraction, achieving decontamination values of approximately 30. The addition of the co-precipitation stage significantly increased the separation (DF of 4800) with less than 0.2% of the original phosphorous concentration present in the final fraction. Considering the insignificant effect on recovery and minimal presence in the final fraction, the scope operational envelope has been determined as equivalent to the 224ppm for the anion method and 504ppm for the full separation approach to reduce the phosphate, therefore total dissolved solid content.

Metalloid (As and B)

A slow elution of arsenic from the resin was observed with the concentration decreasing with each wash however a significant quantity (over 25%) was present in the final elution fraction, achieving decontamination factors of up to 7.5. The addition of the co-precipitation stage significantly increased the separation of arsenic (DF up to 21000) with less than 0.42% of the original concentration in the original fraction. The concentration of boron present in the samples was approximately five times higher compared to arsenic and poor separation observed for both methods with up to 75% present in the final fraction, and achieving a DF values no greater than 51. Despite the poor separation these elements have insignificant impact on Np recovery and do not cause any measurement interferences and as such the operational envelope for the metalloids has been determined to be 673 ppm.

Other metal elements (Al and Sn)

Tin, present in the samples up to 91 ppm, was removed in the load and initial wash fractions from the anion exchange column, achieving decontamination factors of 70000. There was incomplete separation of aluminium at higher concentrations up to 4700 ppm, with 7.5% of the original concentration present in the final fraction reducing the DF to no greater than up to 1800. As with boron, there was a linear relationship between amount of aluminium present in the final fraction and the original concentration level. The p-block elements if present in the final fraction will have minimal impact on the final measurement efficiency and the statistical analysis has shown no significant detrimental effect on Np recovery therefore the operation envelope has been set at 7050ppm.

Transition (Co, Cr, Cu, Fe, Mo, Ni, V)

Iron was analysed at concentrations up to 22,500 ppm reflecting the levels typically present in samples. There was complete elution of Fe from the resin in the load and nitric acid wash fractions achieving decontamination factors for both methods of 220,000. The presence of iron although it has no impact on Np recovery can led to the production of thick electrodeposited sources however the separation efficiency of both methods was good.

Chromium, copper, molybdenum and nickel were all present in the samples at similar concentrations ranging from 3.2 ppm to 3590 ppm. The majority of the elemental concentration was removed in the load and 8M nitric acid wash (between 80% and 97%) with less than 0.5% of Mo and Ni present in the final elution fractions indicating good separation. For Cu up to 2% of the original concentration remained in the Np fraction with the method achieving a DF of 5600. For Cr the concentration in the same fraction was significantly higher at 20% for the anion method however the addition of the co-precipitation stage reduced the value significantly to less than 0.5% achieving a maximum DF of 88000, similar to Mo. The presence of these transition elements is unlikely to interfere with the final measurement efficiency however both Ni, Cu and Mo significantly affect Np recovery so the operational envelope has been set at 2.1 ppm whilst for Cr the impact is minimal so defined at 620 ppm.

Cobalt was present in the samples at between 3.2 ppm to 55 ppm due to the low abundance found in samples typically analysed. For both methods less than 2% of the original concentration was present in the elution fraction with the majority completely removed in the load and initial wash fractions achieving DF values up to 3800. Cobalt if present is unlikely to interfere with the final measurement efficiency and has an insignificant impact on Np recovery therefore the operation envelope has been defined as 55 ppm.

Vanadium was present in the samples at similar concentrations to cobalt. The anion method was inefficient at removing vanadium from the Np elution fraction with between 58% and 100% of the original concentration present. The addition of the co-precipitation reduced the levels to less than 0.2% achieving DF up to 8200. The elution profile indicates that vanadium was present in a number of oxidation states. The majority was retained onto the resin column with approximately 25% eluted in the load and nitric acid washes and present as the pentavalent vanadyl nitrate. Almost half of the v21anadium was eluted in the 9M HCl wash with sequential extraction studies (Brownlee, 1960) showing that pentavalent V is eluted from anion exchange columns in 6M to 9M hydrochloric acid. A further 12% and 21% of the V was eluted as the hydrochloric acid concentration increased (HCl/NH_4I and HCl/HF fractions respectively) indicating the presence of +2, +3 and +4. The oxidation state of V is important as V(III) reduces Np(IV) to Np(III) in perchloric acid (Appleman and Sullivan, 1962) which would not be retained on the resin, affecting the recovery. The low influence on recovery suggests vanadium was not present in the III state or completely removed and was eluted with Np in the IV state. Despite being present in the same oxidation state it had no statistically significant impact and its presence does not interfere with final measurement so the so the operational envelope can be defined as concentrations up to 52 ppm.

Lanthanides (La and Ce)

Ce was shown to have a considerable and significant impact on Np recovery for both methods. This element is often used as an analog and if present in the tetravalent state it will behave similar to Th and be adsorbed onto strongly basic resins in strong nitric acid conditions as $Ce(NO_3)_6^{2-}$ (Korkisch 1989). However, the elution profile of Ce from the anion exchange column showed the majority is eluted, along with La, in the nitric acid load and subsequent wash fraction. It is therefore likely that in the presence of the redox agent Ce is reduced to the trivalent state and not retained onto the resin as reported by Korkisch, (1989) not reflecting the elution profile of Pu (Chapter 3). As Ce is present in the standard solutions in higher concentrations than La (220 ppm compared to 17 ppm) it is likely the difference in influence is due to differing concentrations present with the presence of significant quantities of rare earth elements impacting on the separation efficiency of the column thus decreasing Np retention. It is also possible that Ce, as a redox agent may oxidise Np to the pentavalent state which is not retained on the anion column leading to a detrimental impact on recovery. Therefore the operation envelope for the lanthanides has been defined as the 26ppm where no effect on Np recovery is observed and good separation is achieved.

4.11 Interference on final measurement

The statistical analysis showed uranium and thorium had little impact on Np recovery therefore the operational impact could be set at concentrations up to 9.6 ppm and 2.7 ppm respectively. However, it is critical there is good separation to reduce the radiometric and isobaric interferences with activities less than 0.1 mBq in the final sample fraction. Th was completely removed in the 3M nitric acid and 9M HCl washes at concentrations less than 6.4 ppm achieving a DF in excess of a 1000. However up to 3% of the original concentration remained in the final fraction above 6.4 ppm decreasing the achieving decontamination factor to less than 300. The addition of the co-precipitation step increased the separation efficiency with less than 0.3% present in the final fraction, increasing the DF achieved to 5600. To ensure that the impact of spectral overlap is minimised for Th the addition of the co-precipitation stage maybe necessary for higher concentration samples (i.e. greater than 6.4 ppm). Thorium is absorbed by anion exchange resins as a nitrate complex similar to neptunium as both are present in the IV state with similar ionic radii. The distribution coefficient for Th is lower than Np but still sufficient to quantitatively retain the Th on anion exchange resin from strong acids and therefore if loaded onto the column at a reasonably slow flow rate most of the Th will be displaced by Np but some will concentrate at the front of the Np absorption band (Ryan, 1959). Based on decontamination factors the operational limit will be set at 9.6 ppm for thorium for the full separation method and decrease to 6.4 ppm for the anion method. However, these levels would exceed the 0.1 mBq limit if the sample is analysed by alpha spectroscopy (Table 10).

Anion exchange resin in a chloride matrix will exchange chloride for anionic contaminants e.g. uranium. Unlike other tetravalent actinides, uranium has a lower distribution coefficient in 8M nitric acid and is retained to a lesser extent and generally removed from the column with less than 0.5% of the original concentration (2.7 ppm) present in the final fraction achieving a DF of between 600 and 7700. The addition of the co-precipitation stage had little further impact. The operational limit has been set at the same level as for thorium. The separation achieved for measurement by ICP-MS is probably sufficient to mitigate against tailing of the ^{238}U peak. However for alpha spectrometry the level permittable to prevent any interference in the original concentration is significantly lower at sub ppt (ng/L).

4.12 Operational limits

As a result of the statistical and radiochemical analysis of the thirty five element standards the operational envelope for the method has been defined as outlined in Table 10 in terms of elemental concentrations and not sample matrices.

The operational concentration limits have been calculated for each element in isolation and if more than one is present there is a possibility of a synergistic impact.

The high threshold is set for a limit of 0.1% TDS in the final measurement fraction and the lower based on 0.01% TDS.

Table 10 Elemental concentration limits (ppb) for the method with and without the co-precipitation stage

Periodic Group		Operational Concentration limit (ppb unless stated)			
		Anion Exchange method		Full Separation	
	Element	High threshold	Low threshold	High threshold	Low threshold
Alkaline metal	K	4300	4300	6460	6460
Alkaline earth	Ca	160	160	250	250
	Mg	160	160	250	250
	Sr	160	65	250	65
Polyatomic non metal	P	220	220	500	500
Metalloid	As	88	11	110	11
	B	12	1.2	12	1.2
Lanthanides	La	2.3	0.23	2.3	0.23
	Ce	17	4.6	26	4.6
Post transition	Al	130	13	130	13
	Sn	91	78	140	78
Transition	Co	37	37	55	42
	Cr	410	310	620	310
	Cu	12	1.7	17	1.7
	Fe	15000	12000	22500	12000
	Mo	3.3	0.33	3.2	0.33
	Ni	2.2	0.22	2.2	0.22
	V	34	34	52	52
Actinides	Pu (alpha)	0.0000037 (8.5x10^{-9}Bq/kg)*		0.0000013 (2.98x10^{-6}Bq/kg)*	
	Pu (ICP-MS)	750 (1.7x10^{-3}Bq/kg)*		750 (1.72x10^{-3}Bq/kg)*	
	Th (alpha)	0.000011 (4.5x10^{-11} Bq/kg)**		0.000011 (4.46x10^{-11} Bq/kg)**	
	Th (ICP-MS)	6.4 (2.6x10^{-5} Bq/kg)**		10 (4.06x10^{-6} Bq/kg)**	
	U (alpha)	0.000042 (5.2x10^{-10} Bq/kg)***		0.000093 (1.2x10^{-9} Bq/kg)***	
	U (ICP-MS)	1.80 (2.2x10^{-5} Bq/kg)***		2.70 (3.4x10^{-5} Bq/kg)***	

* Pu activity is based on being present as ^{239}Pu.

** Th activity is based on being present as ^{232}Th.

*** U activity is based on being present as ^{238}U.

4.13 Conclusions

A robust method for the determination of ^{237}Np using the novel approach of experimental design has been developed. It is capable of analysing, for most of the elements, up to the highest levels likely to be encountered in environmental and decommissioning samples with a method scope based on elemental concentration rather than specific sample type (Table 10).

The statistical approach was used to identify the elements and quantify the effect on ^{237}Np recovery for two key separation stages and the method as a whole. Three commonly used co-precipitation methodologies (iron hydroxide, manganese dioxide and mixed carbonate/hydroxide) were investigated. The results showed that ^{237}Np recovery was not effected with over 99% co-precipitating for the elements and concentration levels tested.

Anion exchange is also commonly used to separate and purify ^{237}Np from matrix elements and interferences. This approach was investigated with and without the addition of the co-precipitation stage prior to separation to quantify the degree of interaction of each of the elements with the analyte at each stage of the separation. The neptunium recoveries for both methods showed variation due to the differing sample matrices, with the higher recoveries generally obtained for the samples with a lower elemental concentration. The anion method produced typical chemical average recoveries of 74% with 85% of the results producing a yield greater than 40%. The addition of the co-precipitation stage reduced the method efficiency with less than half of the results (38%) producing a recovery greater than 40%.

The statistical approach identified Mg, Ca, Ce, Ni, Cu, Mo (anion method only) as the elements which effected the recovery of Np across the concentration ranges with K, Sr, P, As, B, La, Al, Sn, Co, Cr, Fe, V, Th, U as having a minimal to insignificant impact.

By assessing the amount of each element present in the final Np elution fraction, the decontamination value achieved and the impact of the element on the final measurement, operational ranges or upper elemental concentration limits for the samples was determined.

The anion exchange resin separation removed more than 90% of the elemental interferences in the load and 8M nitric acid wash indicating the method had good separation characteristics. By analysing each element over a range of concentrations enabled the critical limit which tailing occurred into the other fractions, including the final fraction, to be defined. It was observed that for most of the elements, the amount present in the final fraction increased linearly with original sample concentration once above the critical level. For some elements, e.g. boron, the presence of the element in the final fraction had minimal impact on the final measurement and therefore the operational range could be defined at the maximum concentration analysed. However, for the alkaline metals, phosphorus and potassium, their presence had no detrimental impact on Np recovery but their presence in the final fraction increased the total dissolved solid content above the limit which was the critical parameter for defining the operational concentration.

The anion exchange method produced poor separation for the metalloids (As and B), V and Cr were all present in significant quantities (greater than 5%) in the Np elution fraction. The addition of the co-precipitation stage increased the decontamination factors achieved for As, B and V and their presence has no significant impact on determinand recovery or final measurement efficiency.

Measurement interferences, both radiometric and isobaric, generally originate from the presence of plutonium, uranium and thorium in the final Np fraction. For alpha spectrometry the limit of 0.1 mBq on the source decreased the critical limits to sub ng/L (ppt) concentration levels in the original sample. For final determination by ICP-MS the concentrations of Pu, Th and U can be tolerated (ppb, µg/L in the original sample).

By adopting a combination of statistical and radiochemical analysis the operational elemental range for the ^{237}Np separation method has been defined. Any sample, regardless of matrix, with an elemental composition that falls below the operational limit can be analysed with the procedure producing good method recoveries, efficient separation and a final fraction which is does not contain any final measurement interferences.

4.14 Acknowledgment

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Chapter Five

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

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

5.1 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.

5.2 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 137Cs, Pu-a and 241Am 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 15 km long, 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, 1978a, b; 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 behaviour 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.

5.3 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 et al. (2009) have also been included.

Ravenglass saltmarsh is situated approximately 10 km 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 27). The sampling area was 300 x 250m.

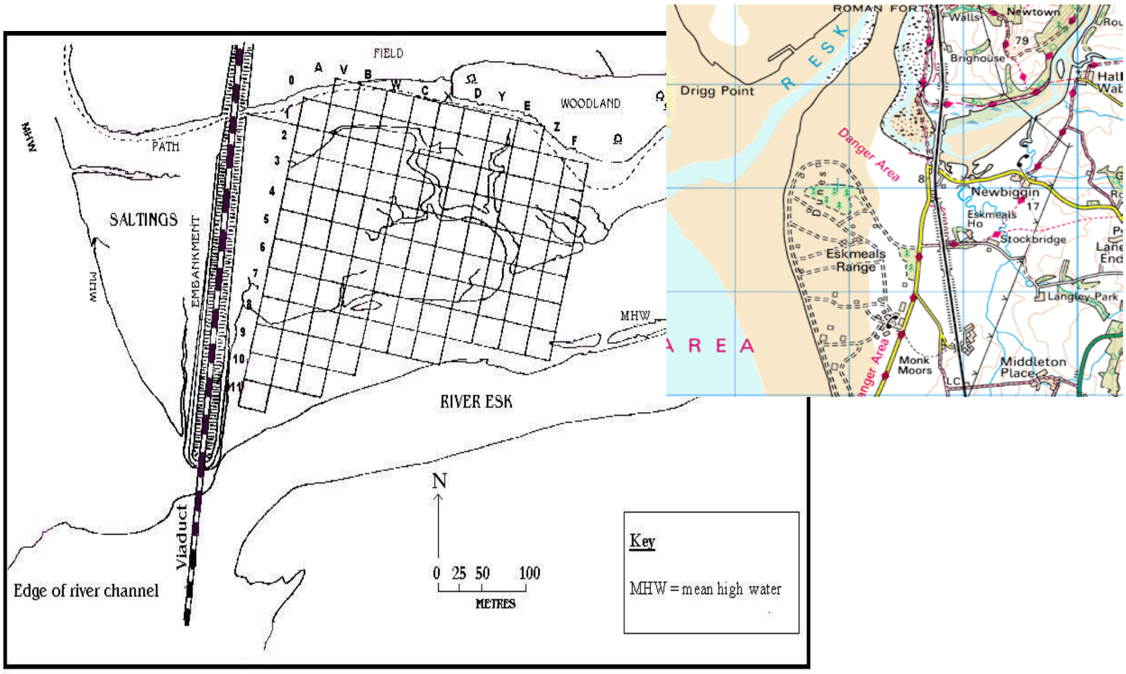


Figure 27: Location of saltmarsh and sampling grid (Ordnance Survey, 2006; Horrill, 1983)

5.3.1 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 25msurvey grid was established on the marsh (*Figure 27*) 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 x250mm 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 siltwas 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.

5.3.2 Site characteristics

A diagram of the saltmarsh in 1980 and the associated sampling grid is given in Figure 27. 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 28). 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 28: Aerial map of Ravenglass saltmarsh (Google Maps, 2015).

5.4 Radiochemical analysis

Following collection, the samples were dried at 105°C, 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 et al., 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 (75-100 g 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 0.5 g 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.

5.4.1 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):

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

where m1 and m2 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):

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

5.5 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 106Ru, 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, 24,100 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 11.6mm 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 - 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, 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.

5.5.1 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 (Kershawet 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 (Kershawet 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 106Ru 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 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 adsorptive capabilities. The sediment at sampling point B5 on the Ravenglass saltmarsh was found to be uniform material to a depth of ~1 m, dominated by silt sized particles (40% 63-125 µm; 24% 32-63 µm; 21% 8-32 µm; 4% 2-8 µm; 7% <2 µm). Due to the presence of plant roots, the top 50 mm 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, 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 and Baxter, 1988a, b; MacKenzie et al., 1999). However particles less than 10 mm 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, b) 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.

Short lived nuclide: ^{106}Ru

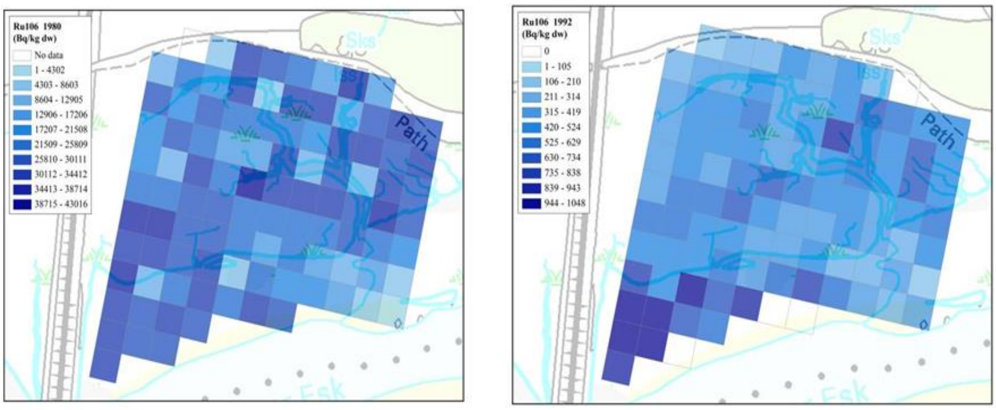
Ru-106 is a short lived radionuclide with a half-life of 368.2 days and exists in many complex species with the +2, +3 and +4 the most common. It is discharged from the pipeline as a nitrosyl complex which has high solubility characteristics. Stanners and Aston (1981) predicted it would take one month 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 4×10^4 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 11). Ru-106 was not determined in the 1997 samples.

Table 11: Ru-106 activity concentrations (Bq kg^{-1} dry weight) across the saltmarsh for the different sampling periods

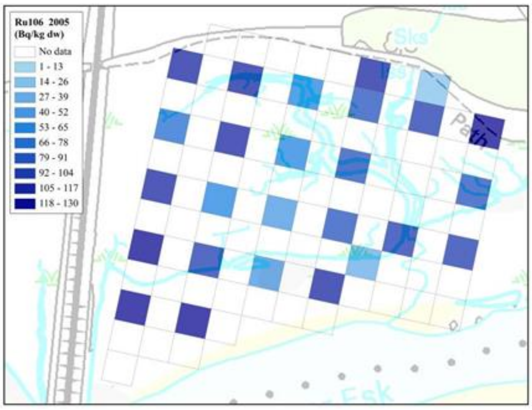
Year	1980	1992	2005
Geometric Mean	17200	468	82.2
Median	20300	463	96.8
Minimum	1620	110	22.4
Maximum	29300	1050	130
Standard deviation	6450	195	30.2
Number of samples	99	97	26

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 29). 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 - 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 29: 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.

Labile nuclide: ^{137}Cs

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 Caesium 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, 1988). 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 trap 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 12). 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.

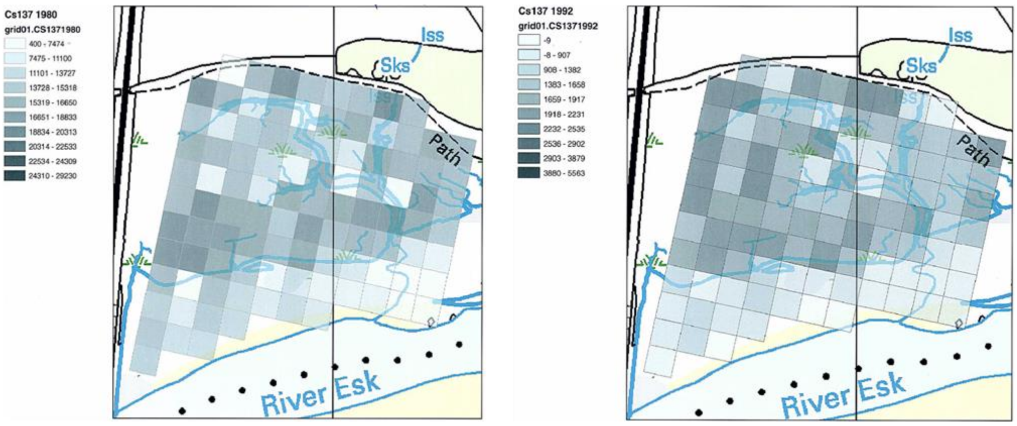
For the 1992 and 1997 time points the calculated geometric mean and median for the results were in good agreement, however there is bias towards the higher and lower activities for 1980 and 2005 respectively.

Table 12: 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

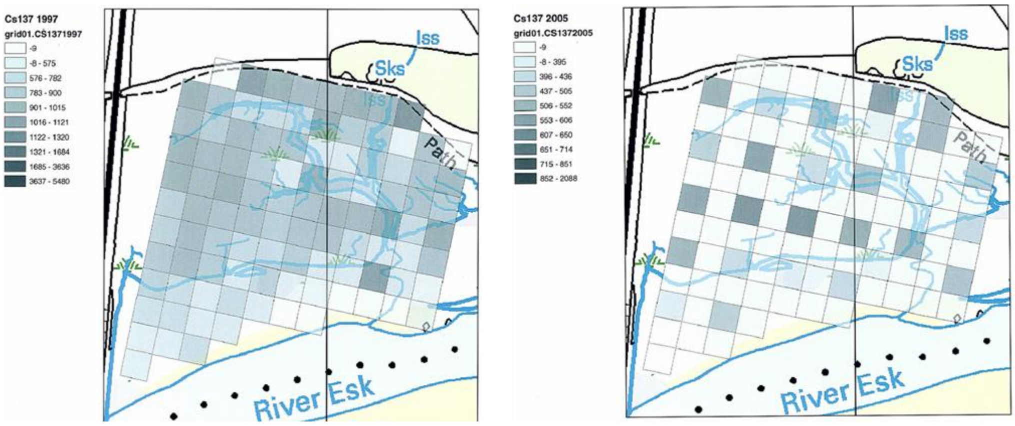
Substantial spatial variation in ^{137}Cs activity concentration occurred on the saltmarsh (Figure 30) with the highest activity concentrations in the low energy areas, at the landward end of the saltmarsh and the slightly elevated middle area. The sediments in these regions experience less tidal movement 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 30: 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.

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) 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 2.2-2.4x10^6 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}.

Resolubilisation at the saltmarsh was not considered to be a significant factor with other physical processes dictating Pu and Am movement (Livens and Baxter, 1988). 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 13). 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 from the offshore mud patch.

As with the other radionuclides, the activity of ^{241}Am decreased over the 25 year period (Table 13), 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 the 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 13: Pu alpha and Am-241 activity concentrations (Bq kg^{-1} dry weight) across the saltmarsh for the different sampling periods

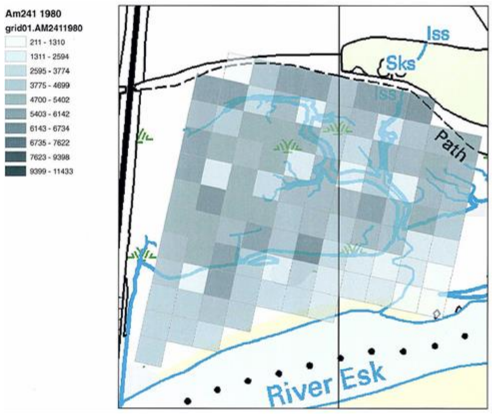
Radionuclide	Year	1980	1992	1997	2005
Pu alpha	Geometric Mean	11500	1540	1190	806
	Median	14700	1580	1190	840
	Minimum	229	519	412	494
	Maximum	26000	9410	4300	2100
	Standard deviation	5490	1060	496	342
	Number of samples	54	97	95	26
Am-241	Geometric Mean	5040	2060	1460	1590
	Median	5980	2620	1470	1460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

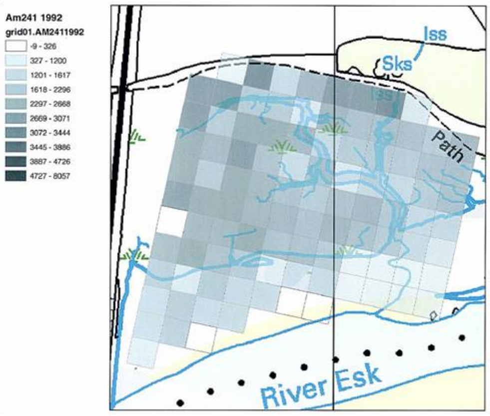
^{241}Am only in Figure 31 as these are the most complete data set with the same trends shown for Pu alpha. Consistent with our data, Tyler (1999) reported high activity concentrations of ^{241}Am in surface sediment towards the landward side of the Caerlaverock saltmarsh in Scotland and also elevated 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.

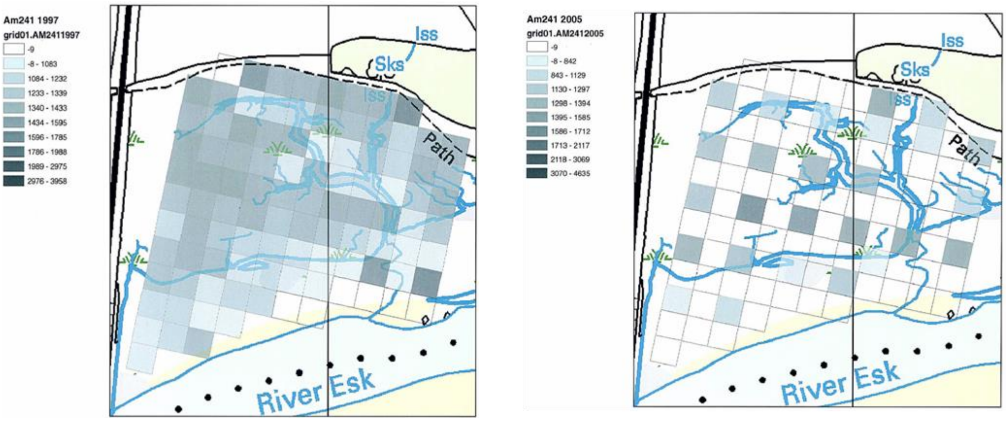
The rate of change in spatial variation has a higher tendency for Pu alpha compared with Am. This may be due to three factors (i) if Pu is present in the (III/IV) state it will be more strongly associated with particles than Am (ii) Pu is not continuously enhanced by nuclide ingrowth as is Am and (iii) 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 31: 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.

5.6 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 27, 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 14).

Table 14: 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 were 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 32) and $^{238+239/240}$Pu.

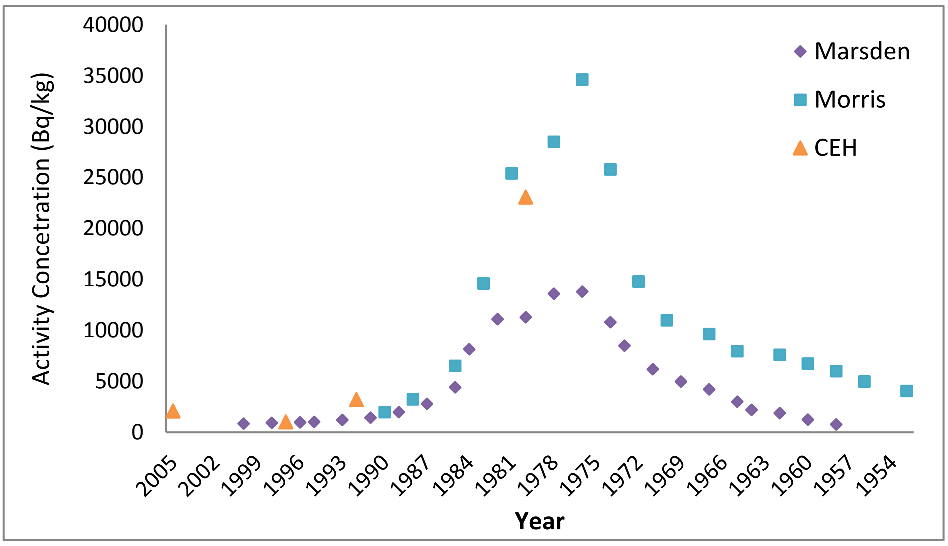


Figure 32: Comparison of ^{137}Cs activity concentrations in surface scrape and sediment core data at sampling point B5.

The indicative sedimentation rates were calculated using the surface sample data with the variation in accumulation rates across the marsh shown in Appendix D . 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.

$$Difference\ factor \quad = \frac{Activity\ at\ sampling\ point\ A0\ at\ t1}{Activity\ at\ sampling\ point\ A0\ at\ t2}$$

Each difference factor 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 the equation below:

$$Sedimentation\ factor\ = \frac{Difference\ factor}{Difference\ factor\ at\ B5}$$

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 15 using:

$$Sedimentation\ rate\ \ = Sedimentation\ factor\ \ x\ \ Sedimentation\ rate\ at\ B5$$

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) which uses a mixing and no mixing sedimentation rate (Table 15). The sediment mixing rate during the transportation from the discharge point to the saltmarsh (Oh, 1999) was calculated as 90% by comparison of the Pu isotopic ratios from cores collected at the saltmarsh with the Sellafield discharge record up to 1996. 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.

Table 15: Comparison of sedimentation rate (mm/yr) reported in the literature for cores taken at four sampling points

Nuclide	**Time interval**	**Data Source**	**Sampling point**		
			A3	**B7/W7**	**X6/X7**
Cs	**1997**	Oh no mixing	5.50	9.00	9.60
	1997	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**	Oh no mixing	8.60	8.60	10.4
	1997	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	

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

Table 16) 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}.

Table 16: Sedimentation rates across the saltmarsh for the different sampling periods

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	9.9	1.7
	1997-2005	15.8	14.6	15.5	4.8	27
	1980-2005	10.9	12.4	2.73	26.7	5.33
Pu (mix)	1980-1992	3.86	4.35	0.7	11	1.97
	1992-1997	5.07	5.13	0.62	20.7	2.62
	1997-2005	13.1	13.5	5.6	37.2	6.26
	1980-2005	8.6	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	5	33.2	5.59
	1980-2005	7.68	8.49	3.17	14	3.59

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.

5.7 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.

5.8 Acknowledgment

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Chapter Six

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6 Variations in the spatial distribution of neptunium-237 in surface samples from an ungrazed West Cumbrian saltmarsh over a 25 year period

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6.1 KEYWORDS

Saltmarsh, Neptunium-237, Plutonium, Caesium-137, radionuclides, spatial variation, temporal variation.

6.2 ABSTRACT

Saltmarshes are dynamic environments with a combination of relatively high sedimentation rates, stabilisation of sediment by vegetation and low sediment mixing rates resulting in the generation of chronologies of pollution history. The saltmarshes in the vicinity of Sellafield act as sinks for radioactivity discharged from the Sellafield site with the sediments interacting with discharges from the Sellafield reprocessing site. Neptunium-237, present in Sellafield Limited's liquid effluent discharges, in the short term pose a low environmental hazard due to the lower activity concentrations relative to other radionuclides such as Pu alpha, ^{137}Cs and ^{241}Am. However, due to its long half-life (2.13 × 10^6y), high radiotoxicity and presence in High, Intermediate and Low Level

wastes, it is considered as a major dose commitment component to the public for the long-term disposal of radioactive waste as such a greater understanding of its behaviour, distribution and mobility in the environment is required.

Analysis of surface scrape samples collected over four sampling campaigns (1980, 1992, 1997 and 2005) over a twenty five year period for ^{237}Np, and previously analysed for Pu alpha, ^{241}Am, ^{137}Cs and ^{106}Ru (Caborn et al., 2016), enabled spatial and temporal variations across the saltmarsh to be observed. The effects of physical processes on radionuclides due to the different sedimentary dynamics across the saltmarsh is demonstrated and identification of the factors that influence radionuclide behaviour. Over time the activity concentration of ^{237}Np reduced due to factors including variations in discharge, remobilisation and redox variations. Comparison of the rates of change showed ^{237}Np activities reflected discharge activity indicating that the radionuclide is more conservative in behaviour, similar to the ^{137}Cs, and the saltmarsh has no significant secondary activity input from either the mud patch or due to ingrowth from ^{241}Am. Considerable spatial variation was observed which became less defined over time and reflected to a lesser degree the distribution of ^{137}Cs, with the highest activity concentrations in the low energy areas where higher rates of sedimentation occurred. Comparison of the Np, Pu and Cs isotopic compositions concluded that Np was most likely to be present in the pentavalent state and therefore highly mobile and susceptible to remobilisation.

6.3 Introduction

Neptunium-237 is released to the environment as a result of nuclear weapons fallout, industrial processing of ^{237}Np produced in nuclear fuel in fission reactors, authorised discharges from nuclear power and reprocessing facilities and *in-situ* decay of previously discharged ^{241}Am (Assinder, 1999). Globally it is estimated that 1.5 tonne of ^{237}Np exists as a result of above ground weapons testing with 70% present in the Northern Hemisphere (Beasley et al., 1998). Np-237 is formed from ^{235}U and ^{238}U by neutron capture in thermal reactors with 760 g of Np being produced per tonne of irradiated fuel (Germian et al., 1987). Liquid discharges from fuel reprocessing operations at Sellafield have contributed 6.87 TBq to the environmental inventory between 1978 and 2014 and prior to this date it was estimated between 2 and 4 TBq was released into the Irish Sea (Kuwabara et al., 1996).

Operations at Sellafield, the UK's largest nuclear site located on the Cumbrian coast, involved the fabrication of Mixed Oxide Fuel (MOX), reprocessing of fuel from civil and military reactors and nuclear waste storage with the reprocessing facilities releasing low level liquid waste into the Irish Sea between the early 1950s and 1992 as part of their authorised discharges. More recently Sellafield's focus has changed to decommissioning its first and second generation nuclear reactors, Windscale and Calder Hall reactors, which includes managing waste arising from the storage and reprocessing of spent fuel at Magnox and THORP reprocessing plants. The liquid effluent discharges contain actinides and fission products from purge water used in waste storage ponds and process liquors from spent fuel reprocessing, with the site's annual discharge summaries reporting the presence of ^{237}Np in effluents since 1978. Over time radionuclide activities have decreased significantly in the Sellafield effluent discharges with the discharge maxima for Pu alpha and ^{137}Cs occurring in the mid 1970's as a result of pond water purging from the site. In 1986 the levels significantly decreased and have continued to decline following the commissioning of the Site Ion Exchange Effluent Plant (SIXEP) treatment facility. Peak ^{237}Np discharges occurred in 1980 (0.66 TBq) reducing to between 0.18 to 0.4 TBq yr^{-1} for the period of 1985 and 1995 and declining further to the present day levels (0.03 and 0.06 TBq yr^{-1}).

$$^{241}_{94}Pu \xrightarrow{\beta\ 14.33\ years} {}^{241}_{95}Am \xrightarrow{\alpha, 432.6\ years} {}^{237}_{93}Np$$

Figure 33 Decay of ^{241}Pu and ^{241}Am to ^{237}Np

Neptunium is present in Sellafield liquid discharges at lower activity concentrations compared to other transuranics, however, due to ingrowth from ^{241}Am the levels will increase over time (Figure 33). Due to its long half-life, presence in High, Intermediate and Low Level wastes, comparative mobility and high radiotoxicity ^{237}Np will become more radiologically important and a major component of the dose commitment to the public (Cohen, 1982; Hill et al., 1982, Assinder, 1999). This has led ^{237}Np to be classed as one of the thirty seven priority radionuclides for RWM's (Radioactive Waste Managements) safety cases (NDA, 2014) and to be predicted to be the "most hazardous material in high-level nuclear waste in geological repositories from 10000 to 30000000 years after disposal" (Thompson, 1982).

Neptunium (atomic number 93) was the first synthetic transuranium element to be discovered and the fifth member of the actinide series. Neptunium can be found in five oxidation states (+3 to +7) with the IV, V and VI the most common existing as Np^{4+}, NpO_2^+ and NpO_2^2 under environmental conditions. Like Pu it is redox sensitive, but tends to be more stable and mobile with low sorption affinity and particle reactivity. Studies have shown that 50% of the total ^{237}Np discharged from Sellafield is present in the tetravalent state. The Np is then slowly oxidised so found exclusively in oxic water in the pentavalent state as the aqua ion (NpO_2^+) (Assinder, 1999, Germian et al., 1987) with only 1% and 0.5% remaining in the tetravalent state in the seawater around Sellafield and the South Scottish coast respectively (Pentreath et al., 1986). The distribution coefficient of Np(V) is estimated at between 10^3 and 10^4 l kg^{-1} (Pentreath and Harvey, 1981), significantly lower than for Pu (10^5 l kg^{-1}) and Am (10^6 l kg^{-1}), therefore in comparison Np has a lower particle affinity resulting in Choppin (1983) classifying the radionuclide as the most environmentally mobile actinide species.

Once the liquid effluent has been discharged from Sellafield 95% of Pu and the majority of Np and Am, along with other radionuclides, become associated with the sediment on the Irish Sea floor within 12 hours of discharge (Sajih and Livens, 2010; Marsden et al., 2006; Morris, 1996; Hetherington et al., 1978). Deposited radionuclides with a high affinity for inorganic particles become strongly associated with the fine grained sediment located in a belt parallel to the Cumbrian coast extending into Liverpool Bay, and across the mouth of the Solway Firth to Wigtown Bay and accumulate (Kershaw et al., 1992) at the mud patch where significant mixing and particle re-working due to bioturbation occurs with redistribution of radionuclides evident to a depth of 1.4 m in core samples taken from the Irish Sea (Kershaw et al., 1984). Compared to other transuranics, Np has a lower affinity for inorganic particulate material and is less particle reactive with fine grained, suspended material which is reflected in its lower K_D (Pentreath and Harvey, 1981). Due to the oxic conditions in the Irish Sea, association is driven by the high concentration of suspended particles (50-150 mg L^{-1}) and with the fine grained sediment within the Irish Sea (Morris et al., 2000). Once sediment-associated, the artificial radionuclides including Pu, Am and Np, are dispersed to the estuarine environment mainly by sediment resuspension from the mud patch, and particulate transport in the water column via open marine and tidal currents, with a proportion being deposited in the estuarine environment. Accumulation in the mud patch and subsequent redistribution results in a delayed, or secondary, contamination source input into the marine environment (Sajih and Livens, 2010; Marsden et al., 2006; Morris, 1996; Kershaw et al., 1986).

With increasing distance from Sellafield the particle affinity decreases as Np changes state from IV to V due to oxidation, grain size distribution and composition of suspended sediments (Assinder, 1999; Edgington & Nelson, 1983). Differences in activity concentrations between suspended and deposited sediments have also been reported as the latter is a mixed sediment grain population in terms of grain size, composition, date of initial contamination and subsequent history (Aston et al., 1985).

Deposition and accretion of sediments occurs in the dynamic saltmarsh environment followed by degradation as a result of perturbations such as sea level rise or storm events (Dyer et al., 2002). The relatively high sedimentation rates, stabilisation of sediment by vegetation and low sediment mixing rates result in the generation of chronologies of pollution history. The saltmarshes in the vicinity of Sellafield act as sinks for radioactivity discharged from the Sellafield retaining discharge profiles and preserving a chronological record of contamination (Caborn et al., 2016; Lindahl et al., 2011; Leonard et al., 1999; MacKenzie & Scott, 1993). This preserved contamination record enables an evaluation of radionuclide behaviour over time. Due to its close proximity to Sellafield, the Ravenglass estuary (NW, England) is one of the most radioactively contaminated, and therefore well-studied estuarine environments, within the Irish Sea (Sanchez et al., 1997). Generally radionuclide activity concentrations in the north-eastern Irish Sea surficial sediments peaked in the late 1970's and early 1980's reflecting the highest discharge rates and have decreased steadily with activity and distance from Sellafield (Kershaw et al., 1999; Mitchell et al., 1999; Sanchez et al., 1997). At the saltmarsh, a similar trend was observed with radionuclide concentrations decreasing over time with the rate of change dependent on the radionuclide and location in the saltmarsh due to the physical and biogeochemical processes which affect the distribution and migration of radionuclides (Caborn et al., 2016; Oh et al., 2009; Leonard et al., 1999).

Due to the highly dynamic ecosystem the rates of deposition of colloidal and particulate radioactivity deposited during high tide across the saltmarsh for the different radionuclides vary spatially. Higher activity concentrations were reported by Oh (1999) lower down the saltmarsh depth profile near to the seaward edge and higher up the profile towards the landward edge. The seaward areas are inundated by the tides daily with the channels across the saltmarsh almost as frequently immersed depending on the distance from the sea and the tidal phase. This results in less sediment accumulation on the saltmarsh occurring and constant tidal reworking of sediments near to the main tidal channels (Friddlington et al., 1997). Sediment core analysis has shown substantial re-distribution of ^{237}Np and a tendency for the associated small particles to become resuspended and distributed elsewhere (Morris et al., 2000; MacKenzie et al., 1999; Friddlington et al., 1997). The elevated activity concentrations in the area are due to either low sedimentat accumulation rates resulting in a compressed historical record of Sellafield discharge or resuspension of historic contamination.

The low energy areas at the landward end of the saltmarsh and to a lesser extent the mid, elevated region, are only inundated by high Spring tides and their sediment is less prone to re-suspension (Howard et al., 1996; Chapman, 1941). Fine grained sediment will accumulate which has not settled out of suspension at the initial stages of the tidal cycle and will become trapped in the vegetation which is more prevalent in these areas (Oh, 2009).

Grain size distribution also influences radionuclide activity, with fine-grained sediments having high radionuclide absorptive capabilities. Pentreath and Harvey (1981) reported varying K_D values for Np following analysis of seawater from the Irish Sea with Edington and Nelson (1984) suggesting a number of factors including grain size, oxidation state changes and the composition of suspended sediments may cause the variation. Sellafield-derived ^{237}Np was found to accumulate in areas of fine grained sediment however due to the lower distribution coefficients and particle affinity, compared to other transuranics, is more available for remobilisation however data is limited (Assinder, 1999). Conversely the tendency for particles less than 10 μm to form aggregates and associate with larger particles, 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). Analysis of a sediment core and hydrological data from the saltmarsh showed the upward migration of Np as water moved upwards through the marsh sediment as the tidal height and hydrostatic pressure increased causing upwelling. As the water receded downward migration was observed (Morris et al., 2000, Carr and Blackley, 1986). Due to its mobility characteristics, the behaviour of Np has a greater similarity to Cs than other radionuclides (Hursthouse et al., 1991).

The degree of association of each radionuclide with sediment is governed by parameters such as geochemical behaviour of the element, chemical form of radionuclide, oxidation state, pH, salinity, organic content, grain size and radionuclide affinity. 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. Np, like other transuranics, has multiple oxidation states enabling it to complex with different chemical species resulting in different physiochemical forms being released into the environment with differing geochemistry and radionuclide affinity. A sequential leaching study (Hursthouse et al., 1991) determined the geochemical association for Np on the Ravenglass saltmarsh as the following:

Adsorbed (35%) > Hydroxide (27%) ≈ Organic 29% > Exchangeable (5.7%) > Residual (3.5%)

The order of association differs from that of Am which was:

Organic (49%) > Adsorbed (22%) > Hydroxide (17%) > Residual (7.8%) > Exchangeable (<3.9%).

The saltmarsh sediments are comprised of 18.6% clay, which is mainly illite with a fraction of montmorillonite, 74.5% silt and 6.5% sand with the surface scrape samples having a relatively high organic content (3.1%) due to the presence of plant root matter in the top 50mm (Marsden et al., 2006, Morris et al., 2000). Pentavalent Np is more soluble than tetravalent (10^{-4}M compared to 10^{-10}M at neutral pH) and has moderate interactions with bentonite and rocks (Nagasaki *et al.,* 2016) with NpO_2^+ weakly sorbing to mineral surfaces hence the favoured absorption association mechanism. High Np(V) sorption to illite has been observed due to the partial reduction to Np(IV) at the surface, decreasing the solubility and increasing the strength of interaction (Marsac *et al.,* 2015). The exact mechanism was hypothesised to be a surface meditated process due to electron transfer from adsorbed or structurally bound Fe(II) to surface bound Np(IV) resulting in a redox/sorption reaction.

This study focuses on ^{237}Np distribution within the saltmarsh environment and is a continuation of previous work carried out investigating the spatial and temporal variation of radionuclides on the ungrazed saltmarsh at Ravenglass over a twenty five year period (Caborn et al., 2016). Significant temporal variation across the area was observed for other actinides with the rate of change dependent on the radionuclide and location with ^{241}Am showing the least decline partially due to ingrowth from ^{241}Pu and as a result of transport of sediment from the offshore Irish Sea mud patch. There was statistically significant spatial variation across the saltmarsh which became less distinct with time as activity concentrations declined with the differences in areas of accumulation (high and low energy) dependent on the radionuclide.

Surface scrape samples are routinely taken for environmental monitoring programmes with the data ultimately used to calculate dose and estimate risk of exposure to the general public. It is important to understand the variation in the results that can be obtained due to inconsistent sampling and geographic variation for selection of sampling locations to produce a representative result.

The objectives of this project were to:

- Evaluate the temporal changes in activity and relate these to known discharge histories to identify the source terms of ^{237}Np on the Ravenglass saltmarsh;

- Determine the spatial variation in the deposited ^{237}Np activity concentrations over a period of 25 years to gain a better understanding of the depositional regime;

- Compare the findings with other studied radionuclides to identify the mechanisms of association and behaviour of ^{237}Np in the environment.

6.4 Experimental Site and Sampling Details

Ravenglass saltmarsh is situated approximately 10 km 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 34). The sampling area was 300 x 250 m.

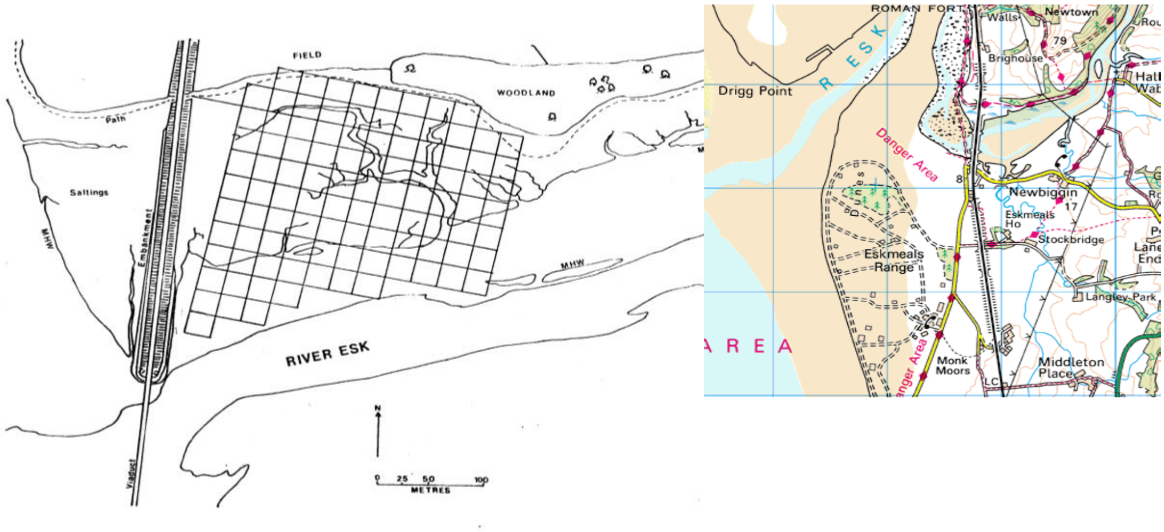

Figure 34: Location of saltmarsh and sampling grid (Ordnance Survey, 2006; Horrill, 1983)

6.4.1 Site characteristics

A sampling grid was originally established on the Ravenglass saltmarsh in 1980 (Figure 34) with the vegetation in a linear distribution pattern related to height (Horrill, 1983). Over time, the size and shape of the saltmarsh has changed due to continuous accretion and erosion with the formation of a bank by 1992 at the lower end of the marsh and the loss of three sampling sites (B10, X8 and D8) but little change in vegetation cover compared to that recorded during the original survey (Horrill, 1983). By 2005 the degree of erosion had increased significantly, markedly reducing the number of available sampling points near the river with a new triangular area of saltmarsh covered in vegetation present at the lower end of the sampling transect. Over the sampling period, the extent of vegetation biomass markedly increased across the saltmarsh except at sites B5, C5 and C7 where there was a decrease and no vegetation coverage.

6.4.2 Site sampling

The site was originally selected in 1980 on the basis that the total gamma radiation levels, determined 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 34) with a total of 100 sampling points. In August 1992 a survey of all the sample points was carried out similar to that of the original study of July 1980 (Horrill, 1983). This was followed by a less intensive survey in July 2005 comprising of 26 sampling points (targeting alternate rows and columns) as described in Caborn et al., 2016.

For each of the surveys, a 250 x 250 mm quadrat was placed at the grid point. The vegetation within the quadrant was 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.

6.5 Radiochemical Analysis

Samples were dried at 105°C, ground and analysed for radionuclide content. The methodology for the ^{137}Cs and plutonium alpha measurement has been previous reported (Caborn et al., 2016). For ^{237}Np, approximately 5g of sample was spiked with ^{239}Np, ashed and acid leached. The ^{237}Np was separated and purified using ion-exchange chromatography. The purified fraction was then evaporated and redissolved in dilute nitric acid prior to gamma spectrometry measurement, to determine the yield tracer recovery. The ^{237}Np was measured using an ICP-QQQ (Agilent 8800 Triple Quad). All results are reported as dry weights (dw). Quality control samples were analysed along with the samples.

6.6 Statistical analysis

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

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

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 (Caborn et al., 2016).

6.7 Results and discussion

6.7.1 Temporal variation

Over the 25 year period, the ^{237}Np activity in surface scrapes steadily declined from a geometric mean of 7.85 Bq kg^{-1} in 1980 to 1.26 Bq kg^{-1} in 2005 with an overall activity reduction of 84.0% and annual rate of change of -7.80%/annum (Table 17 and Table 18). The geometric mean was slightly lower than the median for the 1980 and 1992 sample sets but similar for the 2005 data with the distribution biasing towards the higher activity concentrations for the earlier years.

Table 17: Np-237 activity concentrations (Bq kg^{-1} dry weight) across the saltmarsh for the different sampling periods

Year	1980	1992	2005
Geometric Mean	7.85	7.82	1.26
Median	8.67	10.5	1.19
Minimum	1.24	0.830	0.703
Maximum	17.0	14.2	5.03
Standard deviation	4.05	3.81	0.869
Number of samples	25	20	23

Between 1980 and 1992 the average activity marginally increased with an annual rate of change of 0.03% due to an increase in ^{237}Np activities at six sampling points (A5, A9, B9, C1, C4, D0). If these points are considered outliers and are not included, the geometric mean for the rate of change showed a decrease of 1.69% per year. Four of the sampling points (A5, C1, C4, D0) were in low energy flow areas with the results showing a marginal increase. The activities increased two fold for the remaining samples (A9 and B9) were situated in the high energy, seaward area of the saltmarsh where the highest frequency of tidal movement and greater potential for radionuclide deposition. For comparison, activities for ^{241}Am and Pu alpha increased in this region (Caborn et al., 2016). In contrast the ^{237}Np activity between 1992 and 2005 significantly decreased (83.9% reduction) with an annual rate of change of -13.1%/annum.

Table 18 Comparison of Annual Percentage Rate of Change for ^{237}Np on the Ravenglass saltmarsh and from Sellafield discharge inventories

Source	Time Period		
	1980-1992*	1992-2005*	1980-2005*
Saltmarsh Scrape	-0.03%	-13.1%	-7.06%
Discharge	-0.42%	-14.6%	-8.07%

* For the discharge data a one-year lag has been applied with the time period used of 1981, 1993, 2006.

The rate of change in ^{237}Np over the twenty five year period, and for each of the individual time periods is in good agreement with the change in activity discharged (Table 18). As the trend reflects discharges it is unlikely that ^{237}Np accumulates in the mud patch leading to a secondary input from a delayed, or secondary, contamination source. This indicates that Np has a lower particle affinity than other transuranics such as Pu and Am, which to a degree concentrate in the mud patch, and is more conservative in behaviour.

The activities determined were compared with those reported independently to ensure there were no abnormalities with the data set and analysis (Table 19). The sediment core analysed by Morris et al., (2000) and Marsden et al., (2006), taken at sampling point B5 on the saltmarsh, was in agreement with the surface scrape sample result from the same sampling point (11.3 ± 0.27 Bq kg^{-1} in 1980 and 10.3 ± 0.49 Bq kg^{-1} in 1992).

Table 19: Reported ^{237}Np activities for the Ravenglass and surrounding area

Location	**Sample**	**^{237}Np activity (Bq/kg)**	**Reference**
Irish Sea	Suspended particulate	0.08-1.44	Pentreath & Harvey, 1981
	Filtrate	0.2-38.9	
River Esk	Intertidal Sediment	4.36	Assinder et al.,1991
Ravenglass	Sediment core at B5	0.68 to 13	Morris et al., 2000
		Surface 13	
Ravenglass	Sediment core at B5	0.18 to 16	Marsden et al., 2006
		Surface 1.87	
Ravenglass	Surface Sediments 1980	1.24 to 17.0	
Ravenglass	Surface Sediments 1992	0.830 to 14.2	
Ravenglass	Surface Sediments 2005	0.703 to 5.03	

When compared to other radionuclides, ^{237}Np activity concentrations in the surface scrape samples were significantly lower; for example the geometric mean activities in 1980 for ^{137}Cs was reported as 15.1 kBq kg^{-1}, Pu alpha at 11.5 kBq kg^{-1}, ^{241}Am at 5.04 kBq kg^{-1} (Caborn et al., 2016). The lower activities resulted in reduced rates of change for ^{237}Np which reflected the decreased discharge activities.

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).

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.

The annual percentage change was used to compare the rate of reduction for the radionuclides studied at the saltmarsh and in Sellafield discharge effluent data. Over the study period the trend changed (Table 20) across the three time period comparisons. The trend observed on the saltmarsh for 1980-1992 agreed with the rate of reductions in effluent discharges. For 1992-2005 and over the twenty five year period there was poor agreement with ^{237}Np and ^{137}Cs showing the greatest rate of decline compared to the Pu alpha and ^{241}Am which was opposite to the trend in discharge. The average annual percentage change on the saltmarsh for ^{137}Cs, like ^{237}Np, was similar to that observed in the discharge data with the overall trend influenced by the lower rates of reduction seen for Pu alpha and ^{241}Am, especially between 1992 and 2005, which indicated a significant secondary input source from the mud patch and consistent with the non-conservative behaviour for these radionuclides. The rate of reduction is lowest for ^{241}Am due to the additional input from ingrowth from its parent nuclide ^{241}Pu, with estimations that 17% of the current sediment inventory for ^{241}Am activity has arisen from the in situ decay of ^{241}Pu (Marsden *et al.,* 2006). The impact of *in situ*, alpha decay of ^{241}Am to ^{237}Np needs to be considered however the impact would be less significant in the short term due to the longer half-life of the parent ($t_{½}$= 432.2 years).

Table 20: Order of annual percentage rate of change for radionuclides on the Ravenglass saltmarsh

Source	**Time period**	**Rate of decline**
Saltmarsh activity	1980-1992	Cs≈Pu>Am>Np
	1992-2005	Np>Cs>Pu>Am
	1980-2005	Cs>Pu>Np>Am
Discharge	1980-1992	Cs>Pu>Am>Np
	1992-2005	Am>Pu>Np>Cs
	1980-2005	Cs>Am>Pu>Np

6.7.2 Spatial variation

The spatial variation for ^{237}Np were less defined and distinct for the three time periods compared to other radionuclides due to the lower activity concentrations of ^{237}Np in the surface scrape samples (Caborn et al., 2016). In 1980 the spatial distribution is distinct (Figure 35) with the highest ^{237}Np activity concentrations generally in the landward areas (low energy) and under the railway viaduct where there is high sediment accumulation, vegetation trapping and less tidal movement reducing the potential for remobilisation. Lower activities were present in, or near, areas of high energy (and low sediment accumulation). Generally the spatial trends are more apparent that those observed for Pu alpha and ^{241}Am but not as distinct as the variation noted for ^{137}Cs reflecting the greater mobility of Np than the transuranics and, like ^{137}Cs, the secondary input from the mud patch is of lesser significance.

The spatial distribution in 1992 (Figure 35) showed the landward, low energy area reducing in activity to become a lower activity region with activities falling by almost a factor of 2. This may be due to the remobilization of ^{237}Np from this area to other parts of the marsh over the twelve year period or, more likely, recent deposition of less contaminated sediment over the surface of the saltmarsh. The highest activity concentrations were located mainly across the middle of the saltmarsh ranging from 9.3 to 13 Bq kg^{-1}. The distribution for 2005 showed that the activities across the saltmarsh are very similar and no significant spatial trend was apparent (Figure 36).

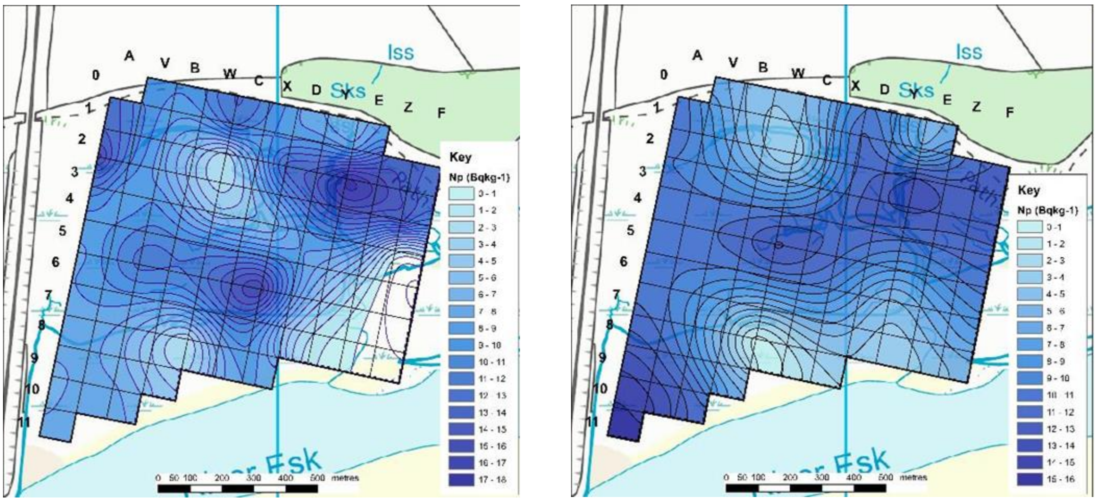

Figure 35: Spatial distribution of ^{237}Np in 1980 (left) and 1992 (right) at Ravenglass saltmarsh. The activity concentration is shown in Bq kg^{-1} dry weight.

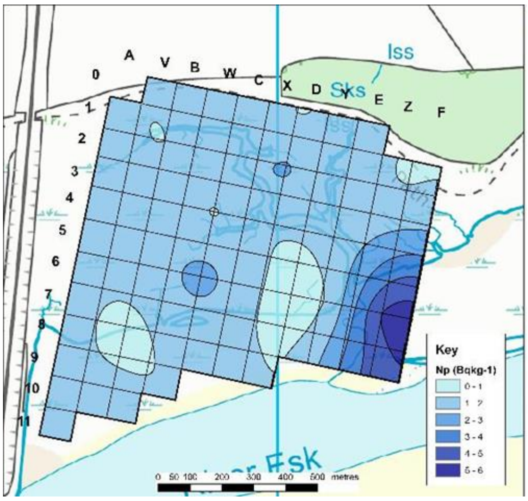

Figure 36: Spatial distribution of ^{237}Np at 2005 at Ravenglass saltmarsh. The activity concentration is shown in Bq kg^{-1} dry weight.

All base maps obtained from Edina. © Crown Copyright and Database Right (2016). Ordnance Survey (Digimap Licence). Distribution plots created in ArcMap™.

To investigate radionuclide behaviour Np, Pu and Cs isotopic compositions were measured in the samples and compared with Sellafield discharges. Variations in $^{239+240}$Pu:^{237}Np ratio in the discharge, Irish Sea and Ravenglass saltmarsh sediments indicate an enrichment of Np relative to Pu, Am and Cs have previously been reported (Hursthouse et al., 1991). It is acknowledged that ^{237}Np has only been reported in Sellafield's annual discharge inventory since 1978 when the activities of most of the radionuclides had started to decline and after the first sampling campaign.

Over time radionuclide activities have decreased significantly in the Sellafield effluent discharges with ^{237}Np activities ranging from 0.18 to 0.67 TBq yr^{-1} between 1979 and 1995 then subsequently reducing (0.03 and 0.06 TBq yr^{-1}) (Figure 37). The ^{237}Np:^{137}Cs ratio for the first reported ^{237}Np discharge results was lower (0.00606) than successive results due to higher ^{137}Cs activities (330 TBq in 1985 reducing to 18 TBq in 1996). Generally the ^{237}Np:^{137}Cs ratios reflected the decreasing activity concentrations, at approximately 0.020 until 1995 and then decreased (ranging from 0.0040 to 0.012) due to the lower ^{237}Np and ^{137}Cs activities in the authorised discharges. The ratios on the saltmarsh for time periods 1980 and 1992 were very similar (0.0043 and 0.0047) and reduced by just over a factor of two in 2005 (0.0019) reflecting the trend in discharge ratio data.

The values obtained for the Pu alpha:^{137}Cs ratios were higher than for ^{237}Np:^{137}Cs due to the greater Pu alpha activity levels in the discharges but reflect the same trend after 1985. On the saltmarsh the Pu alpha:^{137}Cs, reported as geometric mean, is significantly higher than the Sellafield discharge ratios (Figure 37) indicating enrichment of plutonium reflecting the difference in distribution coefficient and retention of Pu in the off-shore mudpatch. Pu alpha, like ^{241}Am, is particle reactive and exhibits non-conservative behaviour with input sources originating from discharge and the mud patch with results reflecting current and historic contamination. The ^{237}Np:Pu ratios observed for the Ravenglass saltmarsh were lower than those in the discharge with the difference becoming more significant over time.

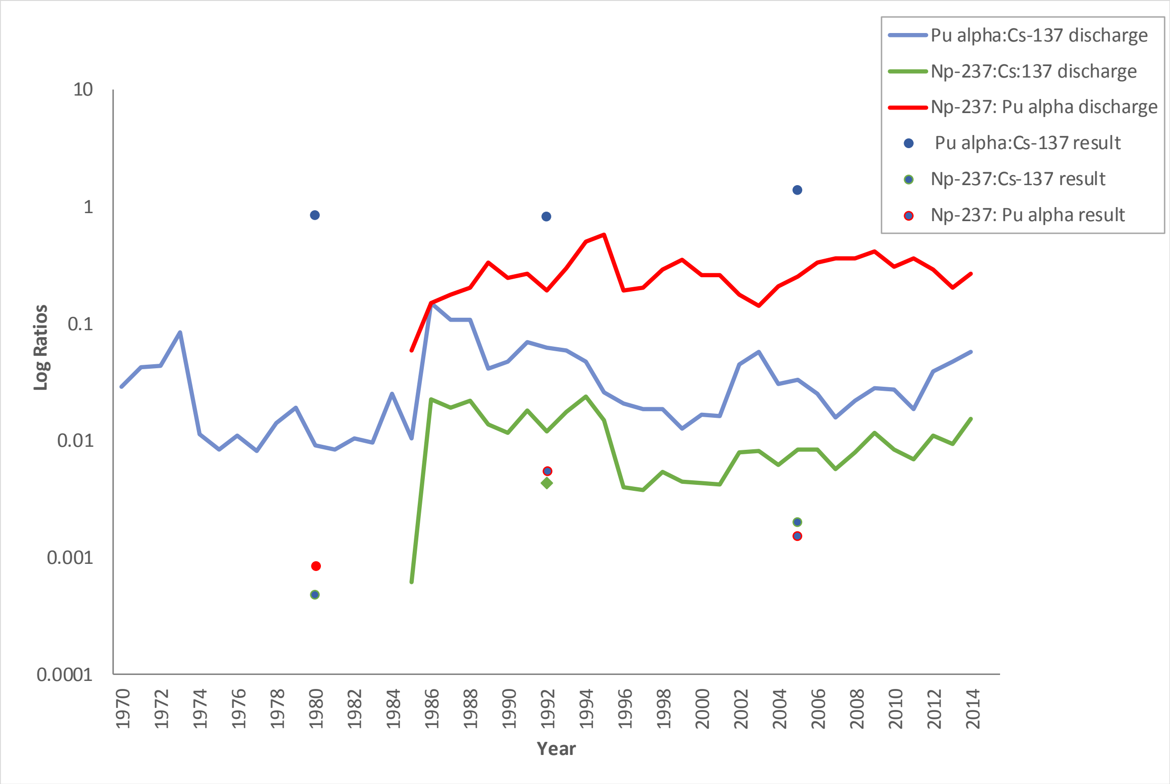

Figure 37: A comparison of ratio data calculated for Pu alpha, ^{137}Cs and ^{237}Np in Ravenglass saltmarsh scrape samples and authorised discharge data from Sellafield site

Although both actinides are from the same source the ratio data shows that the behaviour of Pu alpha and ^{237}Np on the saltmarsh is influenced by differing factors. The comparable ^{237}Np:^{137}Cs ratios indicate Np, like Cs, exhibits more conservative behaviour with higher mobility than other transuranics suggesting that ^{237}Np is present in both the tetra and penta-valent states. This is confirmed by the varying Pu alpha:^{137}Cs which shows Pu is less mobile and probably present in the III/IV oxidation state. The ^{237}Np:Pu alpha ratio changed significantly over the period of 1992 to 2005 linked to the lower rate in reduction of ^{237}Np activities on the saltmarsh over time compared with

Pu alpha. The mobile and soluble pentavalent species of both Np and Pu (NpO_2^+ and PuO_2^+), dominate coastline or surface waters. Unlike Pu, Np does not readily reduce to +3 and +4 in the marine environment, and has a lower particulate affinity, distribution coefficient and higher mobility.

It is therefore likely Np is discharged in the effluent in the IV state with the greater proportion becoming oxidised over time to Np(V). Due to the low solubility of NpO_2^+ the association with particles is weak and the mechanism for association is driven by the high concentration of suspended particles. The lesser proportion of Np present in the tetra valent state does become strongly associated with the fine grained sediment at the mud patch. Np-237 is dispersed from the mud patch via particulate transport in the water column into the estuarine environment and then deposited deposits onto the saltmarsh. Similarly to Cs, Np will interact with clays, especially illite (Marsac et al., 2014, Nagasaki et al., 2016) with the degree of association highly dependent on the oxidation state. Np as mainly present as pentavalent NpO_2^+ (Nagasaki et al., 2016) tends to exhibit mobile behaviour due to the weak absorption association to the clay mineral surface. Tetravalent Np, present to a lesser extent, and as a consequence of reduction of Np(V) at the illite surface, has a strong sorption to the surface, high particle affinity, lower solubility and is immobile in behaviour. It can be inferred the behaviour observed is similar to that of ^{137}Cs but to a lesser extent as influenced by the presence of Np(IV).

The temporal results show that the ^{237}Np activities present on the saltmarsh reflect those reported in the Sellafield discharge inventories and that any secondary inputs from the mud patch, and to a lesser degree ingrowth, are less significant than for the other transuranic radionuclides.

The spatial distribution of ^{237}Np across the saltmarsh is similar to the trend observed for ^{137}Cs with the highest activities present in the low energy areas of the saltmarsh where there is less potential for remobilisation and redistribution. Consideration of the nuclide ratios showed that ^{237}Np exhibited similar conservative behaviour to ^{137}Cs with a higher mobility and lower particle affinity than Pu alpha and ^{241}Am. It is likely that Np is present in the marine environment in the pentavalent state and predominately remains as the relatively soluble NpO_2^+ forming moderate association with sediments but prone to remobilisation.

6.8 Conclusions

Between 1980 and 2005 the activity concentrations of ^{237}Np in surface scrape samples decrease. The rate of change was insignificant between 1980 and 1992 followed by a period of significantly decreasing activity from 1992 to 2005 and in good agreement with the discharge activities results over the same periods. Np-237 behaviour on the saltmarsh closely reflects the discharge profile with little influence from any other source inputs such as the Irish sea mud patch or as a result of ingrowth from ^{241}Am.

The rate of change over the 25 years showed a temporal order for the rate of change in activity of Cs >Pu> Np >Am which was consistent with the discharge inventory trend. Between 1992 and 2005 the agreement was poor due to Pu alpha and ^{241}Am "enrichment" from secondary source inputs (e.g. sediment derived from the mud patch) and for ^{241}Am because of ingrowth from its parent nuclide ^{241}Pu.

The degree of ^{237}Np spatial variation compared to other radionuclides was not as pronounced due to the lower activities present across the saltmarsh. The greatest variation was observed in the low energy landward areas situated to the rear of the saltmarsh which had the highest activities. Consistent with the trends observed for other radionuclides the variation was less distinct with time due to declining activity concentrations.

Although Np can exist in a range of oxidation states comparable to those of Pu and originate from the same source, comparison of the radionuclide ratios showed that Np geochemistry exhibits a conservative behaviour that is more akin to ^{137}Cs. Np-237 behaviour at the saltmarsh also closely reflects discharge data. It is inferred that it is predominantly present in the mobile, pentavalent state, whilst Pu alpha was present as the relatively immobile III/IV on the Ravenglass saltmarsh. Although it has a lower particle affinity than ^{137}Cs (K_D 2 x10^5 l kg^{-1}), Np(V) will be susceptible to remobilisation and therefore concentrated in low energy areas where there are greater sedimentation accumulation rates, less susceptible to reworking and tidal disturbance.

6.9 Acknowledgment

The authors appreciate access to the Agilent ICP-QQQ ICP-MS facility operated by GAU-Radioanalytical.

6.10 Abbreviations

dw, dry weight

GAU, Geosciences Advisory Unit (Uni Southampton)

NPL, National Physical Laboratory

IAEA, International Atomic Energy Authority

SIXEP, Site Ion Exchange Effluent Plant

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7 Distribution and mobility of ^{237}Np in a West Cumbrian ungrazed saltmarsh core

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7.1 Keywords

saltmarsh, ^{237}Np, Plutonium, ^{137}Cs, radionuclides, spatial variation, temporal variation,

7.2 Abstract

The activity depth profile of ^{237}Np in a sediment core taken from the Ravenglass saltmarsh, West Cumbria, UK has been determined. The distribution profile in the sediment core showed the highest activities of ^{237}Np in the upper sections and the presence of two minor peaks at a depth of 3.5cm and 13.5cm, equivalent to 1982 and 1992 with the results falling below the limit of detection at a depth of 21.5 cm, equivalent to 1974. The observed profile was generally reconciled with the Sellafield effluent discharges considering the limited discharge data pre 1978 and was less defined than for ^{137}Cs and other transuranics which showed good agreement.

The radionuclide profile for ^{237}Np in the sediment core was similar in distribution to that reported for other cores analysed from the same saltmarsh. The core analysed had two main differences; geochemistry and location on the saltmarsh. The sediment core exhibits a distinct geochemical redox profile due to fluctuations in the water gradient causing upwelling through the marsh sediments, contributing to the migration of Np. The core originates from a higher energy area with greater rates of sedimentation and frequent tidal inundation. Other cores analysed did not show the redox zonation but did have good agreement with ^{237}Np data obtained despite the different locations and varying geochemistry therefore ^{237}Np is not redox sensitive. The lower ^{237}Np activities

compared to the other cores which were sampled at differing locations reflect the spatial variation observed across the saltmarsh.

Comparison of distribution coefficients and nuclide ratios of ^{237}Np:^{137}Cs and Pu alpha:^{137}Cs alpha at discharge and on the saltmarsh showed that the behaviour of ^{237}Np is more comparable to labile ^{137}Cs. It is likely that Np is less associated with the sediment on the Irish Sea mudpatch due to its low particle affinity, and is readily remobilised in the estuarine environment where it will accumulate over the saltmarsh. Once deposited, significant post depositional migration occurs and the inventory of ^{237}Np is influenced by the location and conditions especially tidal movement but not by the geochemistry.

7.3 Introduction

Since 1952 fission products, activation products and transuranic radionuclides, including ^{237}Np, have been released into the Irish Sea by Sellafield nuclear site as part of their authorised discharges. In Sellafield liquid discharges ^{237}Np is present at lower activity concentrations compared to other transuranics however the levels have not decreased as rapidly and will rise due to ingrowth from ^{241}Am. In addition, its long half-life ($t_{½}$ =2.13 × 10^5y), presence in High, Intermediate and Low Level wastes, high radiotoxicity and mobility increases the radiological importance of the radionuclide. Thompson (1982) predicted that ^{237}Np will be the “most hazardous material in high-level nuclear waste in geological repositories from 10 000 to 30 000 000 years after disposal” and is a major component of the dose commitment to the public from the long-term disposal of radioactive waste (Cohen, 1982; Hill et al., 1982).

The Ravenglass saltmarsh located in West Cumbria has been the focus of research (Horrill, 1983; Morris et al., 2000; Marsden et al., 2006; Livens et al., 1998) as the marsh is located 10 km south of the Sellafield site, acts as a local sink for Sellafield-derived radionuclides, and it’s not disturbed by the general public or by livestock. Actinides and fission products from purge water used in waste storage ponds and process liquors from spent fuel reprocessing are released in the liquid effluent discharges from Sellafield into the Irish Sea and sorb to suspended particulate and colloidal material (IAEA 1985, Hamilton 1989), or plankton suspended in the water column (Masson 1989). It has been estimated that the 95% of Pu and the majority (unquantified) of Np and Am is precipitated and associated with the sediment on the Irish Sea floor within 12 hours of discharge (Hetherington et al., 1978,). As a result of tidal movement and currents in the shallow Western Irish Sea basin (typically 30m in depth) fine grained particles, with associated radionuclides, accumulate in an area of mud and muddy sediments (approximately 15km long x 3 km wide x 30m depth) parallel to the coastline commonly known as the ‘mud patch’ (Hetherington, 1978; Kershaw et al., 1992; MacKenzie et al., 1994; Pentreath et al., 1984). Particulates are redistributed and deposited into the water column via open marine and tidal currents onto the saltmarsh as a result of tidal processes and storm events.

Saltmarshes are dynamic ecosystems in the upper coastal intertidal zone between land and open salt water where frequent tidal inundation occurs. These areas experience varying rates of sediment deposition and accretion followed by degradation due to sea level rise or storm events (Dyer et al., 2002). The relatively high sedimentation rates, stabilisation of sediment by vegetation and low sediment mixing rates result in the generation of chronologies of pollution history. The saltmarshes in the vicinity of Sellafield act as sinks for radioactivity discharged from the Sellafield site producing a historical record which reflects distribution and migration of radionuclides and allows identification of the physical and biogeochemical processes such as location, ingrowth resulting from radionuclide decay, post depositional remobilisation and erosion of radionuclides (MacKenzie & Scott, 1993; Leonard et al., 1999; Oh et al., 2009; Leonard et al., 1999; Lindahl et al., 2011; Caborn et al., 2016b).

To increase our understanding of the behaviour of ^{237}Np in a sedimentary environment, a sediment core from the Ravenglass saltmarsh has been analysed to ascertain activities, depth profile and correlation with core’s geochemistry. The core has previously been analysed for other radionuclides including ^{99}Tc, Pu isotopes, ^{137}Cs, ^{241}Am and minor and major elements (Wigley, 2000 and Oh, 1999). The core exhibits a distinct geochemical profile with varying depth profiles of stable elements reflecting redox zonation and radiochronology with good correlation with Sellafield discharge histories. Presently there is limited information regarding the factors which affect the distribution of ^{237}Np required to underpin waste management solutions and safety cases. The objectives of this studies were:

- Assess the variations in the ^{237}Np activity in the sediment core and compare with the geochemistry redox profile shown by stable element trends;
- Ascertain the temporal changes in the ^{237}Np activity concentrations deposited down the profile of the core and identify if the distribution reflected discharge history.

- Compare the temporal and spatial variation of ^{237}Np with that observed for other studied radionuclides such as Pu alpha and ^{137}Cs to understand the distribution and mobility of neptunium in the environment.
- Use Np, Pu and Cs isotopic compositions and distribution coefficient ratios to determine the chemical state of ^{237}Np in the estuarine environment and the impact on its behaviour including association characteristics.

7.4 Materials and methods

The Ravenglass saltmarsh is situated approximately 10km south of the Sellafield site on the northern shore of the River Esk Estuary in Cumbria, UK. The site (Figure 38) has a sampling area of 300 x 250m (National Grid reference SD089948) and is sheltered by dunes located to the southwest and inland of a railway viaduct. It is not easily accessible and ungrazed therefore undisturbed by the general public or by livestock.

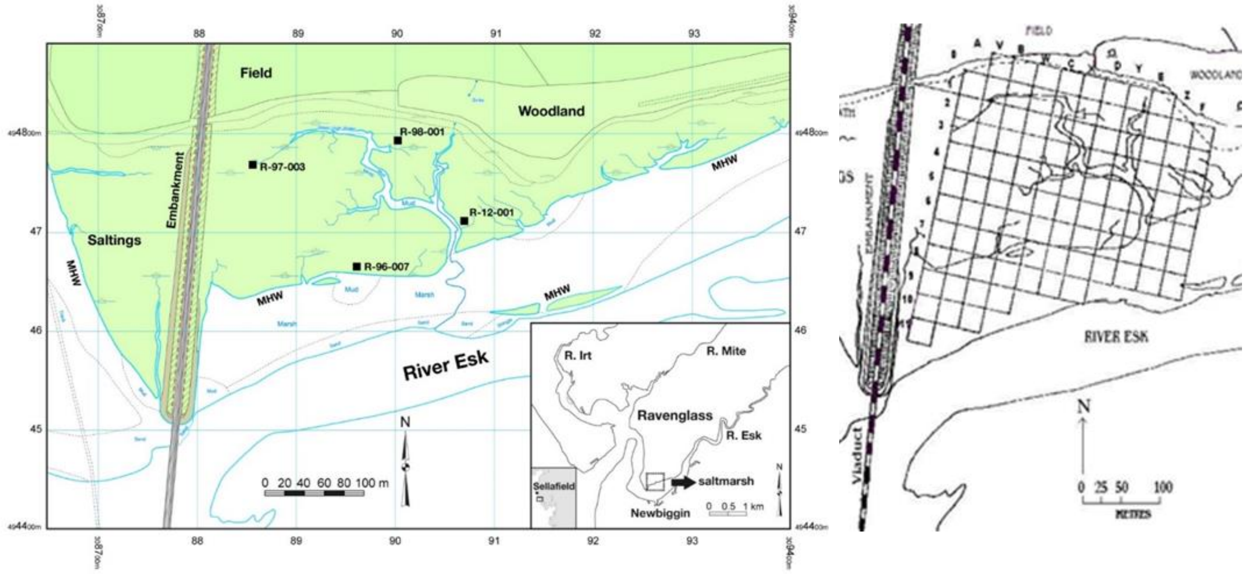

Figure 38: Location of saltmarsh and sampling grid

The core (R-96-007) was collected in 1996 at sampling position W 6.5 which is at the seaward end of the marsh. The core has been well studied, is defined both radiochemically and elementally with a large amount of supporting data and is used in this study instead of collecting a further core sample. The core was taken by driving polyacrylate tubes (10cm ID) into the marsh to obtain a core 60cm in length. The core was transported intact and stored at ~4°C prior to preparation. The core was sectioned at 1cm intervals and freeze-dried to remove water. Visible root matter, if present, was removed and the samples ground in a pestle and mortar. The samples were sieved through a 1mm sieve to remove any stones and organic matter present. As the cores were not stored in non-oxidising conditions porewaters were not extracted as the results obtained could be compromised.

Major and trace elemental analysis was carried out by X-ray fluorescence spectrometry. An aliquot of the sample was taken and ignited at 900°C for a minimum of 2 hours. The ignited material (0.8g) was mixed thoroughly with a eutectic (4:1) mixture of lithium metaborate and lithium tetraborate in a grain stabilised Pt-Au crucible (Croudace et al., 1998a, b). The mixture was heated to 1200°C to melt the flux and dissolve the sediment sample which was then cast as a melt into a Pt-Au mould and cooled to produce a bead suitable for XRF determination of major elements. 10g of ground sample was pressed into a pellet for trace element determination using a pressure of 12 tonnes per square inch. Measurements were performed using a Philips 1400 sequential X-ray fluorescence spectrometer.

High resolution gamma-ray spectrometry was used to obtain data for a range of radionuclides (^{241}Am, ^{57}Co, ^{60}Co, ^{134}Cs, ^{137}Cs, ^{154}Eu, ^{155}Eu, ^{40}K, ^{210}Pb, ^{214}Pb, ^{226}Ra). Approximately 20g of sample was transferred to a 22ml polythene liquid scintillation vial and the exact sample mass recorded. The sample was then counted on a well-type high purity germanium (HPGe) detector. The resulting energy spectrum was deconvoluted and the activity of each identified radionuclide calculated using the Fitzpeaks software package (JF Computing, Stanton in the Vale, U.K.). The gamma spectrometer was previously calibrated for both energy and efficiency against an Amersham QCY-48 mixed radionuclide standard adsorbed onto a sediment matrix (Croudace, 1991).

For the determination of the Pu isotopes, ^{242}Pu was added to approximately 1g of dried sample as the yield tracer and digested using borate fusion (Croudace et al., 1998a,b). The Pu was purified by ion exchange/extraction chromatography and electrodeposited onto stainless steel discs. The ^{238}Pu, $^{239/240}$Pu and ^{242}Pu activities were determined by alpha spectrometry (EG&G Wallac Octete).

Elemental, gamma spectrometric and Pu (alpha) data for the core have been previously reported (Wigley (2000) and Oh (1999)).

The ^{237}Np analysis was carried out by ashing and leaching 5g of sample in *aqua regia* after the addition of yield tracer, ^{239}Np, followed by radiochemical separation using ion-exchange chromatography to purify the neptunium. The purified fraction was then evaporated to near dryness and redissolved in 0.32M nitric acid. The recovery of the yield tracer was determined by HPGe gamma spectroscopy measurement. Neptunium-237 was subsequently measured by ICP-MS using the Agilent 8800 Series Triple Quadrupole® LC/MS (Caborn et al., 2016a).

7.5 Results and Discussion

7.5.1 Geochemistry

A distinct geochemical redox profile often develops in saltmarshes which can be visually evident (Williams et al., 1994). Visual observation of the core (R-96-007) showed an oxic-anoxic boundary at 25cm which is due to the fluctuating concentrations of major elements Mn and Fe. Si, present as SiO_2, was the most abundant element (mean concentration of 67.4% dw) followed by Al (as Al_2O_3) (mean concentration of 10.8% dw). Both of the major elements showed variation with depth indicating a change in sediment composition (Figure 39). Carr and Blackley (1996) characterised the saltmarsh as comprising of fine grained silt/silty sand to a depth of 1m with coarser gravel sand which is water saturated below. The profile data in the core reflects their findings with a decrease in Al_2O_3 and increase in SiO_2 levels occurring at about 50cm depth indicating a lower clay and higher sand content sediment. Higher Ca concentrations (3.8 wt% as CaO) were observed in the upper 2 cm which may be the result of shell fragment which have become incorporated in the subsurface (Figure 39). Thereafter there is slight change in Ca concentration.

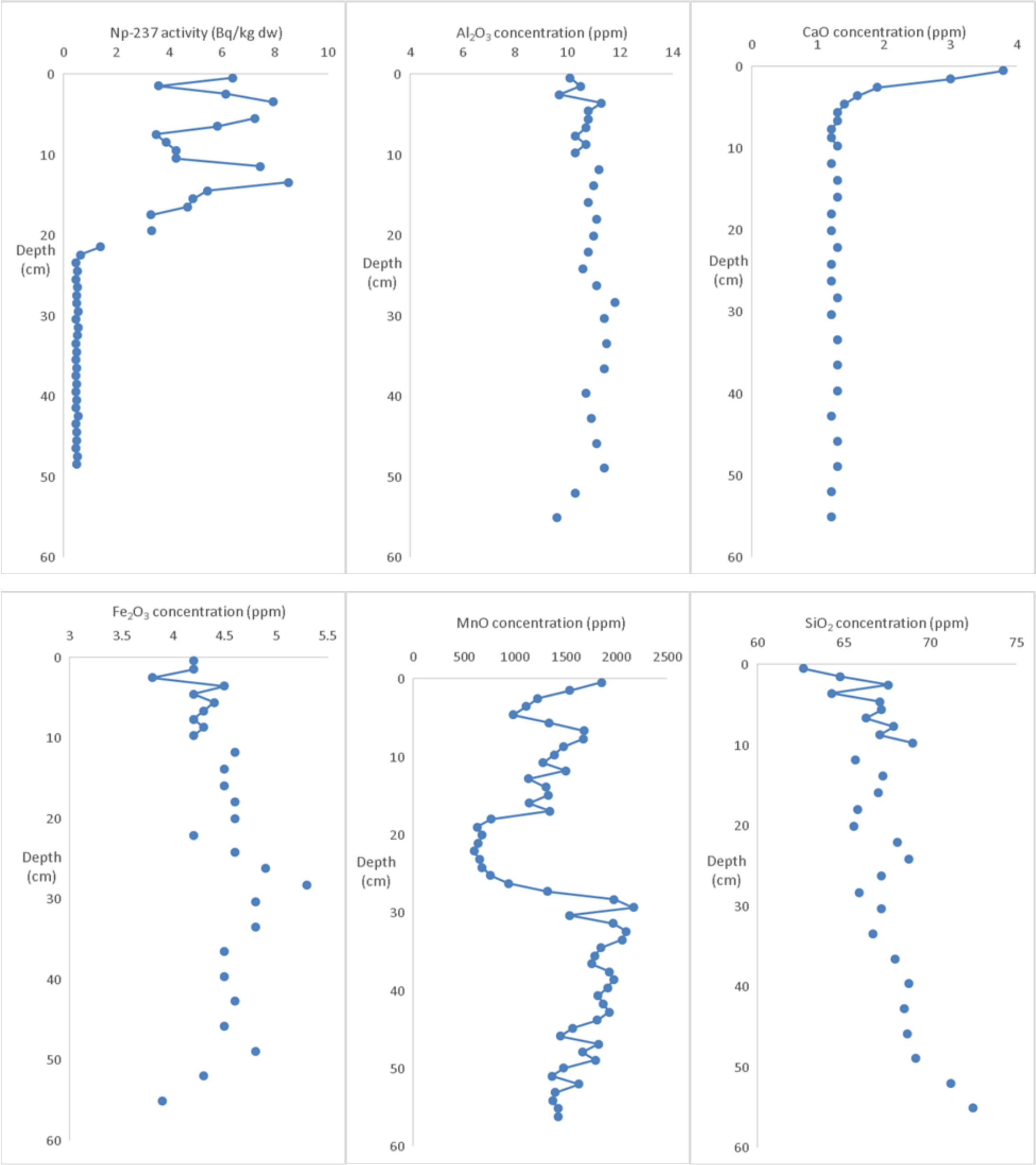

Figure 39 Stable element concentrations and Np-237 activity vs. depth for the Ravenglass saltmarsh core.

7.5.2 Redox zonation

The core analysed by Morris et al (2000) did not show any significant changes in stable element composition from elements such as Al, Si, Ca and Ti in the profile indicating no significant compositional changes. There was also no evidence of redox zonation indicated in the depth profiles of key elements such as Fe and Mn.

Clear redox zonation was observed in this core (R-96-007) with three distinct zones present in the Mn profile (Figure 39) indicating possible redox driven remobilisation and immobilisation processes. The first oxic zone, to a depth of approximately 16.5cm, is due to the oxygen diffusion from the surface resulting in the variation of the Mn which may be due to the formation of manganese (III) and (IV) oxyhydroxides. Between 16.5cm and 26.5cm a sub-oxic zone is observed. Under these conditions oxyhydroxides become solubilised and fully reduced where it is likely Mn(II) dissolved species are produced that diffuse and become remobilised. A second oxic zone is apparent, 26.5cm to base of core, with further Mn solid phase variation observed where the Mn(III) and (IV) oxyhydroxides may again be present. The sampling point is seaward and possible upwelling of water can occur as a result of tidal movement causing an increase in the oxygen content.

Iron, like manganese, is a redox sensitive element however the variation in concentration is not observed (Figure 39). The oxygen tension, or partial pressure of oxygen, in water for manganese oxyhydroxides is higher than that of iron therefore it is likely that the reduction potential (E_h) is in between the two values. For Mn(II) to form the E_h must be below +300mV whilst for Fe(II) reduction a redox potential of less than -100mV is required. The saltmarsh has been found to be mildly anoxic with redox potentials on the saltmarsh ranging between +180 and +230mV (Morris et al., 2000). In addition, the saltmarsh has a low reducible Fe content (7.9% of the total Fe) with the majority present as bound iron which is not redox sensitive (Morris et al., 2000).

7.5.3 Core Radiochemistry

To establish the core radiochemistry the sediment accumulation was estimated at a rate of 0.87 cm year^{-1} based calculations using three methods; excess ^{210}Pb dating, laminations and assessment of ^{137}Cs and ^{241}Am profiles (Warwick, 1999). The time from discharge from the Sellafield pipeline to reaching the saltmarsh (lag time) was previously estimated (Caborn et al., 2016) using Cs and Ru ratio data. At 1980, the contamination was defined as recent with a lag time of less than 0.5 years 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. As a consequence, a lag time correction was not applied with the maxima in ^{137}Cs activities correlating to the discharge maxima in 1975.

For the ^{137}Cs, Pu alpha and ^{241}Am the core retained a chronological profile of radionuclides which was in good agreement with published Sellafield discharge records (Figure 40). The ^{241}Am distribution profile for the core activity is broader than the discharge inventory due to ingrowth and geochemical differentiation in the mud patch. The relationship observed confirms that the sediment was largely undisturbed despite originating from a higher energy area.

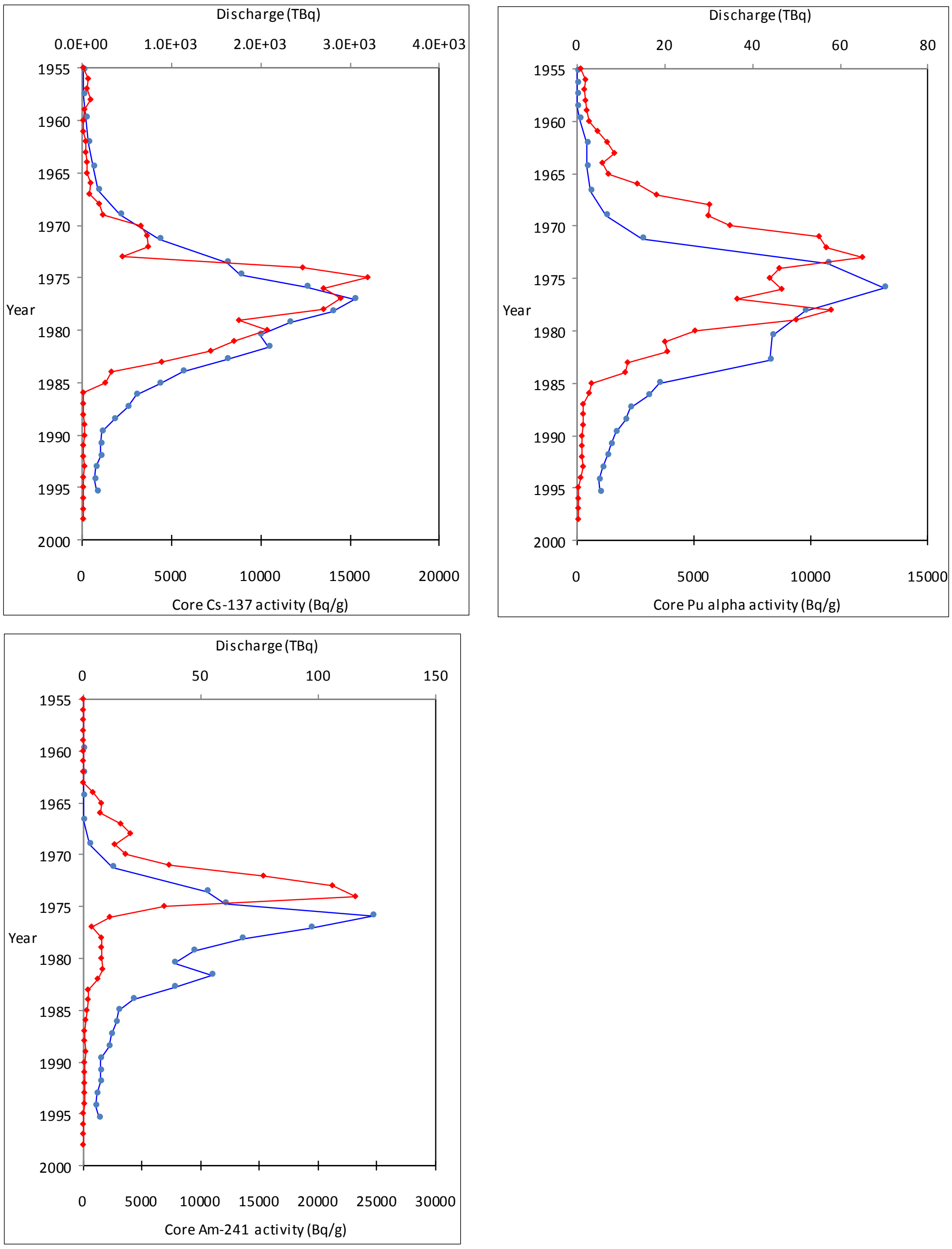

Figure 40 Distribution profile of ^{137}Cs, Pu alpha and ^{241}Am in Ravenglass saltmarsh core with discharge (annual discharges are represented by ● and activity concentrations by ●).

7.5.4 Np-237 activity profile

The annual discharge summaries from Sellafield have only reported the presence of ^{237}Np in effluents since 1978. The discharges from Sellafield were at a maximum in 1980 (0.66TBq), ranging from 0.18 to 0.67TBq yr^{-1} between 1978 and 1995 then subsequently reduced (0.03 and 0.06 TBq yr^{-1}) and prior to 1978 estimated to be between 2 and 4 TBq (Kuwabara et al., 1996).

The ^{237}Np activities were highest (Figure 41) in the upper sections of the core with two minor peaks at a depth of 3.5cm and 13.5cm (7.94 ± 0.77Bq kg dw^{-1} and 8.51 ± 0.55 Bq kg^{-1} dw respectively). Below 22 cm the ^{237}Np results were below the limit of detection (0.5 Bq kg^{-1} dw).

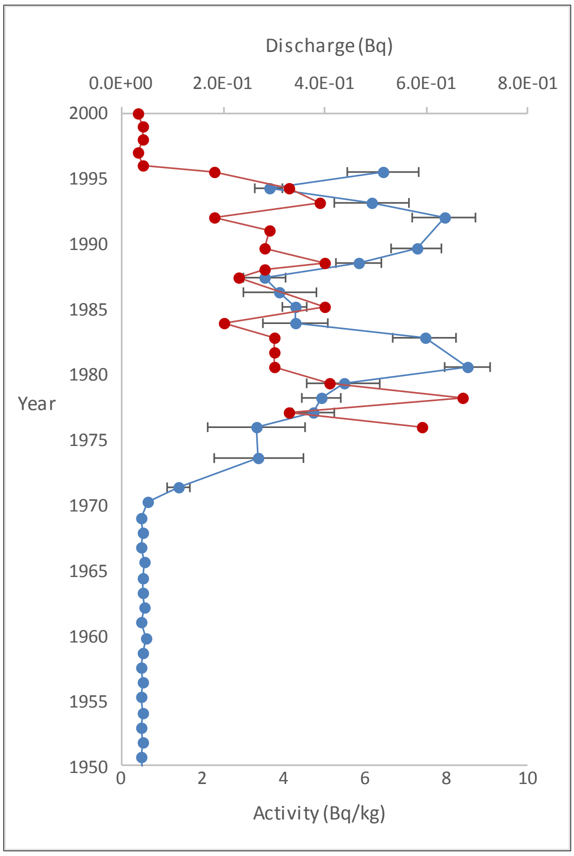

Figure 41 Distribution profile of ^{237}Np in Ravenglass saltmarsh core with discharge (annual discharges are represented by 🔴and activity concentrations by 🔵).

7.5.5 Correlation with discharge

The distribution for ^{237}Np down the core is markedly different and less defined than for other radionuclides with the activities decreasing down the profile to a greater extent, falling below the method's limit of detection (Figure 40 and Figure 41). Using a sedimentation rate of 0.87 cm year^{-1} the peaks at 3.5 cm and 13.5 cm indicate a discharge maximum in 1980 and 1992 if the core has been undisturbed as indicated by the core radiochemistry.

The limited discharge data makes interpretation of the core profile difficult and brings in a level of uncertainty. The increased activity observed in the core at 1980 reflected the high annual discharges however the increase in 1992 did not show the same level of correlation between the activity and discharge data. The activity maxima also do not agree with the depth profiles seen for the other radionuclides analysed. The profile agrees with the findings of Morris et al., (2000) who also reported a distinct peak in the upper two sections (mid points of 0.6 cm and 1.8 cm) which didn't reconcile with discharge pattern or other radionuclide profiles.

As the core was taken from a high energy area where there is frequent tidal inundation, redistribution of ^{237}Np within the sediment may occur accounting for the lack of correlation with discharge and increased activity levels in the upper sections. As the tidal height increases so does the hydrostatic pressure which drives the water column up through the marsh sediments. In the effluent discharge ^{237}Np is present in IV state and becomes slowly oxidised to Np(V) (Assinder, 1999, Germian et al., 1987). Estimates showed Np(IV) made up 50% of the total discharge inventory ^{237}Np but only 1% and 0.5% remained in this form in the sea water around Sellafield and the South Scottish coast respectively (Pentreath et al., 1986) with the majority present as Np(V), especially at suboxic marshes. This dominant species, compared to other more particle reactive transuranics, is highly mobile and susceptible to remobilisation (Caborn et al., 2016b). Therefore it is likely that the ^{237}Np follows the water column flow with the activity migrating upwards leading to the increased activities in the upper section of the sediment core.

7.5.6 Impact of redox changes

The ^{237}Np distribution profile has no significant correlation with the major elemental data (Figure 39). In particular, the geochemical composition showed major Mn composition changes within the core profile with a heterogeneous distribution which did not correlate with the ^{237}Np trend (Figure 42). The ^{237}Np activities instead of showing a maxima at approximately 30cm fell below the limit of detection where the Mn results indicated the presence of a second oxic zone inferring the behaviour observed is similar to that of ^{137}Cs but to a lesser extent as influenced by the presence of Np(IV). Neptunium is redox sensitive element however variations in concentration are not observed due to the oxic environment. At the oxic saltmarsh conditions (redox potential of 180 to 270mV; Morris et al., 2000) the majority of Np will be stable in the pentavalent state (NpO_2^+). For variations to occur and the formation of Np(IV) the reduction potential must be below -120mV (Runde, 2000). Np(IV) is likely to be present to a lesser extent as a consequence of reduction at the illite surface (Nagasaki et al., 2016).

Analysis of a core taken by Morris et al., (2000) from the Ravenglass saltmarsh at sampling position B5 reported a strong correlation between the CaO and Np results with depth however for this core (R-96-007) the agreement was poor ($r^2 = 0.0836$).

Both the activity concentrations and depth profiles for the core were comparable with those obtained by Morris et al., (2000) and Marsden et al., (2006) (Table 21 and Figure 42) who also analysed cores sampled from the Ravenglass saltmarsh. The activity concentrations for the R-96-007 core were lower by approximately 25% in comparison to the other cores however the distribution profiles were similar (Figure 42) with the two minor peaks present. Morris et al., (2000) also reported poor correlation with discharge in the upper sections of the core (Morris et al., 2000). Although the ^{237}Np distribution is different from that of other radionuclides, it appears to be consistent across the saltmarsh despite the differing sampling locations.

Table 21 Np-237 activity concentrations (Bq kg^{-1} dry weight) for cores taken across the Ravenglass saltmarsh

	Core Details		
	Marsden (2006)	**Morris (2000)**	**R96-007**
Geometric mean	3.58	3.20	2.74
Median	5.62	3.10	4.07
Minimum	0.400	0.680	0.484
Maximum	10.7	13.0	8.51
Standard deviation	3.74	4.36	2.61
Number	24	17	24

The core analysed by Morris et al (2000) showed no redox zonation with “the major element composition relatively stable with depth”. The agreement in activity distribution profile despite the varying geochemistry indicated that ^{237}Np is not redox sensitive and other factors impact on its distribution.

7.5.7 Spatial variation

Scrape data from the sampling point R-96-007 core was taken at time periods 1980, 1992 and 2005 (Caborn et al., 2016a) was compared to the depth profiles for the core and those reported by Morris et al., (2000) and Marsden et al., (2006) to ascertain the level of spatial variation. There is good agreement with the distribution profiles observed for the four data sets indicating that the difference in activity concentrations is due to the location on the saltmarsh (Figure 42). Core R-96-007 was taken from a higher energy area than the cores sampled by Morris et al., (2000) and Marsden et al., (2006). A recent spatial study which assessed the activities in surface scrape samples across the same marsh (Caborn et al., 2016a) showed higher ^{237}Np activities concentrations at the sampling point the R-96-007 core originated and was in an area of high sedimentation, less frequent tidal inundation and vegetation trapping. The sedimentation rates for the two cores are in contrast with the high energy area core (R-96-007) having a lower rate sedimentation accumulation of 6.86mm year^{-1} and between 4.8 and 5.6mm year^{-1} (Marsden et al., 2006; Morris et al., 2000 respectively) compared to a value of 0.87cm year^{-1} for the R-96-007 core.

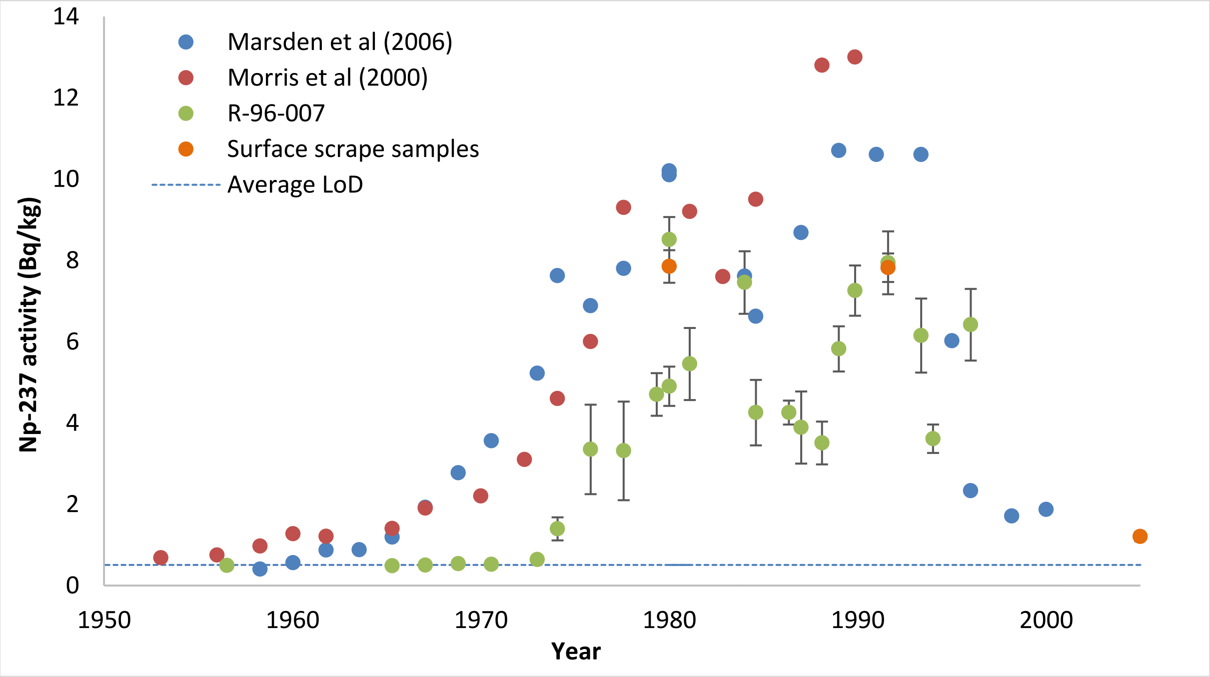

Figure 42 Comparison of ^{237}Np distribution in cores from the Ravenglass saltmarsh

7.5.8 Nuclide ratios

The oxidation state of ^{237}Np can potentially influence its behaviour in the environment with the mobile and soluble pentavalent species dominating in coastline or surface waters. Unlike Pu, Np does not readily reduce in the marine environment to the tri or tetra valent states and has a lower particulate affinity and distribution coefficient, and higher mobility. The main source of ^{237}Np is from the liquid effluent discharges into the Irish Sea where the radionuclides become associated with fine, suspended material to differing degrees, depending on their particle reactivity. The distribution coefficient (K_D) indicates the level of association and is estimated at between 10^3 and 10^4 l kg^{-1} in the Irish Sea for Np(V) (Pentreath and Harvey, 1981). This is significantly lower than other transuranics, with typical values for Am and Pu in the Irish Sea at 10^6 and 10^5 respectively. The distribution coefficient for Np decreases with increasing distance from Sellafield due to oxidation of neptunium from IV to V, grain size distribution and composition of suspended sediments (Edgington & Nelson, 1984, Assinder, 1999). For ^{137}Cs when the discharges were at their peak in the Irish Sea the distribution coefficients were reported as 350 l kg^{-1} (Baxter et al., 1979) but significantly increased with time to 2 x 10^5 l kg^{-1} (Pulford et al., 1998) with the rise reflecting the reduction in liquid effluent discharge activities and release of a labile Cs fraction out of the Irish Sea basin.

Unlike ^{137}Cs, transuranic radionuclides are particle reactive with 95% of Pu and the majority of Np and Am, estimated to have precipitated and associated with the sediment on the Irish Sea floor within 12 hours of discharge (Hetherington et al., 1978, Marsden et al., 2006). They become associated with the fine grained sediment in the belt parallel to the Cumbrian coast extending into Liverpool Bay, and across the mouth of the Solway Firth to Wigtown Bay, commonly referred to as the mud patch. The radionuclides associated with the particles are transported and dispersed into the water column via open marine (both surface and current) and tidal currents into the estuarine environment which acts as a sink and ultimately a secondary source of the radionuclides.

To ascertain the behaviour of ^{237}Np and allow comparisons with other radionuclides of which the nuclide ratios of ^{237}Np:^{137}Cs and Pu alpha:^{137}Cs alpha at discharge and on the saltmarsh were calculated. If a radionuclide is particle reactive there will be poor correlation between the discharge and activity isotope ratios indicating a secondary input source for example activity released from the mud patch. If the radionuclide exhibits conservative behaviour there will be good correlation between the data sets indicating that the radionuclide is mobile and is not significantly retained during sediment transport to the saltmarsh. To verify the data the same approach was used for the saltmarsh scrape sample activity concentration data at W6 sampling point (Caborn et al., 2016a) at three time periods (1980, 1992 and 2005) and shows excellent agreement with the discharge and core data obtained.

The trend in isotopic composition for ^{237}Np:^{137}Cs in the core data generally reflected the ratios for Sellafield liquid effluent inventory with maxima in the mid 1980's to 1995, followed by decline due to the reduced discharges. The activity concentration ^{237}Np:^{137}Cs ratios reflected the increasing activity concentrations until 1986 and then increased to a maximum at 1993 (8.07×10^{-03}) due to the ^{137}Cs activities decreasing at a greater rate than ^{237}Np. Although the results are lower, the difference is just over a factor of two and considering the variation in data there are similarities between the profile for the discharge and sediment core ratios which indicate similar behaviours.

The Pu alpha:^{137}Cs ratios in the saltmarsh were significantly higher than for ^{237}Np:^{137}Cs due to the greater Pu alpha activity levels in the discharges but reflect the same trend since the mid 1980's. The ^{237}Np:Pu alpha ratios for the activities on the Ravenglass saltmarsh were far higher than those for discharge with an average 33 fold difference.

A comparison of the ^{237}Np:^{137}Cs and ^{237}Np:Pu alpha data for the core, surface scrape and discharge data illustrates the contrasting behaviours of the transuranics (Figure 43). For the ^{237}Np: ^{137}Cs ratios there is a similar trend between the core activities and discharge data indicating conservative behaviour with the most significant source term being the Sellafield discharges.

For the ^{237}Np:Pu alpha and ^{237}Np:^{137}Cs ratios the trends were similar for between the discharge and activity data however several orders of magnitude different (Figure 43) indicating the input from a secondary source e.g. the mud patch of Pu alpha activity.

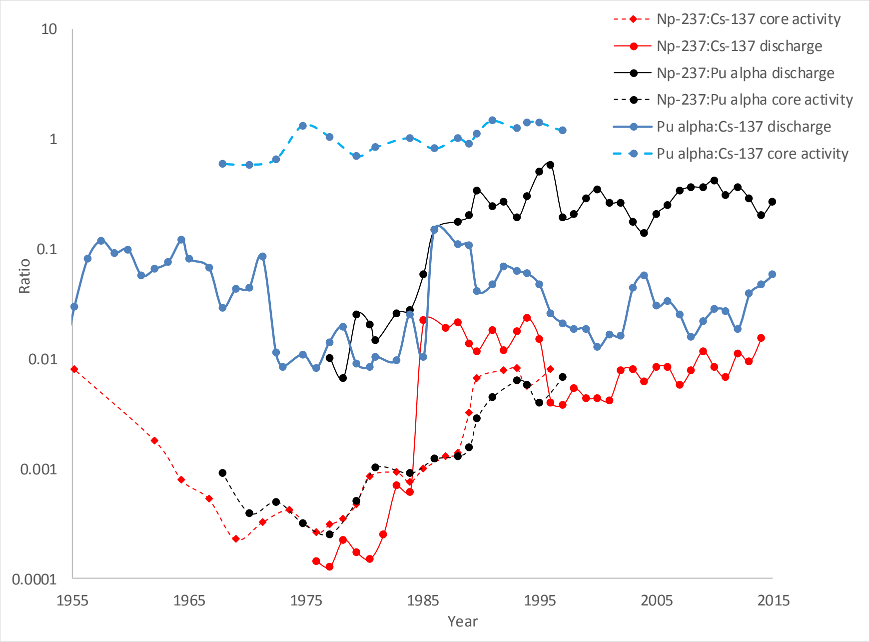

Figure 43 Comparison of ^{237}Np:^{137}Cs and ^{237}Np:Pu alpha activity ratios in discharge and core samples

The ratios reflect the lower particle affinity of ^{237}Np, and ^{137}Cs, compared to Pu alpha and indicate conservative behaviour with the data correlating more closely with discharges and mud patch as a secondary source having less influence. Although both actinides are from the same source, the ratio data shows that the behaviour of Pu alpha and ^{237}Np on the saltmarsh is influenced by differing factors. Although not entirely comparable, the behaviour of Np prior to deposition on the saltmarsh is similar to that of ^{137}Cs and has an analogous chemistry and mobility characteristics.

7.6 Conclusions

The Ravenglass saltmarsh sediment core showed a distinct geochemical redox profile with previous analysis of other radionuclides (^{137}Cs, ^{241}Am and Pu alpha) which showed a chronological profile which had a strong correlation with published Sellafield discharge records indicating that the sediment was largely undisturbed.

The distribution profile for ^{237}Np in the sediment core shows the highest activities in the upper sections and the presence of two minor peaks at a depth of 3.5cm and 13.5cm, equivalent to 1982 and 1992. The results below a depth of 21.5 cm, equivalent to 1974, which fell below the limit of detection (0.508 Bq kg^{-1} dw). The profile was partially reconciled with the Sellafield effluent discharges however less defined than for other radionuclides. The lack of correlation was due to limited discharge data, increased of ^{237}Np activity in the upper sections and a differing profile distribution compared to the other transuranic nuclides possibly indicating redistribution of Np within the core.

The depth profile for ^{237}Np in the sediment core was comparable with others analysed from the same saltmarsh and confirmed spatial variation does occur as previously reported (Caborn et al., 2016a). Lower activities were observed in this core due to the differing locations which had a higher sedimentation rate and was present in a higher energy area so more frequently tidally inundated.

The core's geochemical composition showed major Mn composition changes with a heterogeneous distribution profile which was not seen in other cores. However, the radiochemical data was in general agreement despite the different locations and varying geochemistry. In addition, the distribution of ^{237}Np down the core cannot be reconciled with the redox profile. It can be concluded that ^{237}Np is not redox sensitive and it is the inventory, location and conditions, which effect its distribution.

Comparison of the nuclide ratios showed that ^{237}Np is influenced by different factors compared with Pu alpha and its characteristics are more akin to ^{137}Cs. It has a lower particle affinity than Pu alpha, is more mobile and the mud patch as a secondary source has less influence. It is likely that Np is less associated with the sediment on the Irish Sea floor as has a low particle affinity, and is readily remobilised in the estuarine environment where it will accumulate over the saltmarsh. Once there, significant post depositional migration occurs and the inventory of ^{237}Np is influenced by the location and conditions especially tidal movement but not by the geochemistry.

7.7 Abbreviations

dw, dry weight

GAU, Geosciences Advisory Unit

NPL, National Physical Laboratory

IAEA, International Atomic Energy Authority

SIXEP, Site Ion Exchange Effluent Plant

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8 Summary and Conclusions

8.1 Comparison of methods

The review of cited methods for ^{237}Np determination in environmental samples showed that there were common approaches. These included:

- Addition of the yield tracer in the initial stages with half utilising ^{239}Np;
- Reduction of Np to the tetravalent state was critical to achieve good recoveries with a range of reducing agents cited;
- Co-precipitation was widely used and a number of complexing agents cited. As a well-established approach for actinide determination it is non-specific to Np with other transuranics and matrix elements also co-precipitating.
- Anion exchange was the most commonly used separation technique with Np(IV) strongly retained and the chemistry well characterised for the isolation from other transuranics present, allowing for sequential separations.
- Twenty one different techniques were cited. Alpha spectroscopy was most commonly used, along with twelve mass spectroscopy techniques and highly specialised instrumentation such as AMS and NAA.

Most significantly the majority of the methods focused on the analysis of a specific sample matrix and final measurement technique for example soil and sediment or water or seawater and seaweed or lichen by alpha spectrometry.

8.2 Optimisation of a method for the determination of Neptunium-237

A method was been developed for the analysis of ^{237}Np in samples which had high elemental concentrations with the final measurement carried out by ICP-MS or alpha spectrometry. The method included the production of a readily available and regenerating source of ^{239}Np.

The method development process showed that losses of ^{237}Np did not occur at temperatures up to 1000°C and the utilisation of ferrous sulphamate as a reducing agent completely converted Np(IV) to Np(V). Co-precipitation of ^{237}Np is not dependant on the reagent used however the efficiency of elemental separation is method dependent.

The sample matrix has a significant impact on the ^{237}Np recoveries and decontamination factors achieved for the resin column chemistry especially at higher elemental concentrations with anion exchange providing a more robust separation with less practical, flow issues.

For alpha spectrometry the plating times were shown to be optimum at 90 minutes using the sodium bisulphate/sodium sulphate methods with a plating time of 90 minutes.

8.3 Development and validation of a robust method for ^{237}Np determination

A robust method capable of analysing a wide variety of environmental and decommissioning samples for ^{237}Np was developed with final measurement performed using alpha spectrometry or by ICP-MS for added flexibility. Key stages optimised included:

- Production of a readily available and regenerating yield tracer source (^{239}Np);
- Identification of a suitable reducing agent to convert Np(IV) to Np(V);
- Assessment of different complexing agents for the co-precipitation pre-concentration stage and of the elemental behaviour;
- Comparison of ^{237}Np recoveries and decontamination factors achieved for two resin separation and purification methodologies;
- Optimisation of plating conditions for the preparation of alpha spectrometry discs;
- ICP-MS measurement using the Agilent 8800 Series Triple Quadrupole.

The development and validation of the method was carried out using the novel approach of experimental design. It is capable of analysing, for most of the elements, up to the highest levels likely to be encountered in environmental and decommissioning samples with a method scope based on elemental concentration rather than specific sample type. The statistical approach was used to identify the elements and quantify the effect on ^{237}Np recovery for the pre-concentration, separation stages and the method as a whole.

The results showed that ^{237}Np almost completely co-precipitated with three complexing agents with elemental concentration having no statistical impact on recovery. The degree of interaction of each elements on the separation and purification stage (anion exchange resin) was quantified and the impact on ^{237}Np recovery both as a standalone procedure and used in conjunction with the pre-concentration step.

Decontamination factors for each of the elements were calculated and the impact on the final measurement by radiometric, isobaric and matrix elements determined. By adopting a combination of statistical and radiochemical analysis the operational elemental range for the ^{237}Np separation method was defined. The approach demonstrates how any sample, regardless of matrix, with an elemental composition that falls below the thresholds stated can be analysed with the procedure producing good method recoveries, efficient separation and a final fraction which is does not contain any final measurement interferences.

8.4 Spatial and temporal variation of radionuclides over a 25 year period at Ravenglass

The Ravenglass saltmarsh is one of the most radioactively contaminated marshes within the Irish Sea due to its close proximity to the Sellafield reprocessing site. The highly dynamic saltmarsh ecosystem leads to spatially varying rates of deposition of different radionuclides which also vary with time. The radionuclides analysed, ^{241}Am, ^{137}Cs, Pu alpha and ^{106}Ru, showed considerable spatial variation across the sampled site however only ^{137}Cs and, to a lesser extent, ^{241}Am, had detectable systematic spatial trends over the different sampled time periods. The short lived radionuclide ^{106}Ru, accumulated in areas of high energy, whereas long-lived radionuclides were more prevalent in low energy areas.

Over the twenty five year period the specific activity in surface sediment decreased for all radionuclides considered, but the rate of decline varied with the different radionuclides and their location in the saltmarsh. The rate of reduction declined in the order: ^{106}Ru> ^{137}Cs> Pu alpha >^{241}Am with the decay of ^{241}Pu to ^{241}Am measurably affecting the rate of decrease in ^{241}Am specific activity.

There was also spatial variation in the sedimentation rates calculated across the saltmarsh and despite this, good agreement between the discharge data and specific activities obtained for four independent data sets demonstrating that the use of surface scrape samples is therefore suitable as an indicative tool for long term environmental radioactive monitoring. Comparison of ratios over the twenty five years estimated liquid discharges from Sellafield with lag times of less than 0.5 year estimated for 1980 which increased with time (1992 and 2005) 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.

8.5 Distribution and mobility of ^{237}Np in a West Cumbrian ungrazed saltmarsh

The temporal variation for ^{237}Np in surface scrape samples showed a decrease in activity concentration over the twenty five year period. Between 1980 and 1992 the rate of change was insignificant followed by a period of significantly decreasing activity with the results in good agreement with the rate observed for the discharge activities over the same periods. The behaviour of ^{237}Np on the saltmarsh closely reflects the discharge profile and there is little influence from any other source inputs such as ingrowth from ^{241}Am or the mud patch.

Comparison with other radionuclides produced a temporal order of Cs >Pu> Np >Am for the period as a whole which was consistent with the discharge inventory trend. Between 1992 and 2005 the agreement was poor due to Pu alpha and ^{241}Am “enrichment” from secondary source inputs e.g. the mud patch and for ^{241}Am as a result of ingrowth from its parent nuclide ^{241}Pu.

Spatial variation of ^{237}Np across the saltmarsh was observed with the highest activities generally in the low energy, landward areas. The variation, although still present, become less distinct with time as activity concentrations declined.

Although Np can exist in a range of oxidation states comparable to those of Pu, comparison of the isotopic compositions showed that Np geochemistry exhibits a conservative behaviour that is more akin to ^{137}Cs. It is inferred that it is predominantly present in the mobile, pentavalent state, whilst Pu alpha was present as the relatively immobile III/IV on the Ravenglass saltmarsh. Although it has a lower particle affinity than ^{137}Cs (K_D 2 x10^5 l kg^{-1}) Np(V) will be susceptible to remobilisation and therefore concentrated in low energy areas where there is greater sedimentation rates and least tidal disturbance.

8.6 Distribution and mobility of ^{237}Np in a West Cumbrian ungrazed saltmarsh core

The Ravenglass saltmarsh sediment core showed a distinct geochemical redox profile with previous analysis of other radionuclides (^{137}Cs, ^{241}Am and Pu alpha) which showed a chronological profile which had a strong correlation with published Sellafield discharge records indicating that the sediment was largely undisturbed.

The distribution profile for ^{237}Np in the sediment core shows the highest activities in the upper sections and the presence of two minor peaks at a depth of 3.5 cm and 13.5 cm, equivalent to 1982 and 1992. The results below a depth of 21.5 cm, equivalent to 1974, which fell below the limit of detection (0.508 Bq kg^{-1} dw). The profile was partially reconciled with the Sellafield effluent discharges however less defined than for other radionuclides. The lack of correlation was due to limited discharge data, increased of ^{237}Np activity in the upper sections and a differing profile distribution compared to the other transuranic nuclides possibly indicating redistribution of Np within the core.

The depth profile for ^{237}Np in the sediment core was comparable with others analysed from the same saltmarsh and confirmed spatial variation does occur as previously reported (Caborn et al., 2016a). Lower activities were observed in this core due to the differing locations which had a higher sedimentation rate and was present in a higher energy area so more frequently tidally inundated.

The core's geochemical composition showed major Mn composition changes with a heterogeneous distribution profile which was not seen in other cores. However the radiochemical data was in general agreement despite the different locations and varying geochemistry. In addition the distribution of ^{237}Np down the core cannot be reconciled with the redox profile. It can be concluded that ^{237}Np is not redox sensitive and it is the inventory, location and conditions, which effect its distribution.

Comparison of the nuclide ratios showed that ^{237}Np is influenced by different factors compared with Pu alpha and its characteristics are more akin to ^{137}Cs. It has a lower particle affinity than Pu alpha, is more mobile and the mud patch as a secondary source has less influence. It is likely that Np is less associated with the sediment on the Irish Sea floor as has a low particle affinity, and is readily remobilised in the estuarine environment where it will accumulate over the saltmarsh. Once there significant post depositional migration occurs and the inventory of ^{237}Np is influenced by the location and conditions especially tidal movement but not by the geochemistry.

8.7 Conclusion Summary

The issue of lack of reference materials is widely acknowledged and has a significant impact on radioanalytical laboratories activities including method development, underpinning of method validation and demonstration of laboratory proficiency. Methods are defined by the sample matrices and radionuclides analysed however the range of sample types and radionuclide composition presently available is limited and will require significant investment to address. The approach proposed in this PhD thesis enables laboratories to define the method based on elemental composition potentially reducing the effort required for development and validation and allowing greater flexibility when defining the method scope.

Due to difficulties with analysis there have been limited studies of the behaviour of neptunium in the environment required to understand the impact of its mobility and distribution; important when considering the burial and storage of nuclear waste. A method which is capable of analysing ^{237}Np in a range of sample matrices to increase the capability of laboratories and to meet the future challenges of the nuclear industry has been developed. The scope, which is based on elemental concentration, has been validated using a novel approach; experimental design.

Analysis of ^{237}Np in sediment scrape and core samples has enabled the behaviour in the environment to be ascertained. Such information is essential in assessing the long-term behaviour of ^{237}Np in the environment, importance in radiological dose assessment and mobility and distribution in long term storage options such as geological disposal. The analysis of sediment samples from an ungrazed West Cumbrian saltmarsh over a twenty five period and of a sediment core showed a decrease in ^{237}Np activities over time which can be partially reconciled with discharge history. Spatial variation does occur on the saltmarsh and ^{237}Np has a lower particle affinity, and is mobile than other transuranics. The distribution of ^{237}Np is influenced by the location and conditions especially tidal movement but not by the geochemistry.

9 Further work

This PhD study has raised a number of further questions where additional research may be of benefit.

The shortage of solid reference materials for ^{237}Np prevented a sequential extraction study to be carried out. It would be advisable to understand the extraction characteristics of ^{237}Np in a variety of samples including where the contamination is associated with fused silicates such as originating from nuclear weapon test sites e.g. Semipalatinsk and from areas where high impact explosions have occurred, i.e. Chernobyl.

The partial correlation with discharge data was due to limited discharge data which could be improved upon by re sampling the saltmarsh and analysing for ^{237}Np. This would give almost 30 years of discharge history and possibly an improved reconciliation with the activity profile. In addition speciation of ^{237}Np down the core would identify the oxidation states upon deposition and if that changes over time and with differing redox conditions.

This study suggests that ^{237}Np in the Irish Sea is not particle reactive and therefore the level present in the Sellafield mud patch are likely to be lower than for other transuranics such as Pu alpha and ^{241}Am. However little data exists and a core of the mud patch with analysis of the key radionuclides including speciation would provide valuable confirmation.

The presence of ^{237}Np is now well characterised on the Ravenglass saltmarsh and has been shown to have a higher mobility than other transuranics such as Pu. Analysis of surface scrape samples along the coast line would be of benefit to determine the long term mobility characteristics for example how far from the point of source has the contamination travelled over the time period and if the contamination is localised in the longer term.

As the majority of the surface scrape samples were collected prior to the commencement of this study particle size analysis was not carried out. The literature indicates that this could be a key factor to the distribution of ^{237}Np and therefore it would be advantageous to carry out a further sampling and analysis campaign this time including particle size analysis. This would ascertain if the spatial variation observed is as a result of particle size distribution.

Similarly it is suggested in the literature that there is a change in oxidation state on the surface of illites which are present on the saltmarsh. A study to identify if ^{237}Np is reduced, thus effecting the mobility characteristics and to what extent would be of benefit.

Appendix A

Table A.1 Summary of methods in published literature for the determination of ^{237}Np in environmental samples.

No. *	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
3	Np-235 Np-239	water	1000-2000L	Acidify: HCl.	PPT: Ca & Mg hydroxide & carbonate pH 9-10 (repeat)	An Ex: 9M HCl (RA-1M NH_4I). Wash 9M HCl (Pu, Am, Th). Elute: 4.5M HCl-0.1M HF.	PPT: LaF_3. PPT: hydroxides. SEx: TTA in xylene. Wash: 10M HCl. BEx: 10M HNO_3	EDP: Na_2SO_4 & H_2SO_4 pH 1.9-2.1	20-50%		Pu, Am, Tc, Cs	α spec, x-ray, ɣ spec
4	Np-239	lichen		uses [51]								α and ɣ spec
15	Np-239	soils	10-80g	Ash, L. 1:1 HNO_3/HCl	PPT: OH-	SEx: di-Isopropyl ether (FeIII), HNO_3 (Cl-), RA: Fe sulphamate	PTFE/TOMAN: 1.5M HNO_3 (Fe), elute 0.03% $(NH_4)_2C_2O_4$ in 0.1M HNO_3	Sample added to CaF_2 pellets, ash at 800°C	85-95%	10^{-12}g		Luminescence
17	Np-239	grassland soil	10-40g	uses [30]					70-90%			HR-ICP-MS
18	Np-236	soils	8-15g	d. HNO_3/ HF/$HClO_4$		SE: 2-TTFA	An Ex: not specified				^{239}Pu	TIMS
20	Np-239	lichen	15g	L c HCl	RA: Ferrous(II) chloride. PPT: LaF_3	An Ex: 9M HCl, wash: 9M HCl, elute: 4M HCl. RA: Ferrous (II) chloride	SEx: 0.5ml TTA in xylene BEx: 9M HCl. An Ex repeated	d. 1% HNO_3	70-90%		^{238}U, $^{239/240}$Pu	HR-ICP-MS
24	Np-236	sediment	5-10g	Ash then d. HF/AR/HCl/ H_2O_2/HNO_3	PPT: $La(OH)_3$ & $NH_2OH.HCl$ (RA). PPT: HNO_3, Evap	d. in 0.5N $AlNO_3$-3N HNO_3 & add 0.1N $FeSO_4$ & $NaNO_2$ (PuIV & NpIV).	Based on Maxwell (1997)	Evap, d. 10% HNO_3-0.02% HF, filter	70-95%	0.5fg/g	Pu	ICP-MS

No.*	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
26	Np-239	sediments	5g	Ash & L. c HCl	Evaporation & $NH_2OH.HCl$ (RA)	SEx: MIBK (Fe removal)	An Ex: 9M HCl. Elute with 5M HCl.	Post irradiation- $HClO_4$ addition (^{82}Br removal). SEx: TTA in toulene wash 0.5M HCl + NH_2OH-HCl.		0.1-0.5mBq		NAA, ɣ spec
29	Np-239	acidic media			Red agent: 0.1M Fe(II) and 0.11M NH_3OHNO_3	TRU: HNO_3, Wash: 9M HCl, 4M HCl (Am), 4M HCl-0.1M hydroquinone (Pu), 1.5M HCl (Th). Elute: 1M HCl+0.03M Oxalic acid						
30	Np-239	soil & sediment	upto 200g	L. AR + H_2O_2		SEx: Isopropyl ether (Fe). RA: HI. SEx: 10% TOA-xylene. BEx: 1M HCl-0.1M HF. RA: $HN_2OH.HCl$. PPT: LaF_3	An Ex: 8M HNO_3. Wash: 8M HNO_3 (U), 10M HCl (Th), 10M HCl-HI (Pu). Elute: 4M HCl. An Ex: 4M CH_3COOH	EDP: 2M NH_4Cl pH 2	72-82% water 51-79% soil	0.1mBq/ sample		SF-ICP-MS
31	Np-239	seaweed seawater	20g & upto 200L	used [20] (seaweed) & [32] (seawater)							Pu	SF-ICP-MS

No.*	**Tracer**	**Sample type**	**mass**	**Sample preparation**	**Pre-concentration**	**Separation**	**Purification**	**Source preparation**	**Typical recoveries**	**LoD**	**Other nuclides**	**Measurement**
32	Pu242	seaweed seawater	10g or 200L	Soils/sed-ash, L. AR & filter. Seawater- add 12M HCl, $FeCl_3.6H_2O$ & K_2S_2O5, adjust to pH10 with 6M NaOH, remove supernate. Acidify to 0.1M HCl.		An Ex: wash with 8M HNO_3, 12M HCl. Elute with 2M $HCl/NH_2OH.HCl$ + NaCl. 65% HNO_3 added, Evap and d. in NaOH + K_2S_2O5 & $Fe^{3+.}$	PPT: Fe(OH)2. An Ex: wash 8M HNO_3, 12M HCl. Elute 2M $HCl+NH_2OH.HCl$, add 14.4M HNO_3 & Evap	ICP-MS – d. 14.4M HNO_3, Evap & d. 4% HNO_3. α spec – d. $NaNO_3$, 18M H_2SO_4 & 14.4M HNO_3. Evap, d. 0.05M H_2SO_4, pH to 2.5 (NH_3), plate 4-5 hours at 0.7A/cm^2.	80-90%		Pu239, 240	SF-ICP-MS
33	Np-239, Pu242	Porewater sediment		uses [50]				^{242}Pu added, dispersed in Fe oxide				AMS
36	Np-237 standard addition	Fuel pellets	30g	L.7M HNO_3			Cat Ex: CS10, AgO (OA) & 2,3-$NH_2CH_2CH(NH_2)COOH \cdot HCl$ in 0.6M HNO_3 (eluent)		96-98%		Pu, Am, Cm	IC- ICP-MS
37	Np237 spike addition	Sediment, soil, seawater	10g or 100L	Soils/sed-ash, L: AR, add H_2O_2 & $FeCl_3$ (RA). Seawater- 12M HCl, $FeSO_4.7H_2O$ & $K_2S_2O_5$	PPT: $Fe(OH)_2$-$Fe(OH)_3$	Ex: TIOA in 8-10M HCl by redox with SO_3^{2-}-Fe^{3+}. BEx 2M HCl (Np^{4+})	An Ex: 8M HNO_3 (U), 12M HCl (Th). Elute: 6M $HCl+NH_2OH.HClD$. 14M HNO_3, evap.	ICP-MS -d. 0.5M HNO_3. α spec- d. 2M HNO_3, 18M H_2SO_4 & 3M NaCl. Evap , d. 0.05M H_2SO_4, pH to 2.5 (NH_3), plate 5 hrs, 0.6-0.7A/cm^2	9 3%			ICP-MS, α spec
38	Np237 spike addition	vitrified waste glass		KOH-KNO_3 fusion, acid dissolution		TRU Spec On line. Wash: 2M HNO_3, 2M HNO_3,0.1M $NaNO_2$, 2M HCl . Elute: 1M HCl + 0.07M $H_2C_2O_4$					Am, Pu	SI ICP-MS

No.*	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
39		water, soil & sediment	1L or upto 27g	water: acidify, Evap, d. in conc acid + H_2O_2. Soil/sed: Acid leach, Evap & d. in 3N HNO_3 + 0.5N Al nitrate	RA: ascorbic acid, Ferrous sulphamate	An Ex: UTEVA. Elute Np (Th &U) 5N HCl/0.05N oxalic acid	Evap, d. HNO_3/H_2O_2 repeatedly. D. HNO_3 & HDEHP. Ex: 1N HNO3	Sparge with Ar & seal		0.01 to 0.1Bq	Pu, Am, U, Th & Cm	PEARLS
40	Np-239	water, particulate, sediments & biological		Water -Acidify HNO_3. RA: Fe^{3+}, Nd. Sediments d. hot AR, Bio- Ash, d. HNO_3	PPT: NdF_3, D. HNO_3, boric acid	PPT: $Nd(OH)_3$. Ex: TTA xylene. RA: Fe^{3+}. BEx: 8M HNO_3	An Ex: 8M HNO_3. Wash: 8M HNO_3, 12M HCl, 12M HCl-NH_4I, 12M HCl. Elute: 4.5M HCl	EDP: $(NH_4)_2C_2O_4$ / HCl pH 2-3				α spec
42	Np-239	water	150L		PPT: $Fe(OH)_2$, L PPT: c HCl, PPT with NH_4OH.	SEx: Isopropyl ether + NH_4I (RA)	An Ex: wash 9M HCl/0.1M NH_4I, elute 0.5M HCl. Evap, d. 1M HCl. SEx: 0.5M TTA/xylene. BEx: 8M HNO_3	EDP		100n Bq/ml	Pu238, 239/240, Am241, Cm242, 244	α spec
44	Np-239	water, biota, sediments	20L, 5g	Solids: fuming HNO_3, 1M HNO_3	water: PPT: MnO_2 pH 9-9.5, d. HCl/H_2O_2. RA: hydrazine sulphate & Fe^{2+}	An Ex: 7M HNO_3. Wash: 7M HNO_3, 0.3M HF (Np). An Ex: 10M HCl. Elute: 0.1M HF-4M HCl	Irradiation. Repeat An Ex		>85%	0.013 mBq		NAA
45	Np-239	biota & soil	2g soil	Biota: 8M HNO_3, Soil: d. HNO_3/HF	Uses [111]							
46		sediment		Ash & d. HF/AR			Reduce Np with Fe(II) sulphamate, An Ex: TOA column, wash 2M HNO_3, elute 0.2M oxalic acid/0.16M HNO_3 @95˚C			1.2x10-5 Bq/ml		ICP-MS

No.*	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
47	Np-239	soil & sediment	1-200g	Ash, L 1:1 HNO_3/HCl twice	Evap filtrate, d. 10M HCl, RA: NH_2OH HCl, $(N_2H_5)HSO_4$	SEx. Isopropyl ether, wash 2 x 10M HCl, Ex 1M HCl-0.1M HF. Evap, d 10M HCl. An Ex: load & wash 10M HCl, elute 4M HCl/1M HF. Evap, d. Conc HNO_3. D. 8M HNO_3- 0.05M Hydrazine sulphate	An Ex: wash 8M HNO_3, 10M HCl &HI-HCl. Elute 1M HCl-0.1M HF & Evap. D. in CH_3COOH. An Ex: Np eluted, U retained.	Evap & d. 1M HNO_3		0.02Bq/ml		ICP-MS
48	Np-239	sediment	40-60g	L: AR + H_2O_2							Pu & Am	α spec
49	Np-239	plant	0.1-100g	d. HNO_3, HF, $HClO_4$	PPT: $Fe(OH)_2$	SE: 10% TIOA/Xylene, BEx: 8M HCl, 8M HCl-0.05M NH_4I, 4M HCl-0.02M HF	Cat Ex: NH_4OH/HCl. Wash: 10M HCl, 0.1M HCl in CH_3OH, 1M HCl in CH_3OH. Elute: 12M HCl	EDP: H_2SO_4 pH 2.4	66-89%		Pu, Am, Cm	α spec
50	Np-239	environmental		L. C. HCl/HNO3. RA: $NH_2OH.HCl$	SEx: MIBK. An Ex: 9M HCl. Wash: 8M HNO_3 (U). Elute: 5M HCl	RA: $NH_2OH.HCl$. SEx: TTA. BEx: 8M HNO_3		ICP-MS - 1% v/v HNO3, α spec- repeat separationEDP: $NaHSO_4/Na_2SO_4$, NAA- repeat separation irradiate, repeat separation	ICP-MS & α spec = 50-95%, NAA= 30-80%	Bq per 100g 3.7-19 x 10^{-6} (ICP) 0.9-1.3 x 10^{-6} (α spec) 3.1-12 x 10^{-6} (NAA)		ICP-MS, α spec, NAA

No. *	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
51	Np-239	Env. samples	upto 200g	L: AR, H_2O_2	PPT: LaF_3. D. HNO_3 & boric acid. PPT: hydroxide & carbonate. RA: Ferro ammonium sulphate	An Ex: 9M HCl-0.1M NH_4I, Wash: 9M HCl (Pu, Am, Th, Ln), 1M HNO_3-93% methanol. Elute: 4.5M HCl-0.05M HF		EDP: ammonium sulphate	50%			
52	Np-235/ Np-239	sediments		L. 8M HNO_3	PPT: $Fe(OH)_2$	RA: 1M HNO_3, hydrazine sulphate, 8M HNO_3, $NaNO_2$+H_2O_2,	An Ex: HNO_3 wash: 10M HCl, 10M HCl+NH_4I elute: 4.5M HCl +HF	EDP: H_2SO_4 pH 2.4	74%			α spec
53	Np-239	sediments, soils, biota, natural waters		Ash & d. Conc. HNO3		SEx: 0.1M TOPO in toulene (remove matrix elements). Org phase (containing Np) deposited onto filter, heated & irradiated.	Post irradiation- d. Conc HNO_3, UTEVA Ex condition, load & wash 6M HNO_3/0.3% H_2O_2, elute 2M HNO_3/0.1M oxalic acid					NAA & ɣ spec
54	Pu242	soil, sediment & bio samples	upto 4g	Ash, L. Conc HNO_3	Evap & make up in 5M HNO_3 & re-filter	RA: ascorbic acid. inject into SI system (TEVA resin). Load & wash 5M HNO_3, 9M HCl & 1M HNO_3, elute 0.5M HCl			87-95%		Pu	ICP-SF-MS with SI

No.*	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
55	Np-239	soil		L. c HNO_3	PPT: $Fe(OH)_2$	RA: $N_2OH.HCl$. SolEx: Isopropyl ether. Bac Ex: 10M HCl. An Ex: 10M HCl, elute : 4M HCl/0.1M HF.	SEx: TTA xylene. BEx: 8M HNO_3. An Ex: 8M HNO_3, wash: 10M HCl+0.1M HI, Elute: 1M HCl/0.1M HF. An Ex: 4M CH_3COOH (U).			4.7 x 10^{-6} mBq/ml	Tc99, Pu239/240	ICP-MS
56	Np-239	soil & sediment	upto 10g	L. c HNO_3		RA: hydoxylamine hydrochloride. An Ex: 8M HNO_3. wash: 8M HNO_3, 9M HCl, 0.1M I^-/9M HCl. Elute: 4M HCl.		Thin source prep: NdF_3 ppt	40%	0.02 Bq/kg		α spec
57	Np-239	seawater & biological samples		water: acidify. Shells: fuming HNO_3. Other: nitrosulphuric medium	RA: hydrazine sulphate, Fe & $(NH_4)_2Fe(SO_4)_2.6H_2O$	An Ex: 7M HNO_3. Wash: 7M HNO_3, 0.3M HF (Np). An Ex: 10M HCl. Wash 10M HCl, 9M HCl-0.05M NH_4I. Elute: 0.1M HF-4M HCl	Irradiation. An Ex: 7M HNO_3. Wash: 7M HNO_3, elute 0.3M HF.			0.013mBq		NAA & ɣ spec
59	Np-236	soil	1-3g	Ash. L. HCl & HF , 6N HCl, 6N HCl/ boric acid				see Beasley et al 1998			Pu	TIMS
61	Np-239	water, soil, vegetation & meat	10g	d. HNO_3-HF/HCl		SEx: 10% HDEHP in toluene pH 4.5. BEx: 5N HNO_3. BEx: 1M oxalic acid. PPT: YF_3.	An Ex. Wash: HCl-NH_4I (Pu), Wash: c HCl. Elute: 2N HCl		40-70%		^{239}Pu, ^{241}Am, ^{244}Cm	α spec

No. *	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
63	Pu-242	Soil, sediment, seaweed	1-20g	L. AR	PPT: $Fe(OH)_2$		RA: $K_2S_2O_5$, In line SI: TEVA, Inject 8M HNO_3. Wash: 8M HNO_3, 9M HCl, elute: 0.1M NH_2OH-2M HCl	Evap and d. 0.5M HNO_3	85.70%	16µBq/kg	Pu239, 240	ICP-MS
67	Bi-209			Extract in 1M H_2SO_4 (repeat twice)		Ex: proprietary high molecular wt tertiary amine, repeat		Dilute to 0.3% H_2SO_4	91 ± 7%	0.65Bq/L		ICP-MS
72		geological & biological		Ash. L. 8M HNO_3/H_2O_2			Ext: several extractive scintillator cocktails valence dependant			9.5 pg/L	Th, U, Pu, Am, Cm	PEARLS
73	Not used	Sediment										ɣ spec (^{233}Pa)
75	direct measure	marine sediments	500mg					Pellet formation (8 tonnes). Ta = secondary cathode.		80pg/g		dc-GDMS
76		waste samples								sub ng/L	^{226}Ra, ^{230}Th, ^{238}U, ^{241}Am	ICP-QMS
77		standard solutions								2-8 fg/ml	^{99}Tc, ^{226}Ra, ^{232}Th, ^{238}U, ^{239}Pu, ^{240}Pu	HR-ICP-MS

No.*	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
78	40g	soil	40g	fuel: L. 7M HNO_3, sediment: HNO_3/HF/HCl microwave				d. 1M HNO_3	>80%	2.4 mBq/kg	Pu	HR-ICP-MS
80		spent nuclear fuel samples & sediment	30g	fuel: L. 7M HNO_3, sediment: HNO_3/HF/HCl microwave	Red. Agent: 0.2M $NaNO_3$	I.C: Dionex CS5A & CG5a. Eluent: 100mmol/L oxalic acid, 190mmol/L LiOH & 2M HCl.		0.45ng/ml				IC-ID-ICP-MS
81		Aq waste & soils		L. HNO_3						sub pg/L	^{226}Ra, ^{230}Th, ^{238}U, ^{239}Pu, ^{241}Am	DF ICP-MS
82		rad waste & env samples		Li borate fusion. Fe oxide						pg/g range	^{99}Tc, ^{232}Th, ^{233}U, ^{235}U, ^{238}U	LA- ICP-MS
83	Np-236	sediment	1g	Extract in 1M H_2SO_4 (repeat twice)								TIMS
84	Not used	water	1L	acidified and boiled	PPT: $La(OH)_3$	An Ex: 8N HCl, Wash: 8N HCl, elute: 4N HCl/0.05N HF		EDP: HCl/NH_4OH, heat at 2000°C		160fg%		RIMS
19?	Np-239	sediments	40-60g	uses [30]							Pu & Am	α spec - Si(Au) detector & 1k channel PHA
87	N/A	sediment cores									ɣ	ɣ spec (^{233}Pa)
88	Np-239	sediment	0.5-10g	uses [47]						0.02mBq/ml		ICP-MS

No.*	**Tracer**	**Sample type**	**mass**	**Sample preparation**	**Pre-concentration**	**Separation**	**Purification**	**Source preparation**	**Typical recoveries**	**LoD**	**Other nuclides**	**Measurement**
90	Np-239	Soil / sediment		L. AR	evaporation	SEx: Isopropyl ether, 3 x Ex TOA-xylene. PPT: LaF_3	An Ex: 8M HNO_3, 10M HCl, 10M HCl-0.1M HI, elution 4M HCl. An Ex CH_3COOH (U removal).	EDP: 2M NH_4Cl		0.2mBq/ml α spec, 0.02Bq/ml ICP-MS		α spec, HR-ICP-MS
92	soil			d. C.HNO_3/ tetraflurorborate (microwave) or d. HCl/HF	PPT: oxalate salts-rare earth carrier. RA: hydroxylamine hydrochloride, Fe^{2+}.	I.C. Followed by An Ex					Pu	TIMS
93	Np-236	water	2kg	uses [92]							Pu	TIMS
94				uses [59]								
95	Np-235	soil		minerialisation	PPT: $Fe(OH)_2$	An Ex		EDP				
96	Np-235	seawater & biological samples				An Ex: 9M HCl. Elute: 9M HCl. PPT: $Fe(OH)_3$ pH 8.5. RA:hydrazine, $(NH_4)_2Fe(SO_4)2.6H_2O$ & Mohrs salt	An Ex: 7.2M $HNO_3+NH_2NH_2.H_2O$. Wash:7.2M $HNO_3+NH_2NH_2.H_2O$. Elute: 4.5M HCl	EDP: ammonium sulphate pH 1.95		13mBq for 5-25g dry sample		α spec
97		soil		L. AR	uses [52]							
98	Np-239 & Pu242	porewater	~750 ml	Acidify with HNO_3 & Evap	PPT: Fe oxy-hydroxide in presence of suphite. D. ppt in HCl & Evap. D. residue in 9M HCl	uses [52]		Add ^{242}Pu, Fe & HNO_3. Evap & heat residue to oxidise Fe. Ash at 800˚C, add Fe_2O_3 & Al powder		4µBq		AMS

No. *	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
99		porewater	800-900ml	wet ash with HNO_3	uses [30]						Pu & Am	AMS
100	Np-236	uses [9]										TIMS
101	Np-239	sediments	5-25g	uses [47]						0.01mBq/ml	^{99}Tc, $^{239/240}$Pu	Q-ICP-MS
102	Np-239	sediment		uses [30]								α spec & ICP-MS
103	Np-239	sediment	1-20g	uses [30]							^{241}Pu (LSC), Pu 238, 239/240	α spec,
104	Np-239	sediment	5-20g			SEx & An Ex		EDP			238, 239/240Pu	α spec and HR-ICP-MS
105		weak loess aquifer									Am241	HPGe detector
106	Pu242	sediment	10g	uses [107]								ICP-MS
107	Np-239	sediments		uses [52]								ICP-MS
108	Np239	sediments	2-10g dry	d. AR			uses [33]					ICP-MS
109	Np-239	water, sediment, biota	25-100L	Water: Na sulphite + 0.1M HCl (RA). Sed & biota: L. HNO_3.	Water: PPT: $Fe(OH)_3$ pH 9. RA: Nd & hydrazine nitrate. PPT: NdF_3, PPT: NdOH	SEx: 0.5M 2-thenoyltrifluoroacetone in xylene. BEx: 8M HNO_3	An Ex: HNO_3, wash: 8M HNO_3, 12M HCl, 12M HCl-0.1M NH_4I, Elute: 4M HCl	EDP: KSO_4 & NH_4COOH	50-80%			α spec

No. *	Tracer	Sample type	mass	Sample preparation	Pre-concentration	Separation	Purification	Source preparation	Typical recoveries	LoD	Other nuclides	Measurement
110		nuclear fuel sample			on line. RA: Mohrs salt	UTEVA stationary phase: eluent 2M HCl/0.02-0.1M Oxalic acid				pg/g	^{243}Am, ^{232}Th, ^{239}Pu, ^{238}U	IC-ICP-MS
111	Np-239											α spec
112		bentonite clay samples		L. 20mM $KBrO_3$ in 1M HNO_3		Ex: 1M HDEHP/solvent 70 (x 3). BEx: 5M HNO_3, BEx: 0.2M $NH_2OH.HNO_3$ (Np)			82 ± 3%	10µBq	^{239}Pu, ^{241}Am, ^{244}Cm,	ICP-MS
113		bentonite clay samples		L: 1M HNO_3 + 20mM K bromate		Ex: 1M HDEHP/solvent 70 (x 2). BEx: 5M HNO_3, BEx: 0.2M $NH_2OH.HNO_3$				82%	^{239}Pu, ^{241}Am, ^{244}Cm, ^{90}Sr, ^{154}Eu,	ICP-MS
114	Np-235	air, total deposition sediment samples				An Ex: 9M HCl, wash: 9M HCl, 7M HNO_3, SEx: Di-isopropyl ether, wash: 7M HNO_3, 9M HCl, 9M HCl+0.1M NH_4I, 9M HCl..Elute: 1.2M HCl, combine with SEx	An Ex: repeat column. Elute: 4M HCl/conc H_2SO_4	EDP	78 ±11%	1mBq	Pu, Sr, U and Fe	α spec,
115	Pu-242	Environ-mental		L. c HNO_3/c. HCl (microwave) or d.c HNO_3	RA: ammonium Fe(II) sulphate + Na formaldehyde sulphoxylate		Online E.C: TRU. Inject 0.1M ammonium hydrogenoxalate, wash: 2M HNO_3. Elute: 0.1M ammonium hydrogenoxalate		93%	0.7 fg		SF-ICP-MS

No. *	**Tracer**	**Sample type**	**mass**	**Sample preparation**	**Pre-concentration**	**Separation**	**Purification**	**Source preparation**	**Typical recoveries**	**LoD**	**Other nuclides**	**Measurement**
116	Np-239	sediment		L. c HNO_3/c. HCl (microwave) or d.c HNO_3								SF-ICP-MS
117	Np-239	soil	2-5g	L: 1M HNO_3 + 20mM K bromate								ICP-MS
118		high active waste			RA: $Fe(NH_2SO_3)_2$ & N_2H_4-HNO_3	Ex: 0.5M TTA-xylene, wash: 1M HNO_3 + Fe^{2+}. Elute: 8M HNO_3		95 ± 3%		Pu & Am	LSC	

* denotes reference number as cited in Chapter 2
Ex: extraction
SolEx: Solvent extraction
Bex: Back extraction
RA: Reducing Agent
OA: Oxidising Agent
AR: *aqua regia*
D.: Digestion
L: Leach
PPT: Precipitation
RA: reducing agent
An Ex: Anion Exchange
IC: Ion Chromatography
EDP: Electrodeposition plating
Evap: Evaporate
ICP-MS: Inductively Coupled Plasma- Mass Spectrometry
SI: Sequential Injection
SF-ICP-MS: Sector Field ICP-MS
HR-ICP-MS: High resolution ICP-MS
AMS: Accelerator Mass Spectrometry
TIMS: Thermal Ionisation MS
dc-GCMS: dc Glow Discharge Mass Spectrometry
DF: Double focusing ICP-MS
LA ICP-MS: Laser Ablation ICP-MS
LSC: Liquid Scintillation counting
PEARLS: Alpha LSC
NAA: Neutron Activation Analysis

Appendix B

B.1 Background to Instrumentation

The thesis discusses a number of techniques used to measure ^{237}Np. For background information each technique that is used routinely by laboratories is discussed below:

B.2 Alpha spectroscopy

Alpha spectrometry is traditionally used to determine ^{237}Np post separation and purification. This is a destructive technique which requires source preparation and dependant on the limit of detection required count times can range from several hours to several days. Due to overlapping alpha energies of radionuclides causing spectral interferences simultaneous analysis is often not possible and therefore chemical separation is required.

The technique is based on the emission of alpha particles in the decay process which are used to identify and quantify radionuclides using silicon surface barrier detectors or ion-implanted silicon detectors. The detectors cover an energy range of 2.5-8 MeV usually which is suitable for the measurement of most alpha emitters including ^{237}Np. Samples are usually electrodeposited onto a planchett to produce a plated source which is placed at a known but limited distance below the detectors within a vacuum chamber. The vacuum ensures alpha particles can reach the detector as easily attenuated by air. When an alpha particle strikes the silicon detector a charge pulse is produced which is proportional to the energy of the incident alpha particle. This pulse is converted to a voltage and amplified by a preamplifier before being fed into a pulse height analyser (PHA). The PHA allows the number of pulses whose peak lie within a certain voltage range to be measured. The range of voltages measured is determined by the “window” setting expressed as fixed voltage. Software controls the electronics and analyses spectra producing an energy spectra of the sample counted. Energy calibration of the alpha spectrometry is carried out using multi-nuclide sources to determine the resolution and counting efficiency. Most determinations are carried out in the presence of a yield tracer to enable the absolute counting efficiency to be determined.

B.3 Gamma spectrometry

Gamma ray spectrometry is a technique used to identify and quantify gamma emitting isotopes in a variety of matrices. Unlike alpha spectrometry, gamma spectrometry is a non-destructive technique which requires little sample preparation which can detect several radionuclides simultaneously. Count times ranging from minutes to days dependant on the limit of detection required and activity of the sample.

The radioactive source or sample produce gamma rays, which are of various energies and intensities. The emissions are detected and analysed producing a gamma-ray energy spectrum which is characteristic of the gamma-emitting nuclides contained in the source. Samples are placed on or in a detectors which is a passive material such as high purity germanium or sodium iodide where gamma interactions occur. These interactions include photoelectric effect, the Compton effect, and pair production. The voltage pulse produced by the detector is shaped by a multichannel analyzer (MCA) which reshapes it into a distribution and converts it into a digital signal. The analog-to-digital converter (ADC) classes the pulses by their height and represent the channels in the spectrum. The output is then analysed using tools such as energy calibration, peak area and net area calculation, and resolution calculation to produce an energy spectra of the sample analysed. The energy and efficiency of the detectors is determined by analysis of multi radionuclide sources which cover a wide energy range (usually 59.5keV to 2000keV) enabling identification and quantification of the radionuclide composition.

B.4 Mass spectroscopy

ICP-MS is a relatively new technique, first developed in the early 1980's which has developed extensively over the last thirty years. Initially the technique was used for the determination of elements in particular rare earth elements (REE's) and subsequently developed to analyse long lived radionuclides with a significant half-life. Like alpha spectrometry the technique is destructive and requires source preparation though less extensive with decreased measurement times of several minutes. Because of the greater sample throughput benefit this technique was extensively utilised for the analysis of ^{237}Np and a range of stable elements in this PhD study and included measurement using a conventional ICP-MS (Perkin Elmer Elan-DRcE) and Agilent Triple Quad.

Both ICP-MS and the Triple Quad require the sample to be in low concentration nitric acid (usually 1%-2%) with a total dissolved solid content less than 0.1% and up to 2% respectively. Generally samples are evaporated to incipit dryness and then acidified with nitric acid, usually high purity, and re-evaporated. The samples are then made to a known volume in weak nitric acid and a known internal reference added to enable instrument stability to be assessed.

B.5 ICP-MS

ICP-MS couples a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer which enables the conversion of the atoms of the elements in the sample to ions which are then separated and detected.

Within the ICP a carrier gas is used, usually argon, which flows inside the torch. As power is applied to the load coil via a generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark to the argon electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma. The sample is introduced into the ICP plasma as an aerosol by aspirating into a nebulizer and is completely desolvated by the torch. The elements are converted first into gaseous atoms and then ionized towards the end of the plasma. Once converted to ions they are transmitted into the low pressure region mass spectrometer via the interface cones (sampler and the skimmer). These cones are metal disks with a small hole (~1mm) in the centre which focuses the ion beam coming from the ICP torch. The ions from the ICP source are then focused by the electrostatic lenses into the entrance aperture of the mass spectrometer. The ions enter the mass spectrometer and are separated by their mass-to-charge ratio. The quadrupole mass spectrometers have four rods with alternating AC and DC voltages applied to opposite pairs of the rods. These voltages are then rapidly switched along with an RF-field. The result is that an electrostatic filter is established that only allows ions of a single mass-to-charge ratio (m/e) pass through the rods to the detector at a given instant in time acting as a sequential filter.

B.5.1 Triple Quad

The Agilent Triple Quadrupole ICP-MS (ICP-QQQ) is a recent development and has been used in this study for the determination of ^{237}Np in the sediment core samples. The technique has the ability to remove interferences increasing the accuracy and precision achieved. The ICP-QQQ has two quadrupoles, one before and one after the Collision or Reaction Cell (DRC). The first acts as a mass filter, so it rejects all masses except the target analyte and any on-mass interferences. The ion beam that enters the DRC is simpler in composition. The DRC then enables the reaction of the ions with a carrier gas with interferences reacting to form product ions which allow for separation form the detrminand. The second quadrupole, set to original analyte mass, rejects any off-mass product ion(s) reducing the impact of interferences.

Appendix C

C.1 Activities present in Ravenglass saltmarsh surface scrape samples from 1980

Grid position	Am-241	Cs-137	Pu alpha	Ru-106	Np-237
A1	6253	18389		8140	
A2	8325	21386	1629	20979	15.22
A3	8214	19129		17094	10.98
A4	7215	19092	16220	14615	
A5	7141	29230		19684	7.57
A6	6438	27084	15280	27380	
A7	6031	19166		26529	
A8	4921	16169	14760	28934	
A9	4884	17612		27121	6.83
A10	5069	16391	14290	25012	8.25
A11				25752	
V0	8251	19203			
V1	5365	13653	10310	17797	
V2	7178	19425		16835	
V3	3233	9398	4629	20535	8.2
V4	10582	28601		6919	
V5	6882	23014	16310	18204	
V6	6882	25567		27306	
V7	2594	5957	7644	20572	
V8	5032	12506		8288	
V9	4810	14208	14140	19499	
V10				21867	
B0	4625	12321	13990	3367	
B1	6845	16280		15207	
B2	6438	18241	18070	20683	
B3	7178	17723		19462	8.88
B4	7622	22422	20040	23384	
B5	6660	23088		20646	11.27
B6	8510	21312	19620	24938	
B7	8473	18315		22977	
B8	5698	16650	15850	17908	
B9	4329	15170		26122	7.16
B10				22829	
W0	6734	18241		26381	
W1	7030	18093	17420	24420	
W2	7030	15318		18870	
W3	4144	13727	15620	12432	
W4	7141	21349		16946	
W5	7955	21386	14540	21608	
W6	5402	15540		20609	
W7	5217	15244	11040	20646	

Grid position	Am-241	Cs-137	Pu alpha	Ru-106	Np-237
W8	4921	15244		24383	
W9				22126	
C0	2031	7289	4747	21164	11.06
C1	6882	16576		5365	2.65
C2	3286	10990	9102	17020	
C3	6623	22530		12173	4.69
C4	5513	16540	18860	27824	9.93
C5	6142	17950		20313	11.51
C6	1602	6770	4359	19166	
C7	4625	13650		6105	2.42
C8				19462	
X0	6031	18460		16576	
X1	4810	14320	13390	21645	
X2	6179	20310		19129	
X3	6586	20050	15370	23939	
X4	6290	24310		25123	
X5	11430	21980	16870	19055	
X6	4255	12210		12432	
X7	4329	14730	13270	17316	
X8				24568	
D0	6623	21790	17030	12358	8.53
D1	3996	12990		24235	12.2
D2	2560	7470	6542	15910	
D3	6475	21680		8621	5.53
D4	5402	18390	17980	26048	
D5	4699	14580		19943	15.6
D6	3330	11100	11250	17797	
D7	3774	12690		16095	8.81
D8				21904	
Y0	3434	14210		29341	
Y1	6623	21240	14380	10175	
Y2	5069	15690		26381	
Y3	8066	23130	15540	21053	
Y4	6623	19240		26788	
Y5	3149	11990	5147	18574	
Y6	3027	10400		11618	5.17
Y7				15799	
E0	5735	18320	16110	9546	7.97
E1	6290	19200		22163	16.9
E2	2379	5660	5287	25456	
E3	5920	23870		7511	
E4	5846	18720	17150	21941	
E5	1887	7330		23236	
E6	2893	9250	8281	8251	
E7				13209	
Z1	7289	20170	17750	22052	
Z2	6253	23720		22570	
Z3	6808	21020	16440	25382	
Z4	3278	13170		28157	

Grid position	Am-241	Cs-137	Pu alpha	Ru-106	Np-237
Z5	2945	7252	5742	19092	
Z6	1310	4514		11137	
Z7				5772	
F1	6401	17800		21645	13.3
F2	5883	18280	19580	22903	12.6
F3	5032	16060		21497	1.24
F4	3263	10770	5664	20276	
F5	1299	3700		15096	
F6	603	1706	2749	5328	
F7				1616.9	

C.2 Activities present in Ravenglass saltmarsh surface scrape samples from 1992

Grid position	Am241	Cs-137	Pu alpha	Ru-106	Np-237
A1	4679	3475	1908	280	3879
A2	3879	4181	909	404	3741
A3	3741	4022	1965	372	
A4	4642	5333	2577	414	
A5	3326	2174	1768	378	4642
A6	3247	2757	1834	587	
A7	2551	1518	1358	463	
A8	2202	1319	1082	777	
A9	2287	1301	1256	1048	3326
A10	1419	850	611	1044	4679
A11				896	
V0	4178	5300	2302	110.2	
V1	2570	1630	1323	364	
V2	3296	2412	1832	475	
V3	2441	1894	1319	517	
V4	3606	2793	1985	489	
V5	3444	3404	1951	587	
V6	3775	3052	2394	527	
V7	1333	685	846	430	
V8	2427	1573	1315	432	
V9	2499	1524	1349	1045	
V10				948	
B0	2352	1705	1405	228	
B1	3551	2535	1739	371	
B2	4513	4443	2616	461	
B3	3886	4139	2173	465.3	
B4	3613	2656	1691	415.4	
B5	3378	3212	1892	577.6	3247
B6	2962	2512	1618	437.8	
B7	2619	1340	1246	483.7	
B8	2202	1336	1251	971	
B9				715	2551
B10					
W0	2606	1718	1448	234	
W1	3514	2880	1858	480	
W2	2995	1971	1677	573	
W3	3209	2501	1849	424	
W4	3154	2381	1660	585	
W5	3519	3879	2240	658	
W6	2467	1658	1577	458	
W7	2296	1657	1108	611	
W8	2084	1314	1020	719	
W9				558	
C0	1617	1054	986	508	2202
C1	3338	3238	1786	406	2287
C2	1956	1274	1148	337	
C3	2835	1801	1340	405	
C4	3360	2701	1840	729	1419

Grid position	Am241	Cs-137	Pu alpha	Ru-106	Np-237
C5	2969	2416	1573	429	
C6	1094	813	685	394	
C7	2110	1198	1196	336	
C8				928	
X0	3112	2373	1775	418	
X1	1923	1287	1057	408	
X2	2932	2492	1529	490	
X3	2446	1859	1486	394	
X4	2942	2369	1781	528	
X5	2918	3119	2049	399	
X6	1360	789	856	366	
X7				555	
X8				453	
D0	3071	2107	1642	490	4178
D1	2400	1382	1882	903	2570
D2	1508	900	903	490	
D3	2997	2640	1900	454	
D4	3207	3371	1882	353	
D5	2553	2170	1530	420	3296
D6	2083	1234	1117	821	
D7					
D8					
Y0	3000	2152	1602	211	
Y1	2545	1793	1398	668	
Y2	2019	1318	1056	537	
Y3	3134	2350	1980	527	
Y4	2749	2213	1516	496	
Y5	1024	701	3491	439	
Y6	1192	720	2394	277	
Y7				533	
E0	3006	1917	1616		2441
E1	2478	1711	1392	570	3606
E2	1922	1286	1042	507	
E3	2475	2594	1796	463	
E4	2425	1821	1218	408	
E5	1021	621	924	363	3444
E6	1200	755	840	307	
E7				356	
Z1	2881	1782	1547	456	
Z2	2668	1857	1609	656	
Z3	1984	1482	1346	632	
Z4	2144	1152	1539	435	
Z5	1150	608	1379	284	
Z6	844	432	663	393	
Z7				250	
F1	2998	2067	1697	463	3775
F2	2823	2663	1662	524	1333
F3	2264	1789	1231	524	
F4	1453	907	857	567	
F5	885	487	676	463	2427
F6	963	501	519	201	
F7				401	

C.3 Activities present in Ravenglass saltmarsh surface scrape samples from 1997

Grid position	Am-241	Cs-137	Pu alpha
A1	1988	1673	1408
A2	1777	1154	1379
A3	1969	1506	1495
A4	1944	1407	1517
A5	1550	997	1271
A6	1256	931	1405
A7	1595	1117	1262
A8	1477	948	1246
A9	1265	877	997
A10	1167	749	971
A11	1168	742	968
V1	1683	1106	1272
V2	1536	996	1238
V3	1754	1225	1464
V4	1871	1316	1393
V5	1712	1178	1243
V6	1621	1144	1236
V7	1611	1201	1353
V8	1422	876	1476
V9	1280	852	1132
V10	1241	771	1077
B0	2975	3636	2438
B1	1170	900	961
B2	1859	1155	1453
B3	1763	1222	1459
B4	1947	1590	412
B5	1528	1024	1187
B6	1388	958	1214
B7	1460	941	1066
B8	1172	761	903
B9	1050	693	977
B10	1466	873	
W0	1737	1684	1270
W1	1270	854	989
W2	1698	1121	1294
W3	1471	963	1204
W4	1607	1065	1311
W5	1695	1067	1138
W6	1254	819	1075
W7	1225	765	1050
W8	1300	818	972
W9	1057	653	1011
C0	1772	1320	1329
C1	1338	854	1066

C2	1715	1027	1336
C3	1178	777	925
C4	1549	957	1238
C5	1364	989	1061
C6	1281	814	1030
C7	1172	791	921
C8	1288	773	1017
X0	1883	1221	1556
X1	1494	1444	1027
X2	1083	656	1018
X3	1524	1253	1214
X4	1461	1093	1332
X5	1540	1057	1146
X6	1219	973	966
X7	897	561	782
D0	1785	1360	1325
D1	1484	973	1304
D2	1197	735	1058
D3	1232	795	1095
D4	1709	1229	1458
D5	1382	1020	1162
D6	1073	711	864
D7	875	554	703
Y0	1617	1155	1360
Y1	1536	1000	1477
Y2	1396	997	1115
Y3	1137	753	933
Y4	1669	1218	1389
Y5	1332	841	1160
Y6	1029	667	844
E0	3958	5480	3170
E1	1339	471	1103
E2	1324	872	1087
E3	978	956	1086
E4	1636	1399	1540
E5	1162	782	846
E6	2534	2538	2904
Z1	1561	1047	1208
Z2	1675	1061	1359
Z3	1372	1024	1053
Z4	1213	872	1947
Z5	1060	710	888
Z6	1003	660	866
F1	1661		1372
F2	1521	1178	1091
F3	1643	1015	1444
F4	1433	1366	1214
F5	807	1036	690
F6	3943	575	4297
F7		333	

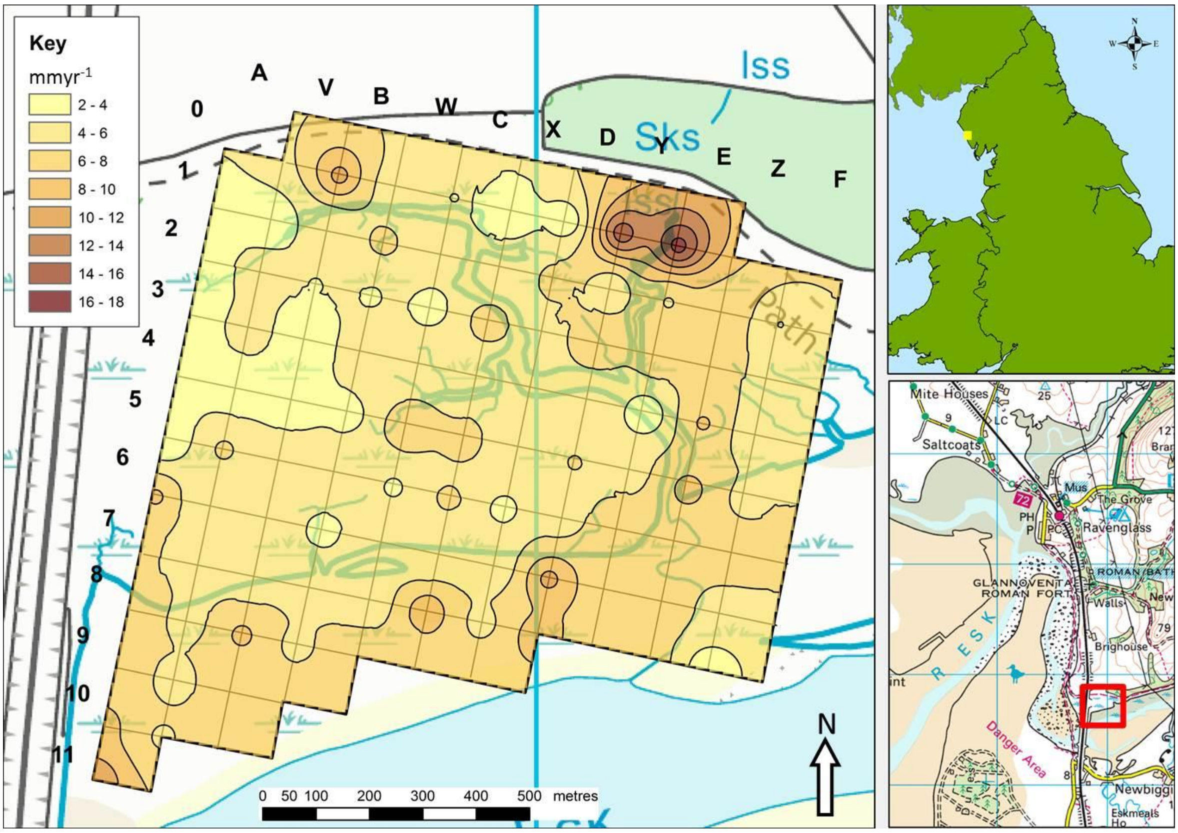
C.4 Activities present in Ravenglass saltmarsh surface scrape samples from 2005

Grid position	Am-241	Cs-137	Pu alpha	Ru-106	Np-237
A1	1394	714	919	114.5	1.22
A2					
A3	1522	547	958	72.83	1.06
A4					
A5	1533	842	1014	105.4	1.21
A6					
A7	1879	706	569	126.6	1.38
A8					
A9	964	436	896	122.2	1.31
A10					
A11					
V1					
V2					
V3					
V4					
V5					
V6					
V7					
V8					
V9					
V10					
B0					
B1	1202	505	898	115.1	1
B2					
B3	1712	851	987	109	1.33
B4					
B5	4635	2088	2095	60.9	
B6					
B7	1539	496	735	104	0.78
B8					
B9	1246	535	700	119.8	1.18
B10					
W0					
W1					
W2					
W3					
W4					
W5					
W6					
W7					
W8					
W9					
C0					
C1	1129	602	783	52.11	1.66
C2					
C3	1660	478	1064	62.71	0.98

Grid position	Am-241	Cs-137	Pu alpha	Ru-106	Np-237
C4					
C5	3069	1447	1830	50.86	2.23
C6					
C7	842	395	494	47.52	
C8					
X0					
X1					
X2					
X3					
X4					
X5					
X6					
X7					
D0	2117	809	969	117	1.19
D1	1045	365	656	79.51	2.06
D2					
D3	1585	581	847	82.77	1.13
D4					
D5	2091	692	882	85.41	
D6					
D7	1349	497	787	108.4	1.11
Y0					
Y1					
Y2					
Y3					
Y4					
Y5					
Y6	790	368	699	34.23	0.703
E0	1297	639	842	22.44	1.27
E1	1108	627	701	91.98	1.23
E2					
E3					
E4					
E5	1901	650	840	103.9	0.94
E6					
Z1					
Z2					
Z3					
Z4					
Z5					
Z6					
F1	1372		693	130.2	0.94
F2		552			
F3	1256		806	86.01	1.06
F4		498			
F5	1828		838	101.7	5.03
F6		606			
F7					

Appendix D

D.1 Spatial distribution of sedimentation rates across the Ravenglass saltmarsh



Appendix E

E.1 ^{237}Np activities in Ravenglass sediment core R-96-007

Sample ID	Distance from top, mid section (cm)	Np-237 activity (Bq/kg)
RC7-01	0.5	6.42 ± 0.88
RC7-02	1.5	3.61 ± 0.35
RC7-03	2.5	6.15 ± 0.91
RC7-04	3.5	7.94 ± 0.77
RC7-05	4.5	N/A
RC7-06	5.5	7.26 ± 0.62
RC7-07	6.5	5.82 ± 0.56
RC7-08	7.5	3.51 ± 0.53
RC7-09	8.5	3.89 ± 0.89
RC7-10	9.5	4.26 ± 0.29
RC7-11	10.5	4.25 ± 0.81
RC7-12	11.5	7.46 ± 0.77
RC7-13	12.5	N/A
RC7-14	13.5	8.51 ± 0.55
RC7-15	14.5	5.45 ± 0.89
RC7-16	15.5	4.9 ± 0.48
RC7-17	16.5	4.7 ± 0.52
RC7-18	17.5	3.31 ± 1.21
RC7-19	18.5	N/A
RC7-20	19.5	3.35 ± 1.1
RC7-21	20.5	N/A
RC7-22	21.5	1.39 ± 0.28
RC7-23	22.5	<0.64
RC7-24	23.5	<0.48
RC7-25	24.5	<0.52
RC7-26	25.5	<0.49
RC7-27	26.5	<0.54
RC7-28	27.5	<0.49
RC7-29	28.5	<0.50
RC7-30	29.5	<0.56
RC7-31	30.5	<0.48
RC7-32	31.5	<0.57
RC7-33	32.5	<0.53
RC7-34	33.5	<0.47
RC7-35	34.5	<0.49
RC7-36	35.5	<0.48

Sample ID	Distance from top, mid section (cm)	Np-237 activity (Bq/kg)
RC7-37	36.5	<0.50
RC7-38	37.5	<0.48
RC7-39	38.5	<0.49
RC7-40	39.5	<0.47
RC7-41	40.5	<0.49
RC7-42	41.5	<0.48
RC7-43	42.5	<0.55
RC7-44	43.5	<0.48
RC7-45	44.5	<0.49
RC7-46	45.5	<0.49
RC7-47	46.5	<0.48
RC7-48	47.5	<0.53
RC7-49	48.5	<0.50