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# The effect of sea level rise on radionuclide mobility at contaminated nuclear sites

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**The effect of sea level rise on radionuclide  
mobility at contaminated nuclear sites**

by

**Jane Eagling**

A thesis submitted to the University of Plymouth in partial fulfilment for  
the degree of

**DOCTOR OF PHILOSOPHY**

School of Geography, Earth and Environmental Sciences Faculty of  
Science and Technology

April 2012

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# **The effect of sea level rise on radionuclide mobility at contaminated nuclear sites**

*Jane Eagling*

Global sea levels are expected to rise as a result of climate change, which will lead to the inundation and erosion of low lying coastal areas and accelerate the intrusion of seawater into sub-surface sediments. Many of the UK's legacy nuclear facilities are located in close proximity to the shore, raising questions regarding the potential mobilisation of radionuclides during sea level rise. Here batch and column experiments were used to simulate and investigate the effect of these processes on the mobilisation of key radionuclides Tc,  $^{90}\text{Sr}$  and U from oxic and reduced sediments under sea level rise scenarios.

Strontium-90 was rapidly mobilised from exchangeable surface sites from oxic sediments during inundation and erosion scenarios with seawater ( $\approx 60\%$ ). Strontium release was driven by ion exchange between  $\text{Sr}^{90}$  and  $\text{Mg}^{2+}$  cations present in high concentrations in seawater.

Uranium release from oxic and reduced sediments was kinetically controlled, characterised by slow release from a range of binding sites, promoted by the formation of U-carbonate complexes. Uranium mobilisation was slower from reduced sediments compared with oxic sediments under seawater flow conditions; therefore reduced sediments would act as a longer term source of U to marine environments. Release was more extensive from initially nitrate reducing sediments (53%) compared with extensively iron reducing sediments (38%), with the difference in release explained by the longer contact period of U(VI) with the iron reducing sediment relative to the nitrate reducing sediment which would lead to slower desorption. Additionally, U(IV) species would be released more slowly than U(VI) species sorbed to the sediments.

The release of Tc was dependent on sediment re-oxidation coupled with the oxidation of Tc(IV) to Tc(VII). Batch experiments showed that only a small proportion of Tc was rapidly (within 5 days) released from the sediments into seawater and groundwater which suggests that the majority of any Tc(IV) contamination will be released slowly as the seawater plume migrates through the sediments. Technetium release was slowest, and ultimately limited to the greatest extent (17%), in initially Fe-reducing sediments, when they were re-oxidised in seawater. Thus the cycling of iron and the impact of the water chemistry on iron mineralogy were important for hindering Tc release. Column experiments showed that iron minerals were less effective at retarding Tc release under flow-through conditions. Kinetically controlled and solubility limited Fe dissolution led to on-going Tc release from the sediments, i.e. the retarding effect of iron phases was temporary and significantly more Tc was mobilised (79-93%) compared with the batch experiments (17-45%).

This study has shown for the first time that radionuclides will be released from reduced and oxic sediments as a result of future sea level rise. Contaminated sediments have the potential to act as a secondary source of radionuclide contamination entering the marine environment from coastal nuclear sites. This information is essential when siting new nuclear facilities and when developing effective remediation, decommissioning and management strategies for legacy coastal sites.

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# **Chapter 1**

## **Introduction**

## **1.1 Nuclear waste and contaminated land**

There are strict regulatory policies for the management of radioactive waste, with international standards, guidelines and recommendations from, e.g., the International Atomic Energy Agency. However, during the early development of military and civil applications of nuclear power, statutory regulations were weaker and poor working practices resulted in the contamination of many sites. Controlled discharges and accidental leaks from plant buildings, waste storage vaults, underground tanks and shallow unlined burial trenches released radionuclides into the environment (Pace *et al.* 2007; Hartman *et al.* 2009). Their subsequent migration through the surrounding environment has resulted in a significant legacy of groundwaters, soils and sediments contaminated with complex mixtures of radionuclides (Riley and Zachara 1992). An important example is the USA where Department of Energy (DoE) sites contain 40 million cubic meters of contaminated soil and debris and 1.7 trillion gallons of contaminated groundwater (Palmisano and Hazen 2003). A summary of the soil and water contamination issues at key nuclear facilities in the UK, USA and Russia is presented in Table 1.1. The long term management or remediation of these sites represents one of the greatest challenges confronting the nuclear industry (Riley and Zachara 1992).

## **1.2 The UK's nuclear legacy**

Although there are a number of sites in the UK where nuclear operations have occurred, the most notable examples with the greatest legacy of waste are Sellafield and Dounreay.

**Table 1.1: Summary of key worldwide nuclear facilities and associated contamination issues adapted from (Kimber *et al.* 2011)**

Site	Former uses	Current use	Soil contamination	Groundwater contamination	Sources
Sellafield (UK)	WW2 explosives production site. Post war; fuel reprocessing & manufacturing, nuclear waste management, nuclear energy generation	Reprocessing, fuel production, waste management & decommissioning	$\approx 1600 \text{ m}^3$ contaminated with radioactive waste; to be treated as ILW $\approx 1 \times 10^6 \text{ m}^3$ to be treated as LLW	Monitoring results from 2009 groundwater plumes contain $^{90}\text{Sr}$ , $^{137}\text{Cs}$ , $^3\text{H}$ & $^{99}\text{Tc}$ Total $\beta$ activity > WHO safe drinking water limit ( $1 \text{ Bq L}^{-1}$ ) with highest annual average of $1.29 \times 10^5 \text{ Bq L}^{-1}$ .	(Hunter 2004; NDA 2010)
Dounreay (UK)	RAF site converted to experimental facility to explore the feasibility of fast reactors	All reactors closed down, site undergoing decommissioning (closure expected 2032)	Irradiated fuel particles (on local beaches) Sediments: $^{137}\text{Cs}$ , $^{90}\text{Sr}$ and $^{241}\text{Pu}$ at activity concentrations of up to 5.4, 2.1 and 2.3 ( $\times 10^5 \text{ Bq kg}^{-1}$ ) respectively	Groundwater monitoring detected $^3\text{H}$ , $^{90}\text{Sr}$ , $^{234}\text{U}$ , $^{238}\text{U}$ & $^{137}\text{Cs}$	(Atherton 2004)
Mayak (Russia)	Nuclear weapons production, reprocessing nuclear material	Fuel reprocessing, decommissioning	HLW tank exploded in 1957 750 PBq released, 90 % of this deposited in the immediate vicinity	Open reservoirs on the site contain $3. \times 10^8 \text{ m}^3$ of contaminated water. In 1993 there were $70 \text{ MBq L}^{-1}$ $^{90}\text{Sr}$ and $100 \text{ MBq L}^{-1}$ $^{137}\text{Cs}$ in reservoir R9 ( $\times 35000 \text{ m}^3$ ). Groundwater pollution plume from R9 covers $10 \text{ km}^2$ , spreading at $80 - 100 \text{ m y}^{-1}$ .	(Siegel and Bryan 2003; Standing <i>et al.</i> 2009)
Hanford (USA)	Pu production, nuclear reactors	Undergoing decommissioning and clean-up	Storage tanks leaked HLW into sediments beneath them. Pu in silt layers up to $9.25 \times 10^6 \text{ Bq kg}^{-1}$ , $^{137}\text{Cs}$ up to $10^8 \text{ Bq kg}^{-1}$ Contaminated area $\approx 183 \text{ km}^2$	Tc, U, Pu, $^{60}\text{Co}$ and $^{137}\text{Cs}$ U (in aquifer) range 0.4 to $1.4 \mu\text{M}$	(Pace <i>et al.</i> 2007; Hartman <i>et al.</i> 2009)

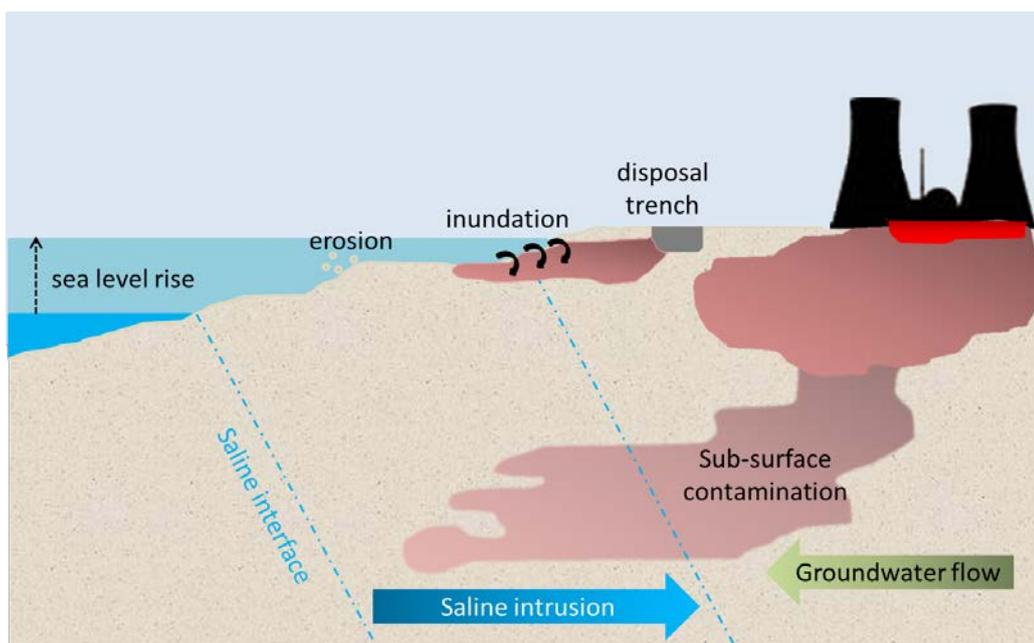
**Sellafield:** Britain's first nuclear reactor and reprocessing plant was launched in 1947 at what is now Sellafield (Cumbria). Current activities are focused on the reprocessing of spent nuclear fuel, fuel manufacture, site decommissioning and clean-up (McKenzie and Armstrong-Pope 2010). A number of historical disposals and leaks of radioactive fluids from buildings, vaults and disposal trenches have resulted in 13 million m<sup>3</sup> of radioactively contaminated material, which is classified as Very Low Level Waste (VLLW) or Low Level Waste (LLW), which remains on the site. However, in the Separation Area where the reactors were historically sited and in the vicinity of the landfills near the southern boundary of the site, a portion of the contamination (1600 m<sup>3</sup>) is classified as Intermediate Level Waste (ILW) (NDA 2010; Kimber *et al.* 2011). The contamination extends downwards to a maximum depth of 55 m and includes soil and shallow subsurface geological material (McKenzie and Armstrong-Pope 2010). The underlying groundwater has therefore been found to be contaminated with <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>3</sup>H, U and <sup>99</sup>Tc, and actinide contamination is also expected (Hunter 2004; Reeve and Eilbeck 2007 ; McKenzie and McCord 2010). The contaminated groundwater discharges into the local marine environment (McKenzie and Armstrong-Pope 2010).

**Dounreay:** Dounreay was built in 1955 and operated as an experimental facility for reprocessing and fuel fabrication in UK's former fast reactor programme. Operations ended in 1996 and 2004, respectively and the site is currently being decommissioned. A 65 m vertical shaft was sunk at Dounreay and was routinely used for the disposal of ILW up to 1970. This was thought to contain approximately 703 m<sup>3</sup> of waste which included contaminated equipment, chemicals, natural uranium fuel, radioactive sources and sludges (Atherton 2004). Operations have begun to isolate the shaft from surrounding groundwaters; however the ground and groundwater have already been contaminated by an explosion in the shaft and leaks from a buried silo (Atherton 2004). High activities of contamination including <sup>90</sup>Sr, <sup>137</sup>Cs & <sup>248/249</sup>Pu have been detected

near the shaft (Table 1.1) and are associated with clays and mica in the rock matrix and iron oxyhydroxides. Groundwater monitoring has identified that tritium,  $^{90}\text{Sr}$ ,  $^{234}\text{U}$ ,  $^{238}\text{U}$  and  $^{137}\text{Cs}$  are the predominant mobile contaminants (Atherton 2004; UKAEA 2005; Savage *et al.* 2009).

### 1.3 Climate change and projected sea level rise

The evidence for climate change is compelling (IPCC 2007) and sea level rise projections estimate a 1.5 – 2 m rise in sea level in the UK within the next 300 years (Nirex 2005), more recently Defra (2012) have estimated that sea levels may increase between 93-190 cm relative to 1990 more recent projections around the UK. There is therefore growing concern regarding the impact of sea level rise on coastal areas. An increase in sea level is expected to lead to the gradual inundation, flooding and erosion of low lying coastal areas, coupled with the intrusion of saltwater into coastal aquifers (Choudhury *et al.* 2001). Figure 1.1 outlines possible sea level rise scenarios for a coastal nuclear facility.



**Figure 1.1: Schematic diagram outlining the possible impacts of sea level rise.**

- **Inundation:** As sea levels rise, mean high tides are expected to gradually migrate landward, leading to the eventual submergence of land. Over time, sea water will engulf areas progressively further inland.
- **Temporary flooding:** As a consequence of rising global temperatures there will be an increase in both the frequency and intensity of storm and tidal surge events which may cause temporary flooding of coastal areas. UKCIP reports that a 1 in 50 year storm event could become a 1 in 3 year storm event by the end of the 21<sup>st</sup> century (Hulme *et al.* 2002).
- **Erosion:** Rising sea levels will lead to the erosion of low lying coastal areas. The most severe erosion is expected to take place during storm events as these generate waves with the highest energy. Increased erosion is expected if storms become more frequent and intense.
- **Intrusion:** Although coastal inundation and erosion of low lying coastal areas are the most obvious concerns from a rise in sea level, the intrusion of sea water into shallow coastal aquifers may also occur (Barth and Titus 1984; IPCC 2007). Elevated sodium concentrations measured during routine groundwater monitoring at Sellafield confirms that seawater is intruding into the site and both the rate and extent of intrusion is likely to increase as sea levels rise (McKenzie and Armstrong-Pope 2010; McKenzie and McCord 2010)

#### **1.4 Mobilisation with increasing salinity**

There is currently a lack of research into the potential mobilisation of radionuclides from terrestrial environments when transferred into a saltwater environment.

Intrusion, inundation and erosion with seawater will have a significant impact on the physico-chemical conditions in the sediments, which may promote or inhibit the mobilisation of sediment associated radionuclides. Results from laboratory and field

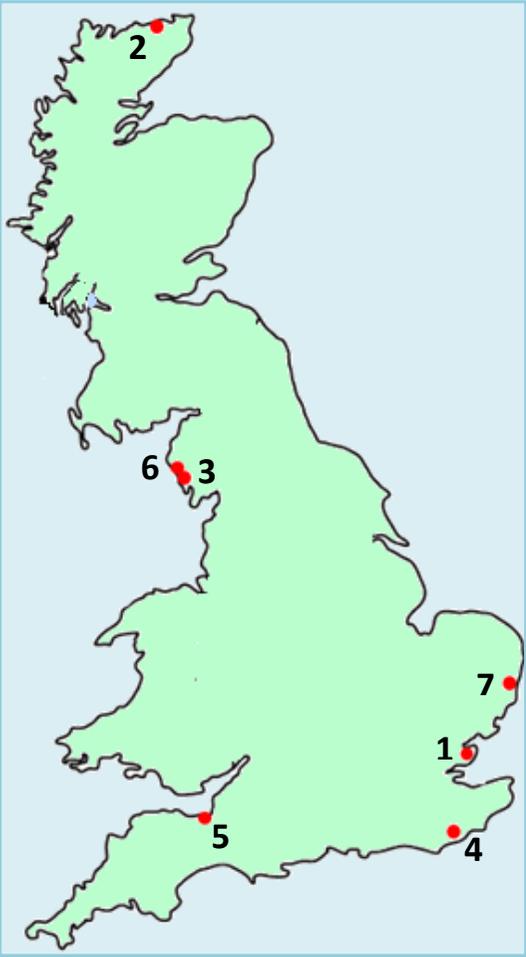
experiments indicate that higher salinity has the potential to promote metal mobility via complexation with seawater anions (including  $\text{CO}_3^{2-}$  and  $\text{Cl}^-$ ) and competition with seawater cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) for sorption sites (Paalman *et al.* 1994; Lores and Pennock 1998; Zheng and Wan 2005; Acosta *et al.* 2011) and promote dissolution-precipitation reactions. Additionally, the inflow of oxygenated seawater into subsurface environments may move sub-surface redox boundaries, enhancing or inhibiting the mobilisation of redox sensitive radionuclides through reoxidation.

The long term fate of contaminated sediments at nuclear sites is of concern, due to their potential to act as a future source of radionuclide contamination. Sea level rise processes may lead to the mobilisation of sediment associated radionuclides which may migrate into local marine environments.

### **1.5 Future vulnerability of the UK's nuclear legacy**

Due to the need for large volumes of water required for cooling purposes, the majority of the UK's nuclear power stations and reprocessing facilities are located on or close to the shoreline (Table 1.2). NIREX produced a report assessing the vulnerability of the UK's nuclear facilities to sea level rise and associated coastal processes, a summary of the results are outlined in Table 1.2.

**Table 1.2: The UK's radioactive waste store locations and their vulnerability to future climate change projections (Nirex 2005)**

	Site	Position on map	Elevation (m AOD)*	Distance from the coast (m)^	Future vulnerability	
					to 2020	to 2100
	<b>Bradwell</b>	1	0-2	500	unlikely	vulnerable to inundation
	<b>Dounreay</b>	2	9-15	50	unlikely	possible for the shaft
	<b>Drigg</b>	3	10-20	500	unlikely	vulnerable to erosion
	<b>Dungeness</b>	4	2-5	160	possible	very vulnerable to erosion
	<b>Hinkley Point</b>	5	10-14	75	unlikely	possible
	<b>Sellafield</b>	6	6-32	50	unlikely	vulnerable to erosion
	<b>Sizewell</b>	7	3-5	50	possible	vulnerable to erosion

\* AOD stands for Above Ordnance Datum where AOD approximates to present-day mean sea level. ^ The sites were located by their postcode, which will not be the exact location of the current radioactive waste stores. Distance from shore is therefore approximate.

Nirex have reported that some sites will be vulnerable to inundation; however the majority of sites are also vulnerable to rapid coastal erosion as a result of rising sea levels. Therefore, understanding the potential release of radionuclides during projected sea level rise processes is of great importance when planning the decommissioning and clean-up of contaminated nuclear sites, as well as for the operation of any coastal radioactive waste stores (Nirex 2005).

### **1.6 Radionuclides produced during nuclear fuel cycle operations**

During the use of nuclear fuel, new radioisotopes are produced through fission (the most abundant of which have atomic masses around 95 and 135) or neutron activation, i.e. when isotopes absorb neutrons. Since actinides are formed by neutron activation, both fission products and actinides are important components of waste (Table 1.3). Fission products with short half-lives, such as  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , pose a higher radiation exposure risk to environmental receptors over the short term. However longer lived fission products (such as  $^{99}\text{Tc}$  and  $^{129}\text{I}$ ) and actinides (including  $^{238}\text{U}$  and  $^{237}\text{Np}$ ) pose the greatest long-term storage and disposal challenges.

Three key radionuclides strontium ( $^{90}\text{Sr}$ ), uranium ( $^{238}\text{U}$ ) and technetium ( $^{99}\text{Tc}$ ) are significant components of radioactive waste (Table 1.3) and are common contaminants reported in groundwater, soils and sediments at nuclear sites in the UK (e.g. Dounreay and Sellafield) and US Department of Energy (DoE) facilities such as Hanford and Oak Ridge USA (Wu *et al.* 2006; Knox *et al.* 2008).

Technetium-99 and  $^{90}\text{Sr}$  are high yield fission products and U is a critical contaminant from the nuclear fuel cycle. For example at Drigg (low level waste repository, Cumbria) U is the most abundant radionuclide in the Drigg inventory and the most significant potential dose contributor (Wilkins *et al.* 2007).

**Table 1.3: Common radionuclides occurring in radioactive waste from the nuclear cycle**

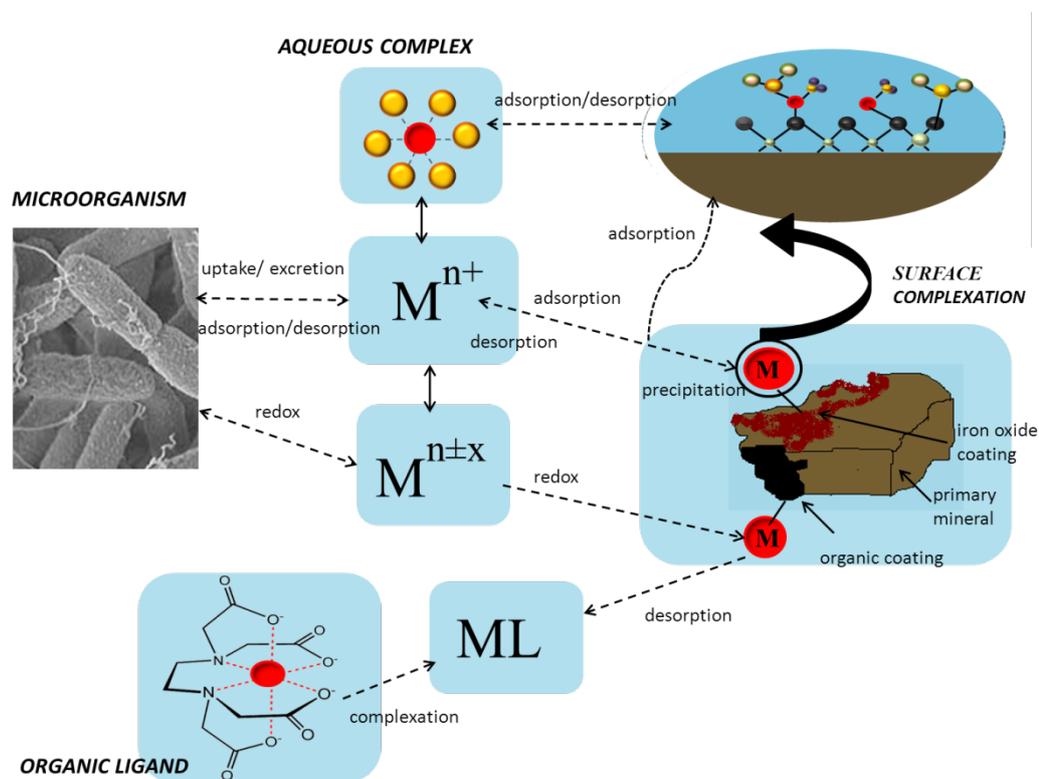
Radionuclide	Half-life (years)	Radiation emitted	% Yield	Energy (keV)	WHO drinking water limits <sup>#</sup> (Bq L <sup>-1</sup> )
<i>Fission products</i>					
<sup>90</sup> Sr	28.9	β	4.50	546	10
<sup>137</sup> Cs	30.23	β	6.34	546	10
<sup>135</sup> Cs	16 x 10 <sup>6</sup>	β	6.9	269	100
<sup>99</sup> Tc	2.1 x 10 <sup>5</sup>	β	6.14	249	100
<sup>129</sup> I	16 x 10 <sup>6</sup>	β	0.84	0.841	
<i>Actinides</i>					
<sup>238</sup> U <sup>^</sup>	4.47 x 10 <sup>9</sup>	α	99.3*		10
<sup>237</sup> Np	2.1 x 10 <sup>6</sup>	α			
<sup>239</sup> Pu	2.4x10 <sup>5</sup>	α			1
<sup>242</sup> Pu	3.8 x10 <sup>5</sup>	α			1

<sup>^</sup> <sup>238</sup>U is a common contaminant from the nuclear fuel cycle.\*The isotopic composition of natural uranium consists of <sup>238</sup>U-99.3 %, <sup>234</sup>U-0.00545 % & <sup>235</sup>U-0.720 % in equilibrium.<sup>#</sup> WHO World Health Organisation (see [http://www.who.int/water\\_sanitation\\_health/dwq/gdwq0506\\_9.pdf](http://www.who.int/water_sanitation_health/dwq/gdwq0506_9.pdf))

### 1.7 Sorption and solid phase associations of radionuclides

The ultimate fate and mobility of radionuclides within the environment is determined by their partitioning between the particulate and aqueous phases. Processes such as sorption and precipitation can lead to the accumulation of radionuclides in sediments. Sorption occurs as a function of mineralogy, particle size and the concentration and affinity of sorbing radionuclides for surface binding sites, including organic coatings, iron (oxy)-hydroxides and carbonates. Sorption is also controlled by the pH, ionic strength and the concentration of complexing agents in the solution phase. If radionuclides are redox sensitive (such as Tc and U) their partitioning will also depend

on the Eh of the system and the presence of materials that lead to reduction, such as organic matter and the presence of oxidants such as O<sub>2</sub>. Figure 1.2 outlines possible interactions between radionuclides and solid phases.



**Figure 1.2: Possible interactions between radionuclides and solid phases.** Adapted from [http://esd.lbl.gov/research/projects/ersp/generalinfo/molec\\_scale.html](http://esd.lbl.gov/research/projects/ersp/generalinfo/molec_scale.html)

**Strontium:** Strontium occurs in the +2 oxidation state and sorbs to soils and sediments through ion exchange reactions and this generally involves the formation of outer-sphere complexes and is reversible (Chen and Hayes 1999; McKinley *et al.* 2007). Studies have shown that the extent of <sup>90</sup>Sr sorption depends on particle characteristics, particularly mineralogical composition (Solecki 2005), including the presence of Fe, Mn and Al metal oxides (Trivedi and Axe 1999; Axe *et al.* 2000; Bellenger and Staunton 2008), clays (Chen and Hayes 1999), organic coatings and carbonates (Sheppard and Thibault 1990; Van Bergeijk *et al.* 1992; Agapkina *et al.* 1995; Zhao and

Chen 2006). Strontium retention in soils and sediments is therefore strongly influenced by pH and ionic strength (Twining *et al.* 2004; Hull and Schafer 2008).

**Uranium:** Uranium exists in two oxidation states in the natural environment, U(VI) and U(IV). Uranium (VI) is present as the uranyl ion,  $\text{UO}_2^{2+}$  and this sorbs reversibly to a variety of minerals (Bostick *et al.* 2002; Krupka and Serne 2002; Qafoku *et al.* 2005) including clays (Whicker *et al.* 2007; Rodriguez *et al.* 2008), iron(oxy)-hydroxides (Martinez *et al.* 1995; Gómez *et al.* 2006; Duquene *et al.* 2008; Sherman *et al.* 2008), aluminium oxides and silica oxides (Sylwester *et al.* 2000), and is retained by organic coatings and aggregates (Crancon and van der Lee 2001; Petrescu and Bilal 2007; Oliver *et al.* 2008). Adsorption of U(VI) is influenced by mineralogy and ionic strength and is pH dependent (Krupka and Serne 2002; Liu *et al.* 2009). In circumneutral to alkaline pH waters, U forms strong  $\text{UO}_2^{2+}$ -carbonate aqueous complexes (Zhou and Gu 2005; Choy *et al.* 2006), which are less likely to interact with negatively charged minerals and are therefore highly mobile. In natural waters, aqueous  $\text{UO}_2^{2+}$  also forms complexes with phosphate, silicate and dissolved organic matter (Lenhart *et al.* 2000; Bostick *et al.* 2002; Giammar and Hering 2004). However as conditions become increasingly reducing, the reduction of U(VI) to U(IV) by abiotic and biotic processes occurs. Uranium(IV) is relatively immobile due to the low solubility of  $\text{UO}_2$  and the high surface affinity of U(IV) ions (Langmuir 1978).

**Technetium:** In oxic environments, Tc is present as  $\text{Tc(VII)O}_4^-$  and interacts weakly with sediments and soils. However, under reducing conditions (Eh 200 - 100 mV at pH 7 (Lieser and Bauscher 1987; Icenhower *et al.* 2010)  $\text{TcO}_4^-$  is reduced to Tc(IV) and is retained in soils and sediments as hydrous  $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$  phases (Burke *et al.* 2004; Fredrickson *et al.* 2004; Maes *et al.* 2004; Wildung *et al.* 2004; McBeth *et al.* 2007; Morris *et al.* 2008) or by sorption to aluminium and iron oxides (Lloyd *et al.* 2000;

Wildung *et al.* 2000; Abdelouas *et al.* 2005) and organic matter (Tagami and Uchida 1996; Keith-Roach *et al.* 2003).

### **1.8 Potential mobilisation of radionuclides from sediments and soils**

Investigating the potential for radionuclide mobilisation under changing biogeochemical conditions is important for understanding radionuclide mobility in natural environments. Important solid phase associations and release mechanisms controlling the release of  $^{90}\text{Sr}$ , U and Tc are outlined in Table 1.4.

**Strontium:** Mobilisation of  $^{90}\text{Sr}$  from soils and sediments is generally controlled by cation exchange reactions and depends on sediment type (Standring *et al.* 2002). Release of  $^{90}\text{Sr}$  increases with increasing ionic strength, particularly the presence of dissolved  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$ , which can effectively compete for sorption sites (McKinley *et al.* 2007; Benkdad *et al.* 2008). Complexation with dissolved organic matter (Dupre *et al.* 1999) and low molecular weight humic acids (Tanaka *et al.* 1997) and association with colloids, such as silica and Ca montmorillonite, have also been reported to increase  $^{90}\text{Sr}$  mobility (Mason *et al.* 1999; Lu and Mason 2001). Strontium forms weak aqueous complexes with nitrate, carbonate, sulphate and chloride (EPA 1999) but is normally present in groundwater and seawater as the free  $\text{Sr}^{2+}$  cation. Despite its generally weak interactions with solid phases, irreversible sorption of  $^{90}\text{Sr}$  onto oxic aquifer sediments has been reported (Jackson and Inch 1980; Jackson and Inch 1983) and was attributed to specific adsorption by Fe, Al and Mn oxide coatings on sand grains (Jackson and Inch 1989). However under reducing conditions Fe and Mn oxide coatings are liable to dissolve resulting in the release of Sr (Andersson *et al.* 1994).

**Table 1.4 Important solid phase associations and release mechanisms controlling radionuclide release.**

Rad.	Oxid. state	Sorption/ (co) precipitation	Important solid phase associations	Aqueous species	Release mechanisms	Important environmental variables	References (also see references in text)
<sup>90</sup> Sr	+2	ion exchange (outer sphere complexes)	iron oxides, clays, organic coatings	Sr <sup>2+</sup> (pH 3-10) DOM complexes	cation exchange: [Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> ]	pH, ionic strength	(Jackson and Inch 1989; Dupre <i>et al.</i> 1999; McKinley <i>et al.</i> 2007)
U	+6	sorption	U(VI):Fe, Mn minerals, silicates, organics, carbonates & clays	UO <sub>2</sub> <sup>2+</sup> UO <sub>2</sub> <sup>2+</sup> -carbonates: UO <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> <sup>2-</sup> , UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> UO <sub>2</sub> <sup>2+</sup> -Ca-carbonates: Ca <sub>2</sub> UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>0</sup> , CaUO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>2-</sup>	complexation with carbonates, cation exchange [Ca <sup>2+</sup> , Mg <sup>2+</sup> , Na <sup>+</sup> ]	oxidation/reduction conditions, pH, concentrations of complexing ligands e.g. carbonates, ionic strength, mineralogy	(Bostick <i>et al.</i> 2002; Dong <i>et al.</i> 2005; Zhou and Gu 2005)
U	+4	accumulates under reducing conditions	U(IV): Fe minerals	U(IV) organic species U(IV) carbonates	re-oxidation (O <sub>2</sub> , complexation with carbonates & organic matter		(Zhong <i>et al.</i> 2005; Wu <i>et al.</i> 2006; Senko <i>et al.</i> 2007)
<sup>99</sup> Tc	+7	none	no sorption	Tc(VII)O <sub>4</sub> <sup>-</sup>		redox conditions, dissolved O <sub>2</sub>	(Icenhower <i>et al.</i> 2010)
<sup>99</sup> Tc	+4	accumulates under reducing conditions	TcO <sub>4</sub> .nH <sub>2</sub> O, iron minerals (eg goethite), sulphide phases	Tc(IV) organic complexes, Tc(IV) carbonate complexes Tc(IV) chloride complexes	re-oxidation (O <sub>2</sub> , NO <sub>3</sub> <sup>-</sup> ) Tc(IV)complexion with; carbonate, dissolved organic matter and colloids	redox conditions , dissolved O <sub>2</sub>	(Livens <i>et al.</i> 2004; Maes <i>et al.</i> 2004; Burke <i>et al.</i> 2005; Begg <i>et al.</i> 2008)

**Uranium:** Uranium(VI) sorption is generally reversible, consistent with surface complexation (Barnett *et al.* 2000; Bostick *et al.* 2002; Qafoku *et al.* 2005). At circumneutral/alkaline pH and in the presence of carbonate, U(VI) carbonate complexes form, such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Zhou and Gu 2005; Choy *et al.* 2006). At higher ionic strength ternary calcium uranium carbonate complexes including  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  and  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  (Krupka and Serne 2002; Dong *et al.* 2005; Fox *et al.* 2006; Stewart *et al.* 2010), may enhance U mobilisation. However (bi)carbonates produced during microbial respiration have also led to the mobilisation of U under reducing conditions, via the formation of uranyl carbonate complexes (Zhou and Gu 2005; Wu *et al.* 2006). Both oxidised and reduced U(VI) and U(IV) can be mobilised through complexation by organic ligands such as siderophores, humic substances and anthropogenic contaminants such as EDTA (Lenhart *et al.* 2000; Frazier *et al.* 2005; Gu *et al.* 2005; Luo and Gu 2009; Luo and Gu 2011). For U(VI) species complexation with organic ligands is generally most important under pH conditions that exclude carbonate complexation.

Sediment-associated U(IV) can be rapidly mobilised when reduced sediments are re-oxidised by  $\text{O}_2$  and intermediates of dissimilatory nitrate reduction (Finneran *et al.* 2002; Senko *et al.* 2002; Wu *et al.* 2007). However the presence of these oxidants does not necessarily lead to the complete release of U(IV). Release may be inhibited by co-precipitation with, or incorporation into the structure of, Fe(III)oxides or by sorption of U(VI) onto Fe(III) oxides produced during Fe(II) oxidation (Payne *et al.* 1994; Ohnuki *et al.* 1997; Sato *et al.* 1997; Zhong *et al.* 2005; Stewart *et al.* 2009). The nature of the  $\text{UO}_2$  precipitates formed during reduction can also affect the rate of re-oxidation and release. For example, studies have shown that relatively slow rates of U(VI) reduction can result in the production of large, aggregated  $\text{UO}_2$  precipitates, which are oxidised at

a slower rate and to a lesser extent than those formed via rapid reduction (Senko *et al.* 2007).

**Technetium:** Although  $\text{Tc(IV)O}_2 \cdot n\text{H}_2\text{O}$  is relatively immobile in the environment, its mobilisation under anoxic conditions can be promoted by the formation of carbonate complexes such as  $\text{Tc(OH)}_2\text{CO}_3^0$ ,  $\text{Tc(OH)}_3\text{CO}_3^-$ ,  $\text{Tc(OH)(CO}_3)_2^-$ , and  $\text{Tc(OH)}_2(\text{CO}_3)_2^{2-}$  (Paquette and Lawrence 1985; Wildung *et al.* 2000; Alliot *et al.* 2009) organic complexes (Boggs *et al.* 2011; Gu *et al.* 2011) and colloids (Maes *et al.* 2004). Technetium is rapidly oxidised and mobilised from reduced sediments when exposed to oxygen (Burke *et al.* 2006; McBeth *et al.* 2007; Begg *et al.* 2008; Morris *et al.* 2008) and nitrate (McBeth *et al.* 2007); however the extent of oxidation depends on the oxidant used (Burke *et al.* 2006). The incomplete mobilisation of Tc has been observed even when the Eh of the system (+150 mV) was sufficient to expect Tc re-oxidation (McBeth *et al.* 2007; Begg *et al.* 2008; Moon *et al.* 2009). For example; Tc incorporated into the structure of goethite [ $\alpha\text{FeO(OH)}$ ] has been shown to be recalcitrant to mobilisation (Lukens *et al.* 2005; Um *et al.* 2011). Additionally Tc associated with iron and sulphide phases, including mackinawite (FeS) and green rust, can be incorporated into the goethite lattice during the re-oxidation of Fe and remain in the +4 oxidation state, resistant to re-oxidation and release (Wharton *et al.* 2000; Pepper *et al.* 2003; Livens *et al.* 2004). Once mobilised Tc(VII) exists as the pertechnetate anion  $\text{TcO}_4^-$  over the pH range of natural waters (Krupka and Serne 2002) and is therefore highly mobile, e.g. discharges of Tc(VII) from Sellafield (UK) have been traced towards the Arctic (Dahlgaard *et al.* 1995; McCubbin *et al.* 2002; Keith-Roach *et al.* 2003; Orre *et al.* 2007).

## 1.9 Experimental strategies for investigating radionuclide mobility in sediments

A wide range of experimental approaches have been adopted by other workers in order to develop the understanding of the processes controlling radionuclide release from sediments.

**Microcosm experiments:** A microcosm can be defined as an intact, minimally disturbed piece of an ecosystem brought into the laboratory for study under controlled experimental conditions (Prichard and Bourquin 1984). Microcosm experiments have been used extensively to study the biotic and abiotic transformations of redox sensitive radioactive contaminants, including U and Tc (Burke *et al.* 2005; McBeth *et al.* 2007; Senko *et al.* 2007; Komlos *et al.* 2008), as reducing conditions develop. Microcosm experiments are particularly useful for these studies as they provide control over environmental variables (for example the exclusion of air) and changes in a sealed microcosm can be monitored over time. However microcosm experiments may not represent the natural environment as they exclude the effects of groundwater flow, seasonal change and physical disturbance (Handlley-Sidhu 2008).

**Solid phase associations of radionuclides with sediments:** The association of radioactive contaminants with soils and sediments influences their mobility. Therefore identification of the main binding sites, the associations of contaminants in sediments and the redox state of radionuclides will aid the evaluation of the mobilisation potential (Sutherland *et al.* 2000; Gleyzes *et al.* 2002). The association of radionuclides with sediments can be studied using synchrotron-based instrumental techniques, including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy (Maes *et al.* 2004; Morris *et al.* 2008; Peretyazhko *et al.* 2008; Burke *et al.* 2010). Unfortunately these techniques have relatively poor detection limits and so can only be applied to heavily contaminated sediments [e.g. 550

$\mu\text{M}$  of pertechnetate was used to investigate Tc binding in Oak Ridge sediments with, nM to sub-nM concentrations found in contaminated areas (McBeth *et al.* 2007)] and so may not represent real environments where concentrations of radionuclides can be significantly lower (Bacon and Davidson 2008). Therefore, in these cases, sequential extractions may provide useful information on the solid phase associations of radionuclides.

Sequential extraction schemes can be used to assess the partitioning of radionuclides into operationally defined sediment fractions by the sequential application of extractants of increasing strength. These extraction schemes have been successfully applied to various environmental matrices including; soils, lake and marine sediments (Pueyo *et al.* 2001; Patinha *et al.* 2012; Reis *et al.* 2012; Zhu *et al.* 2012) and in the study of radionuclides, including Tc, U and Sr (Sheppard and Thibault 1992; Standring *et al.* 2002; Keith-Roach *et al.* 2003; Dali-Youcef *et al.* 2004; Burke *et al.* 2010). A sequential extraction scheme (5 steps) was first described by Tessier (Tessier *et al.* 1979), and was subsequently modified to a 3 step scheme by the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission (1996) in an attempt to standardise the method for which they also provided a dedicated certified reference material (e.g. BCR-601, BCR-701) (Quevauviller *et al.* 1997; Rauret *et al.* 1999; Pueyo *et al.* 2001). Sequential extractions have also been adapted for use in anoxic sediments (Kersten and Förstner 1987; Wallmann 1993) and have been successfully applied to the analysis of anoxic sediments naturally radiolabeled with Tc (Keith-Roach *et al.* 2003).

Due to the operational definition of the solid phase association derived from extraction schemes, the results are dependent on the chosen extraction scheme and any modifications to the method (e.g. the extraction time and washing between steps) may influence the results (Moral *et al.* 2002). The chemical leaches also give information on

the chemical leachability of metals rather than true geochemical associations (Bacon and Davidson 2008). Sequential extractions are often criticised for the lack of selectivity of some leaching agents, re-absorption of released metals, incomplete extraction and precipitation of new mineral phases during extraction (Rauret and Rubio 1997; Mossop and Davidson 2003; Bacon and Davidson 2008). For example, sequential extraction of mineral phases illustrated the non-specificity of the BCR procedure as the iron oxyhydroxide-bound metals were released in Step 1 (the exchangeable step), rather than Step 2 (the reduction step) as would be expected (Whalley & Grant, 1994). Additionally low recoveries for Cu and As were observed using the extraction scheme initially described by Tessier (1979) as it under-estimated the Fe-oxide fraction (Dybowska *et al.* 2005). The most common problem with anoxic sediments is that amorphous monosulfides, such as FeS, dissolve in acidic media, and so will dissolve to some extent in the carbonate (NaOAc, pH 5) and reducible (ammonium oxalate, pH 3) leaches (Parkman *et al.*, 1996; Keith-Roach *et al.*, 2003). Additionally Burke *et al.*, (2010) suggest that these extractions may provide an over-estimation of the association of Tc with organic matter and are indicative of the ability of H<sub>2</sub>O<sub>2</sub> to oxidise Tc(IV)O<sub>2</sub> to Tc(VII).

Due to these limitations results should be interpreted with caution. Sequential extractions have been identified as being of particular use in comparative studies, they can provide insights into general changes in the association of contaminants with soils and sediments as a function of time or variables (Bacon and Davidson 2008). Good examples of these applications include assessing if contaminants become less exchangeable over time, i.e. during ageing (Ma and Uren 2006), determining differences in the association of contaminants with different soils and sediments (Lo and Yang 1998; Standring *et al.* 2002) and assessing whether sediment associated

contaminants become more strongly bound to sediments after bioreduction (Begg *et al.* 2011).

**Mobilisation of radionuclide from sediments:** Traditional batch studies are widely used to study the mobilisation of radionuclides, including  $^{90}\text{Sr}$ , U and  $^{99}\text{Tc}$  from soils and sediments (Porro *et al.* 2000; Standring *et al.* 2002; Standring *et al.* 2002; Zheng and Wan 2005). Advantages of batch studies include low costs and a relatively simple methodology. Batch experiments provide information on the environmental fate of contaminants but they are conducted under static conditions and the equilibrium situation reached in these studies may not be reached in the natural environment. (Hinz and Selim 1999; Quaghebeur *et al.* 2005). Batch experiments may not represent of the leaching behaviour of contaminants under variable hydrological conditions (van der Sloot *et al.* 2006), or under the moisture regime of environmental systems such as paddy soils (Chang and Wang 2002) where the environment is in a state of continuous change and the desorbed products are continuously removed from solution because of the dynamic processes occurring.

Column experiments are now used to study the release of radionuclides such as U and Sr from sediments under flow conditions (Turner *et al.* 1996; Qafoku *et al.* 2005; Solovitch-Vella and Garnier 2006; Liu *et al.* 2008; Liu *et al.* 2009). Column experiments are used to complement batch experiments and provide an opportunity to study radionuclide behaviour under more environmentally relevant conditions (Schweich and Sardin 1981). For example the release and transport of radionuclides can be studied under non-equilibrium conditions and in the presence of hydrodynamic effects, including dispersion and colloid transport (EPA 1999), to investigate release from binding sites with slower desorption kinetics (Keller 2004). Columns are especially useful if contaminants are associated with multiple sorption sites with different release kinetics (EPA 1999). An example of this is the transport of U(VI)

through a terrestrial dune sand, where U elution from the column was retarded with respect to the conservative Br<sup>-</sup> tracer, suggesting non- conservative behaviour (Handley-Sidhu *et al.* 2009). The elution peak was not symmetrical and the tailing observed suggested that release involved kinetically controlled movement between different binding sites. Column experiments are, however, often run at high flow rates not representative of the environment being simulated and this can lead to an underestimation of slow reactions (e.g. dissolution), which are important in low flow field conditions (Gabriel *et al.* 1998). Therefore, flow rates should be chosen to represent the environment being studied.

Stop-start flow events can be utilised to investigate if contaminant release from sediments is equilibrium or kinetic controlled (Ilton *et al.* 2008; Liu *et al.* 2008). During the stop period, species have more time for kinetically controlled desorption processes to occur, increasing the concentration eluted for a period once flow is restarted (Quaghebeur *et al.* 2005). However during stop flow column experiments may behave in a similar fashion to batch experiments. Re-adsorption of the desorbed species, attaining of equilibrium conditions and saturation of the pore waters can hinder desorption.

### **1.10 Project aim and hypotheses**

Sediments and soils local to coastal nuclear facilities are important sinks for radionuclides, and hence it is necessary to understand and predict their behaviour in response to the sea level rise processes of inundation, flooding, erosion and intrusion outlined in Figure 1.2.

Mobilisation can result in a flux of radionuclides to local marine environments where they may (ultimately) pose a threat to human health (Sanchez-Cabeza and Molero 2000; Keogh *et al.* 2007). Furthermore, any discharges into the marine environment may result in national and international controversy. A better understanding of the processes

controlling radionuclide release from contaminated sediments is required when considering the siting of new nuclear waste storage facilities and developing effective remediation and decommissioning strategies for the management of legacy coastal nuclear sites.

The key radionuclides  $^{90}\text{Sr}$ , Tc and U, which display contrasting environmental behaviour, were selected for this study. The half-lives of these radionuclides are relevant, especially when considering the intermediate ( $^{90}\text{Sr}$ ) and the long term (for Tc and U) timescales involved in sea level rise processes. To maintain site relevance two surface sediments were sourced for use in this project; one from the nuclear facility at Dounreay (Scotland) and one sourced from Crediton (Devon, UK) with characteristics similar to the Quaternary unconsolidated flood plain deposits that underlie the Sellafield region (Cumbria).

The overall aim of this project was to test the hypothesis that Tc, U and Sr are mobilised from Dounreay and Crediton sediments during sea level rise processes. The hypotheses underpinning each chapter are outlined below.

*Chapter 2 Mobilisation of  $^{90}\text{Sr}$  from contaminated sediments during inundation and erosion scenarios.* The hypothesis underlying the work described in this chapter is that the release of  $^{90}\text{Sr}$  from oxic sediments will be promoted by cation exchange under seawater inundation and erosion scenarios. To test this hypothesis, sediments from Dounreay and Crediton were contaminated with  $^{90}\text{Sr}$  and aged for 6 months prior to use in mobilisation experiments. Changes in the association of  $^{90}\text{Sr}$  with the sediments during the ageing period were assessed using sequential extractions.

The rate and extent of  $^{90}\text{Sr}$  mobilisation from aged sediments under inundation and flooding scenarios was investigated using batch experiments with a high (1:1) sediment:solution ratio and slow vertical shaking. The effect of increased porewater

salinity on the mobilisation of  $^{90}\text{Sr}$  was studied by comparing release into groundwater, low salinity water (salinity 4) and seawater (salinity 35) during long term (90 day) contact. The mobilisation of  $^{90}\text{Sr}$  under an erosion scenario was investigated using a lower (1:10) sediment: solution ratio and fast horizontal shaking into groundwater and seawater over a 24 h period. Finally, the release of  $^{90}\text{Sr}$  into seawater was examined under dynamic saturated conditions and compared with release in batch seawater experiments.

Chapter 3 Mobilisation of U(IV) from contaminated sediments during inundation and

erosion scenarios The hypothesis underlying the work described in this chapter is that the release of U(VI) from oxic sediments will be promoted by the formation of U(VI) carbonate complexes under seawater inundation and erosion scenarios. To test this hypothesis, sediments from Dounreay and Crediton were contaminated with U(VI) and aged for 6 months prior to use in mobilisation experiments. Changes in the association of U(VI) with the sediments over time were assessed using sequential extractions.

The rate and extent of U(VI) mobilisation from aged sediments under inundation and flooding scenarios was investigated using batch experiments with a high (1:1) sediment:solution ratio and slow vertical shaking. Long term (90 day) experiments were used to study the effect of increased porewater salinity on the mobilisation of U(VI) by comparing release into groundwater, low salinity water (salinity 4) and seawater (salinity 35). The release of U under an erosion scenario was investigated using batch experiments with a low (1:100) sediment: solution ratio and fast horizontal shaking into groundwater and seawater over a 48 h period. Finally the release of U into seawater was investigated under more environmentally relevant, dynamic conditions using column experiments.

#### Chapter 4 Uranium mobilisation from reduced sediments during saltwater intrusion

The hypothesis underlying the work described in this chapter is that the intrusion of oxic seawater into reduced sediments will lead to the mobilisation of U. In order to test this hypothesis, Crediton sediments were amended with U(VI) and allowed to become increasingly reducing over time. Changes in the association of U with the sediments during reduction were monitored using sequential extractions.

The release of U from sediments during different stages of geochemical reduction (nitrate reduced, iron reducing and extensively iron reducing) were compared. The effect of increased porewater salinity and the re-introduction of dissolved oxygen on the mobilisation of U was studied using long term (120 day) batch experiments to compare release into oxic groundwater and oxic seawater and degassed seawater over time. Column experiments were used to investigate the mobilisation of U into oxic seawater during sediment re-oxidation.

#### Chapter 5 Tc mobilisation from reduced sediments during saltwater intrusion

The hypothesis underlying the work described in this chapter is that the intrusion of oxic seawater into reduced sediments will lead to the re-oxidation of Tc(IV) to Tc(VII) thereby promoting Tc(VII) release. In order to test this hypothesis Crediton sediments were amended with Tc(IV) and allowed to become increasingly reducing over time. Changes in the association of Tc(IV) with the sediments during reduction were monitored using sequential extractions.

Technetium mobilisation from sediments during different stages of geochemical reduction (nitrate reduced, iron reducing and extensively iron reducing) were compared. Sediments were re-suspended in oxic groundwater and oxic seawater and degassed seawater over time to investigate the effect of increased porewater salinity and the re-

introduction of dissolved oxygen on the mobilisation of sediment associated Tc(IV). Column experiments were used to investigate the mobilisation of U into oxic seawater during sediment re-oxidation.

### **1.11 Experimental design**

In order to address these hypotheses appropriate experiments were devised and used in this study and are outlined below.

**Inundation:** A rise in sea level will cause coastal inundation, potentially leading to the penetration of seawater into previously freshwater sediments. Therefore, in this study batch experiments were designed to simulate inundation scenarios. A slow vertical shaking protocol was adopted to ensure that the sediments were in constant contact with the overlying water. A 90 day desorption period was selected to investigate the effect of extended periods of seawater intrusion on the release of radionuclides. In these experiments a sediment:solution ratio of (1:1) was chosen to be within the range solid:solution ratios found in geological media, soils and aquifers (Limousin *et al.* 2007). The effect of increased porewater salinity was studied by comparing release into the end member waters i.e. groundwater (salinity 0) and seawater (salinity 35). A low salinity water (salinity 4) was chosen to represent the mixing of the inundating seawater with fresh porewater during the early stages of seawater intrusion. Column experiments were used to investigate the mobilisation of radionuclides over time as increasing volumes of seawater percolated into the sediments.

**Erosion:** Coastal erosion will primarily result in waves carrying contaminated sediments offshore. Therefore batch experiments were designed to simulate erosion scenarios using a lower sediment:solution ratio (1:10 and 1:100). To investigate the transfer of particles from a freshwater to a saline environment, sediments were resuspended in groundwater and seawater. Erosion scenario experiments were

conducted over a short timescale (< 48 h) and, because they represent more dynamic environments, centrifuge tubes were shaken horizontally at a speed sufficient to keep the sediment particles in suspension. The results from seawater column experiments were used to investigate the release of radionuclides at lower sediment:solution ratios encountered as eroded particles are advected seawards.

**Column experiments:** In this study column experiments were conducted to more closely simulate the flow of seawater through contaminated sediments and hence complement and expand on the findings from the batch experiments. Stop-start events (or flow interruptions) were used to study the impact of a period of no flow or slow flow on the release or sorption of radionuclides from soils and sediments. This may occur, for example, when seawater enters an area of lower permeability. Stop-start flow events can also be used to evaluate kinetically-limited processes over the course of an experiment. An increase in radionuclide concentration following a stop-flow event suggests that radionuclides are desorbed during extended equilibration times and suggests that steady-state conditions are not reached under continuous flow conditions, i.e. that mobilisation is rate-limited (Tinnacher *et al.* 2011).

## **Chapter 2**

# **Mobilisation of $^{90}\text{Sr}$ from contaminated sediments under inundation and erosion scenarios**

## 2.1 Introduction

The high energy,  $\beta$ -emitting fission product  $^{90}\text{Sr}$  ( $t_{1/2}$  29 years) is an important component of radioactive waste and has been reported in contaminated soils, sediments and groundwater at legacy sites in the UK such as Sellafield and Dounreay (Hunter 2004; Savage *et al.* 2009; McKenzie and Armstrong-Pope 2010). Strontium occurs in most ground and surface waters as the hydrated divalent ion,  $\text{Sr}^{2+}$  and can accumulate in soils and sediments (Chorover *et al.* 2008; Chiang *et al.* 2010). Strontium sorbs to a variety of clays including kaolinite, illite and montmorillite (Chen and Hayes 1999; Cole *et al.* 2000; Bellenger and Staunton 2008), iron oxide minerals (Chiang *et al.* 2010), quartz (Chen *et al.* 2006), silica (Lu and Mason 2001) and zeolitized tuffs (Um and Papelis 2004). In all of these studies, strontium was electrostatically bound to the matrix surfaces as outer-sphere complexes with ion exchange the dominant sorption mechanism. Outer-sphere complexes are weakly associated with surface binding sites and so are generally reversibly bound and mobilised as porewater pH decreases or ionic strength increases (Dzombak and Morel 1990; Stumm and Morgan 1996; Chen and Hayes 1999; Langley *et al.* 2009). Surface associated strontium can readily exchange with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Na}^{+}$  in solution (Ahmad 1995; Jeong *et al.* 1996; Bunde *et al.* 1997; Bunde *et al.* 1998; McKinley *et al.* 2007); however divalent cations have a greater effect than  $\text{Na}^{+}$  due to similarities in the size of the hydrated ion and charge.

In addition to ion exchange there is also some evidence of the specific adsorption of strontium on hydrous Fe, Al and Mn oxide coatings on streambed sediments, sand grains and mineral phases (Cerling and Turner 1982; Jackson and Inch 1989; Trivedi and Axe 1999) and amorphous hydrous ferric oxide (Mishra and Tiwary 1999), the formation of inner sphere complexes on hematite (Karasyova *et al.* 1999) and incorporation of strontium into the interlayers of the montmorillonite structure (Lu and Mason 2001). These associations resulted in a slower release of strontium.

Strontium has a relatively weak affinity for solid particles in seawater (Benes and Poliak 1990) and can be readily released from marine sediments (Benkdad *et al.* 2008) and river sediments, (Standring *et al.* 2002) however the mobilisation of  $^{90}\text{Sr}$  from iron rich terrestrial sediments during sea level rise is poorly understood.

The aim of this Chapter was to investigate the release of  $^{90}\text{Sr}$  from sediments during inundation, temporary flooding and erosion scenarios as a result of projected sea level rise. The effect of increased porewater salinity during inundation and flooding was studied by comparing release into the end member waters i.e. groundwater (salinity 0) and seawater (salinity 35). A low salinity water (salinity 4) was chosen to represent the mixing of the inundating seawater with fresh porewater during the early stages of seawater intrusion. Short term (< 24 h) batch experiments were designed to simulate erosion scenarios using a lower sediment:solution ratio (1:10). To investigate the transfer of particles from a freshwater to a saline environment, sediments were resuspended in groundwater and seawater. Finally the release of  $^{90}\text{Sr}$  into seawater was examined using fully saturated, dynamic, seawater column experiments.

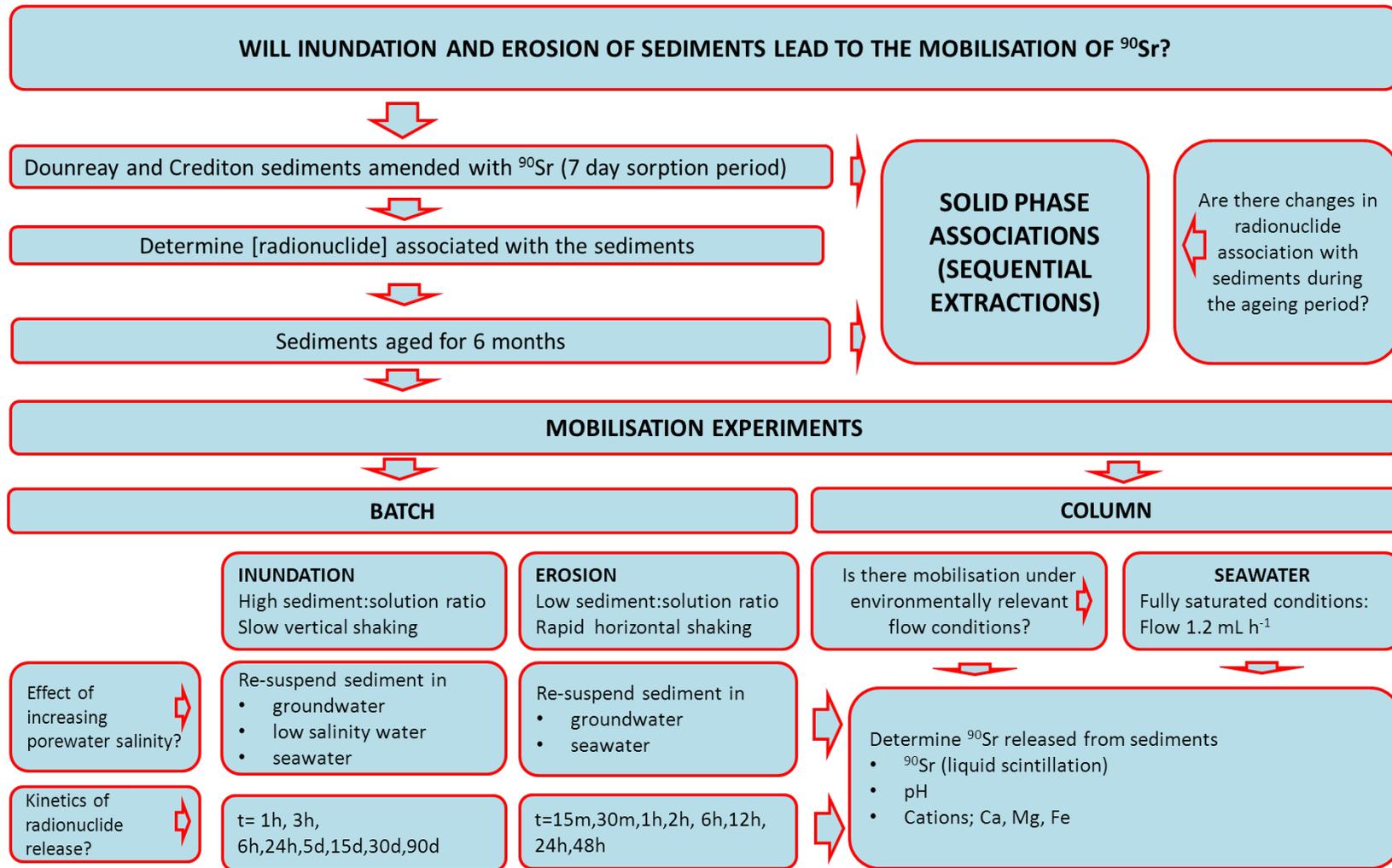
## **2.2 Experimental**

### **2.2.1 Experimental design**

An overview of the experimental strategy adopted in this Chapter is outlined in Figure 2.1.

### **2.2.2 Reagents**

All glassware and plasticware were washed in 2 % (v/v) Decon for at least 24 h, rinsed 5 times in Milli-Q water (Millipore,  $18 \text{ M}\Omega \text{ cm}^{-1}$ ), transferred to a 10% (v/v) HCl bath for 48 h and rinsed with Milli-Q water.



**Figure 2.1 Experimental design adopted in <sup>90</sup> Sr erosion and inundation experiments.**

Plastic and glassware were then dried under laminar flow (Bassaire S6) and stored in double zip lock plastic bags until use to avoid contamination. All chemicals used in the experiments were of analytical grade and obtained from Fisher (Fisher Scientific, Loughborough, UK), AnalaR BDH Chemicals Ltd (Poole UK) or Sigma Aldrich (Sigma Aldrich Chemicals, Gillingham, UK) unless otherwise stated. Standard used in ICP-MS and ICP-OES determinations were dilutions of 10000  $\mu\text{g mL}^{-1}$  atomic emission standards (Fisher Scientific, UK).

### **2.2.3 Sediment and water collection and preparation**

**Water:** Surface seawater (< 1 m depth) was collected from the L4 coastal monitoring station located in the western English Channel (see [www.westernchannelobservatory.org.uk](http://www.westernchannelobservatory.org.uk)) using the RV Plymouth Quest. Seawater was collected in an acid washed carboy that was rinsed 3 times with the local seawater before collection, and the salinity was determined to be 35 using a portable salinity meter (YSI-55). On return to the laboratory seawater was filtered (0.4  $\mu\text{m}$ , Nuclepore track edge membrane, Whatman) and stored at 4  $^{\circ}\text{C}$  in the dark until use.

**Sediment sampling:** Sediments sampled from a depth of 10-20 cm at the nuclear facility at Dounreay (Scotland, UK) were supplied by the Land Remediation Site Decommissioning Project Delivery Unit. Sediments overlying a sandstone bedrock with characteristics similar to those found near the Sellafield (NSRI 2012) were sampled from Crediton, Devon, UK ( Lat: 50<sup>0</sup>.8091'N;Long: 03<sup>0</sup>.6815'W) from below the organic horizon to avoid root material. On return to the laboratory, sediments were homogenised by hand and sieved through a 2 mm nylon mesh. Both sediments were stored in a field moist state in clean polythene bags in the dark at 4  $^{\circ}\text{C}$ . The bags were opened periodically (every 14 days) to ensure that the sediments remained aerobic. The

sediments were not dried in order to avoid potential mineralogical and microbial changes.

#### **2.2.4 Sediment Characterisation**

The bulk mineralogy of the sediments was determined by X ray diffraction (Siemens D5000). The particle size distribution of the < 2 mm fraction of the Dounreay and Sellafield sediments was determined by laser diffraction (Malvern Long-bed Mastersizer X with wet sample unit MS17, Malvern Instruments Ltd, UK) following digestion of the organic content with 30 % hydrogen peroxide. The specific surface area (SSA) was determined using BET N<sub>2</sub> adsorption (Micromeritics Gemini 2375 V4.01 surface area analyser). Freeze dried particles were used and hence the resulting SSA values were likely to be lower than for hydrated particles (Bottero *et al.* 1993; Trivedi and Axe 1999). Total carbon, hydrogen and nitrogen (CHN) content was determined using an elemental analyser (EA 1110 CHN Analyser) in which the sediment was completely combusted and the gases produced were analysed by chromatography with thermal conductivity detection. The organic carbon content was determined after digestion of inorganic carbon (4 M HCl for > 48 h) prior to analysis. Ethylenediamine tetraacetic acid-disodium salt (Analytical grade Merk) was used to calibrate the instrument. A certified reference material (CRM) PACS 1 sediment (National Research Council of Canada) was used to validate the method and the results of CRM analysis (3.66 % ± 0.04 %) compared well with the certified value (3.69 % ± 0.11 %). The cation exchange capacity (in mEq per 100 g of dry sediment) was determined by cation exchange with sodium following the US Environmental Protection Agency (EPA) SW-846 Method 90812 (EPA 1986). The sodium concentration was measured using a flame photometer (Corning 400 Falem Photometer) calibrated with sodium chloride standards. The pH of the sediment suspensions was measured in Milli-Q water using a 1:1

sediment: solution ratio with a conventional pH meter (Mettler Delta 340). Finally, the major elemental composition of the sediments was determined using an inductively coupled plasma mass spectrometer (ICP-MS) following aqua regia digestion of the sediments (1 g of sediment; 8 mL 16 M HNO<sub>3</sub>; 3 mL 12 M HCl).

### 2.2.5 Preparation of simulated groundwater and low salinity water

Salts were dissolved in Milli-Q water to create a synthetic groundwater that was representative of the low level waste repository near Drigg (Cumbria, UK); the constituents are shown in Table 2.1. Strontium 90 (Amersham International, UK) was added to give a final concentration of 200 Bq mL<sup>-1</sup> (4.4 x 10<sup>-10</sup> M); the pH of the groundwater was 7.35.

**Table 2.1: Constituents of Drigg synthetic groundwater (Wilkins *et al.* 2007).**

Salt	Concentration, g L <sup>-1</sup>
KCl	0.0066
MgSO <sub>4</sub> ·7H <sub>2</sub> O	0.0976
MgCl <sub>2</sub> ·6H <sub>2</sub> O	0.0810
CaCO <sub>3</sub>	0.1672
Na <sub>2</sub> SiO <sub>3</sub>	0.0829
NaNO <sub>3</sub>	0.0275
NaCl	0.0094
NaHCO <sub>3</sub>	0.2424

A low salinity water (salinity 4) for use in the batch mobilisation experiments was prepared by mixing the groundwater and seawater end members.

### 2.2.6 Generation of aged <sup>90</sup>Sr contaminated sediments

A 'bulk' of contaminated sediment (< 2 mm fraction) was generated for use in batch and column mobilisation experiments. Dounreay and Crediton sediments (n= 8) were

accurately weighed into separate 1000 mL centrifuge pots and amended with a simulated groundwater solution ( $^{90}\text{Sr}$  200 Bq mL<sup>-1</sup>) using a high (1:1) sediment to solution ratio. Sediment slurries were then incubated in the dark at 20 °C for 7 d with constant shaking (120 rpm). After the 7 d sorption period sediment slurries were centrifuged for 30 min at 4000 g (Legend RT centrifuge). A 5 mL aliquot of the supernatant was removed for immediate determination of pH and a 10 mL aliquot was acidified (HCl, 50 µL, 6 M) and stored at 4 °C for 3 weeks to allow  $^{90}\text{Y}$  ingrowth before analysis of  $^{90}\text{Sr}$  remaining in solution. The concentration of  $^{90}\text{Sr}$  associated with the sediments was determined from the difference between the initial and final aqueous  $^{90}\text{Sr}$  concentrations. Blank experiments (i.e.  $^{90}\text{Sr}$  and groundwater with no sediment) showed that no  $^{90}\text{Sr}$  adsorbed to the vessel walls. The final concentration of  $^{90}\text{Sr}$  sorbed to the sediments was  $178 \pm 5$  Bq g<sup>-1</sup> (Sellafield sediments) and  $160 \pm 3$  Bq g<sup>-1</sup> (Dounreay sediments) respectively.

Contaminated sediments were then transferred into separate plastic storage boxes and homogenised by stirring with a plastic spatula and shaking for 5 min. To validate the homogenisation process, 5 random sub-samples were taken from the bulk sediments, freeze dried and digested with aqua regia (1 g of sediment; 8 mL 16 M HNO<sub>3</sub>; 3 mL 12 M HCl) for determination of the total  $^{90}\text{Sr}$  concentration. There was no statistically significant difference ( $p = 0.064$ ) between the concentrations of  $^{90}\text{Sr}$  in the random sub-samples using a multiple sample ANOVA test (StatGraphics Version 5.1). Sub-samples of the homogenised sediments were then removed and stored (-20 °C) in sealed plastic vessels for later characterisation by sequential extraction.

The remaining contaminated Crediton and Dounreay sediments were then incubated in the dark at  $21 \pm 0.5$  °C for 6 months, with periodic opening (every 10-20 days) to re-supply O<sub>2</sub> to the sediments, before use in batch and column mobilisation experiments.

Changes in the solid state chemical fractionation of  $^{90}\text{Sr}$  during the ageing period were monitored using a modified Tessier five step sequential extraction scheme (Kersten and Förstner 1987; Wallmann 1993) that has been successfully applied to study the association of radionuclides with sediments in marine and freshwater environments (Keith-Roach *et al.* 2003).

### **2.2.7 Mobilisation of $^{90}\text{Sr}$ from sediments during erosion and inundation**

Batch experiments were used to investigate the mobilisation of  $^{90}\text{Sr}$  from sediments during inundation and erosion with seawater. Complementary column experiments were used to investigate  $^{90}\text{Sr}$  release under more environmentally relevant saturated flow through conditions.

**Batch Experiments:** All experiments were carried out under aerobic conditions at room temperature, using laboratory contaminated moist sediments. Batch mobilisation experiments were performed on Crediton and Dounreay sediments that had been aged for 6 months. All mobilisation experiments were prepared on the same day and carried out in triplicate for each pre-determined time point.

**Inundation (1:1) Experiments:** In order to simulate inundation, high (1:1) sediment:solution (m/v) ratios were adopted with slow vertical shaking. Over a lined tray approximately 5.0000 g of aged Dounreay and Crediton sediment samples were accurately weighed (Salter Electronic Balance ER-128A) into clean 50 mL polycarbonate centrifuge tubes (Fisher Scientific, UK). Sediments were then amended with 5 mL of groundwater, low salinity water or seawater; the centrifuge tubes were then capped and slowly shaken in an upright position in the dark at 70 rpm and 21 °C for pre-determined time periods (t= 1 h, 3 h, 6 h, 24 h, 5 d, 15 d, 30 d, 90 d). Centrifuge

tubes were opened periodically to the air to ensure that anaerobic conditions did not develop.

**Erosion (1:10) experiments:** In order to simulate erosion lower (1:10) sediment:solution (m/v) ratios were adopted with rapid shaking over short timescales (<24 h). Approximately 1.0000 g of aged Dounreay and Crediton sediment samples were accurately weighed (Salter Electronic Balance ER-128A) into clean 50 mL polycarbonate centrifuge tubes (Fisher Scientific, UK) over a lined tray. Sediments were then amended with 10 mL of groundwater or seawater. Centrifuge tubes were then capped and shaken horizontally in the dark at sufficient speed to ensure that the particles were in suspension for pre-determined time periods (t=15 min, 30 min, 1 h, 2 h, 6 h, 12 h and 24 h).

At each pre-determined time point, a 2 mL aliquot of the slurry was removed for immediate determination of pH. The remaining slurry was then centrifuged at 4000 g for 30 min. The supernatant was decanted into clean 10 mL polycarbonate centrifuge tubes (Fisher Scientific, UK) and acidified before being stored at 4 °C prior to the determination of dissolved <sup>90</sup>Sr, Ca, Mg and Fe.

### **2.2.8 Dynamic flow through seawater column experiments**

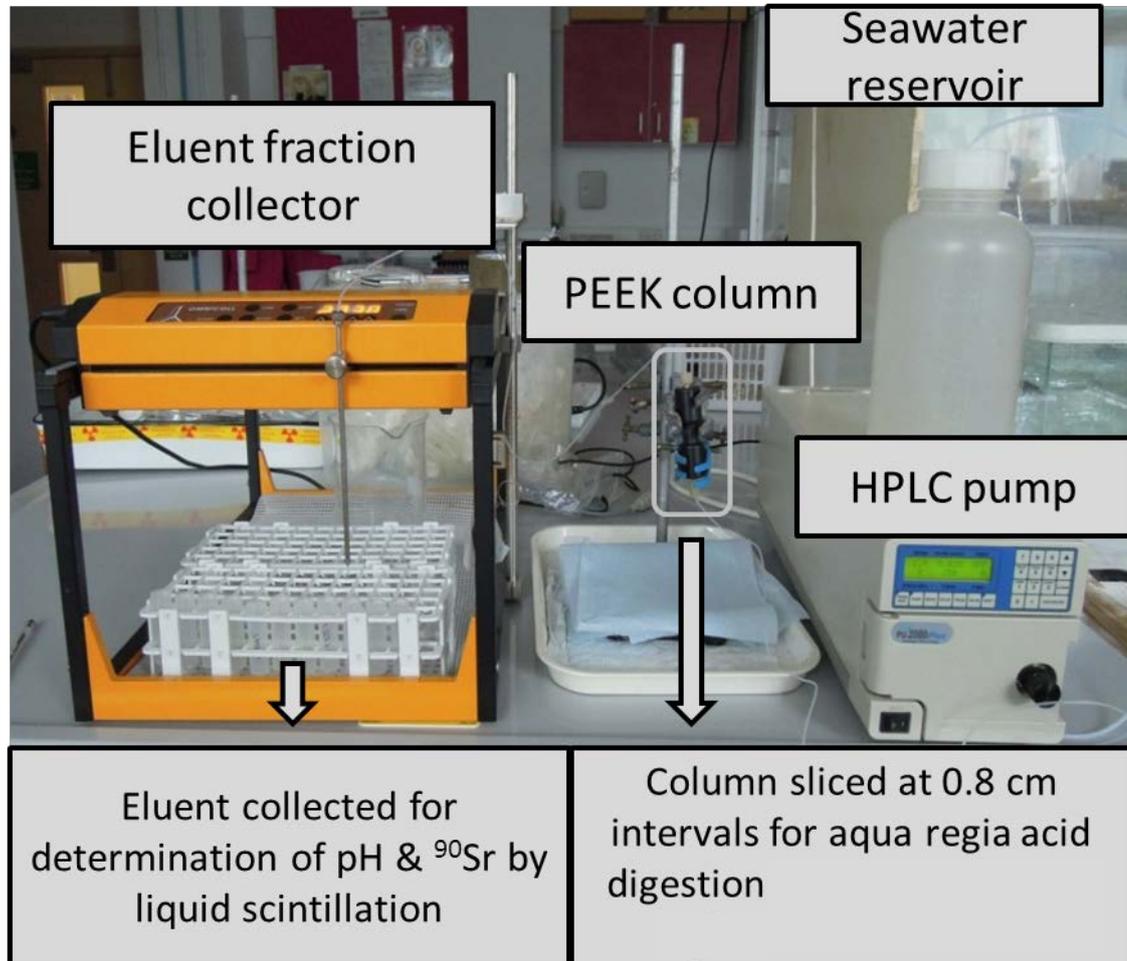
Column experiments were conducted under fully saturated seawater flow conditions to investigate the mobilisation of <sup>90</sup>Sr from Crediton and Dounreay sediments during sea water inundation. Contaminated sediments were packed into a polyetheretherketone (PEEK) self-pack column (50 mm × 10 mm; Applied Biosciences, Foster City, USA). Frits (0.2 µm pore size) located at the top and bottom of the column were used to confine the sediment and allow an even distribution of the column influent (Liu *et al.* 2008). The column and tubing were acid washed (10 % v/v HCl) and thoroughly rinsed

with ultra-pure water between each run. Columns were packed in small increments and tapped gently to achieve constant packing, eliminate air pockets and remove excess water; this step was repeated until the column was full. The sediment mass in the column was then determined gravimetrically. A high-performance liquid chromatography (HPLC) pump was used to slowly saturate the column with seawater at a constant rate ( $1.2 \text{ mL h}^{-1}$ ). An upward flow direction was used to maintain saturated conditions and prevent the formation of preferential flow channels. The eluate was collected using a fraction collector (Omnicoil, Lambda, Zurich, Switzerland), in 1.2 - 3.6 mL fractions. The pH of the eluate was measured as soon as possible after collection, and samples were then acidified prior to determination of  $^{90}\text{Sr}$  by liquid scintillation counting. Pre-weighed vessels were placed at regular intervals (every 10 vessels) on the collection grid and were re-weighed after sample collection to monitor the flow rate. Uncertainty associated with the flow rate was  $< 5 \%$ .

After completing each mobilisation experiment, a conservative tracer (200  $\mu\text{L}$  of 75 mM  $\text{Br}^-$ ) was injected into the column to obtain the physical parameters of each column;  $\text{Br}^-$  was determined by ICP-MS. Column pore volume was calculated gravimetrically by mass difference between the column packed with contaminated sediments and the mass of the saturated column under steady flow conditions. The linear flow velocity through the column was  $253 \text{ m y}^{-1}$  (Sellafield) and  $240 \text{ m y}^{-1}$  (Dounreay) respectively; this is consistent with flow velocities observed in sandy aquifers under natural hydrogeological conditions (Mackay *et al.* 1985). During the experiment; 180 mL (Sellafield) and 189 mL (Dounreay) of seawater flowed through the columns. The column set up is shown in Figure 2.2.

After each run the column was opened and the packed sediment extruded using a clean polypropylene rod. Sediment was sliced at approximately  $0.8 \pm 0.2 \text{ cm}$  intervals and collected in pre-weighed petri dishes. Samples were then freeze dried, re-weighed and

total  $^{90}\text{Sr}$  determined after aqua regia digestion (1 g of sediment; 8 mL 16 M  $\text{HNO}_3$ ; 3 mL 12 M  $\text{HCl}$ ).



**Figure 2.2** Column experimental set up.

### 2.2.9 Determination of solid phase associations

Differences in (a) the association of  $^{90}\text{Sr}$  with Dounreay and Crediton sediments and (b) changes in the solid phase associations of  $^{90}\text{Sr}$  with sediments during the 6 month ageing period were determined using sequential extractions.

**Sequential extraction scheme:** The sequential extraction procedure adopted was a 5 step scheme (Tessier *et al.* 1979) modified for use with anoxic sediments (Kersten and

Förstner 1987; Wallmann 1993) which has been successfully applied to study technetium binding in environmental samples, including anoxic marine environments (Keith-Roach *et al.* 2003) freshwater sediments (Standring *et al.* 2002) and sediments contaminated in laboratory microcosm experiments (Burke *et al.* 2010). An outline of the sequential extraction procedure is shown in Table 2.2.

Approximately 1.00 g of contaminated sediment was accurately weighed into 50 mL centrifuge tubes (Fisher Scientific, UK). For each batch of extractions, a separate aliquot of sediment was freeze dried to constant weight to determine the water content, which was applied to all analytical values reported. All extractions were performed in triplicate using horizontal centrifuge tubes with continuous horizontal shaking at a speed that ensured particles remained in suspension throughout the extraction period. Reagent blanks were analysed for each extraction solution used and a procedural blank (centrifuge tube with no sediment) was taken through the entire procedure and analysed at the end of each extraction step.

*Step 1:* 8 mL of 1 M MgCl<sub>2</sub> adjusted to pH 7 (NaOH) was added to 1 g of sediment within the anaerobic chamber. Centrifuge tubes were sealed and double bagged before shaking the suspension for 1 h at room temperature (25 °C). The extract was separated from the solid residue by centrifugation at 4000 g for 20 min. The supernatant was carefully decanted into a clean polyethylene container, ensuring no loss of the solid residue. Extracts were acidified with HCl and stored at 4 °C prior to analysis.

*Step 2:* 50 mL of 1 M sodium acetate adjusted to pH 5 using acetic acid was added to the residue from step 1 in the centrifuge tube.

**Table 2.2 Outline of the modified 5 step sequential extraction scheme**

<b>Fraction name</b>	<b>Targeted phase</b>	<b>Leachate composition</b>	<b>Reagent: sample ratio (v:m)</b>	<b>Incubation time</b>
Exchangeable	Exchangeable metals retained on the sediment surface by relatively weak electrostatic interactions and can be released by ion exchange processes.	Magnesium chloride (1 M adjusted to pH 7 with NaOH).	8:1	1 h
Carbonate	Metals adsorbed or bound to carbonates, this will also release metals/phases that are sensitive to the pH change.	Sodium acetate (1 M), adjusted to pH 5 with acetic acid.	50:1	5 h
Reducible	Metals bound to Fe/Mn oxides	Ammonium oxalate (0.1 M, adjusted to pH 2-3 with HCl).	50:1	16 h
Oxidisable	Metals bound to sulphides or organic matter	Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> ) 25% digest adjusted to pH 2-3 with HNO <sub>3</sub> , heated to 85 °C, then leached with ammonium acetate (1 M) in 6% (v/v) HNO <sub>3</sub> adjusted to pH 2.	50:1	2 h H <sub>2</sub> O <sub>2</sub> 16 h ammonium acetate
Residual	Metals associated with the mineral matrix	Aqua regia ( 8 mL of 16 M HNO <sub>3</sub> and 3 mL of 12 M HCl)	10:1	1 h cold 2 h reflux

Centrifuge tubes were then placed in a vortex generator (Fisher Scientific, UK) to break up the compacted sediment surface formed during centrifugation and extracted by mechanical shaking for 5 h at room temperature. The extract was separated from the solid as in step 1 and again acidified with HCl and stored at 4 °C prior to analysis.

Step 3: 50 mL of 0.1 M ammonium oxalate adjusted to pH 2-3 using HCl was added to the residue from step 2 in the centrifuge tube. Centrifuge tubes were then placed in a vortex generator (Fisher Scientific, UK) to break up the bund formed during centrifugation and then extracted by mechanical shaking for 16 h at room temperature in the dark to prevent photo-oxidation artefacts. The extract was separated from the solid as in step 1 and again acidified with HCl and stored at 4 °C prior to analysis.

Step 4: The residue from step 3 was transferred to PTFE (polytetrafluoroethylene) digestion vessels (Savillex, Minnetonka, USA). A 10 mL aliquot of hydrogen peroxide (30%, pH = 2) was carefully added to the residue and digested at room temperature for 1 h with occasional manual shaking. The suspension was then refluxed for 30 min at  $85 \pm 2$  °C in a sand bath for 1 h; the volume was then reduced to < 3 mL. A further aliquot of 10 mL of hydrogen peroxide was added to the residue and refluxed again at  $85 \pm 2$  °C, the lid was then removed and the volume reduced to approximately 1 mL. Care was taken not to allow the residue to become completely dry. Once cool the residue was transferred to a 50 mL centrifuge tube and a 50 mL aliquot of ammonium acetate (1 M), adjusted to pH 2 with concentrated HNO<sub>3</sub> was added. The suspension was shaken as described previously and again the supernatant retained for analysis.

Step 5: The residual and total aqua regia metal content of the sediment (using a separate 1 g sub-sample that had not been subjected to the sequential extraction procedure) was then determined using a modified Laboratory of the Government Chemist method based

on ISO 1146 (1996) for the certification of aqua regia soluble analyte concentrations in sediments.

In order to aid transfer of sediment to the digestion vessel, the residue from the sequential extraction was freeze dried to constant weight and stored in a desiccator until use. Samples were transferred into dry pre-cleaned, long necked digestion tubes (Tecator type) and 8 mL of HCl (12 M) followed by 2 mL of HNO<sub>3</sub> (16 M) were added, suspensions were left to pre-digest at room temperature in an aluminium Tecator block (Tecator digestion system 12 1009 digester) for 1 h prior to heating. A further 1 mL of HNO<sub>3</sub> was then added and the suspension was allowed to gently reflux for 2 h at 95-100 °C. After cooling, the suspension was filtered (hardened ashless, Whatman) and the filtrate and washings were transferred quantitatively to a 25 mL volumetric flask. The aluminium Tecator block method was adopted as it has been shown to be optimal for samples with a low organic matter and carbonate content (Sastre *et al.* 2002).

As an internal check on the sequential extraction procedure the total concentration of <sup>90</sup>Sr extracted in each of the separate steps of the sequential extraction procedure (including the aqua regia digest) was compared with that obtained using an aqua regia digest of a separate 1 g of sediment. This was achieved using a statistical analysis outlined by the European Reference Material Commission (Linsinger 2005). Equation 2.1 was used to determine if the sum of the steps was significantly different from the measured total corresponding to a confidence interval of 95 %.

$$mean \Sigma steps - mean aqua regia < 2 \sqrt{sd_{\Sigma steps}^2 + sd_{aqua regia total}^2} \quad (2.1)$$

Where  $\Sigma steps$  is the sum of each of the sequential extraction steps and *mean aqua regia* is an aqua regia digest of the residual fraction. Means of 3 separate experiments, *sd* is the standard deviation of 3 separate experiments.

### 2.2.10 Metal determinations

**Strontium-90:** Aqueous  $^{90}\text{Sr}$  was determined by liquid scintillation (Beckman LS6500 scintillation counter) after a 28 day delay to ensure equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  was re-established. A 2 mL aliquot of the acidified supernatant was added to 10 mL of scintillant (OptiPhase HiSafe 3) in a plastic scintillation vial (low diffusion PE Vial, 20 mL). The vial was shaken carefully to ensure that the sample was mixed thoroughly with the scintillant whilst avoiding depositing the mixture on the walls of the vial. Samples were kept in the dark for 3 h prior to counting to minimise analytical interferences from photoluminescence and chemiluminescence reactions. Each vial was counted for 360 min or until the counting error was within 5 % using a programme to account for efficiency and chemical quench. A blank ( $^{90}\text{Sr}$  and no sediment) showed that there was no adsorption to the vessel walls and a sample of the extractant without a  $^{90}\text{Sr}$  spike was also counted to determine the counting background. Aqueous  $^{90}\text{Sr}$  concentrations were calculated from the total counts in  $\text{DPM mL}^{-1}$  (disintegrations per minute) minus the background (in  $\text{DPM mL}^{-1}$ ).

**Cations:** Acidified samples were stored at  $4\text{ }^{\circ}\text{C}$  prior to analysis. Samples were diluted 10 fold before stable isotope determinations (Ca, Mg, Si, Fe, Mn and Al) by ICP-OES (Varian 725-ES, Yarton, Oxfordshire, UK). Indium was added to all blanks, samples and matrix matched standards as an internal standard to give a final concentration of  $50\text{ }\mu\text{M}$  In. Calibration blanks and checks were run after every 10 samples to check for instrument drift; if the drift exceeded 10 %, samples were re-run. Instrument parameters are shown in Table 2.3.

Trace concentrations of Al, Mn and Fe ( $<0.2\text{ }\mu\text{M}$ ) were determined by ICP-MS (Thermo X Series 2, Hemel Hempstead, UK). Operational ICP-MS parameters are

shown in Table 2.4. A collision cell used to overcome polyatomic interferences such as  $^{40}\text{Ar}^{16}\text{O}^+$  on  $^{56}\text{Fe}^+$ . Calibrations gave  $R^2$  values  $> 0.999$ .

**Table 2.3: ICP-OES parameters for the determination of Ca, Mg, Si, Fe, Mn and Al.**

Instrument:	Varian 725-ES ICP-OES
Matrix:	seawater, groundwater and sequential extraction solutions diluted in 2% $\text{HNO}_3$
Eluant:	Argon
Power	1.4 kW
Coolant gas	12.0 $\text{L min}^{-1}$
Auxiliary flow	1.5 $\text{L min}^{-1}$
Plasma Flow	15 $\text{L min}^{-1}$
Nebuliser flow	0.68 $\text{L min}^{-1}$
Viewing height (above load coil)	8 mm
Replicate read times	4 s
$\lambda$ , nm	Al (396.152), Ca(422.7), Fe(238.204), Mg(285.213), Mn(257.61), Si(251.611)

**Table 2.4: ICP-MS parameters for the determination of trace metal concentrations.**

Instrument	Thermo Scientific X-series 2 ICP-MS
Matrix:	seawater, groundwater and sequential extraction solutions diluted in 2% $\text{HNO}_3$
Eluant:	Argon
Forward Power	1.4 kW
Coolant gas	13.0 $\text{L min}^{-1}$
Auxiliary flow	0.8 $\text{L min}^{-1}$
Plasma Flow	15 $\text{L min}^{-1}$
Nebuliser flow	0.85 $\text{L min}^{-1}$
Nebuliser	Glass concentric
Spray Chamber assembly	ESI PC <sup>3</sup>
Collision cell * 7% $\text{H}_2$ in He	3.5 $\text{mL min}^{-1}$
Dwell time, ms	U, Mn, Fe and Al 10, Tc 40
Mass:charge ratio (m/z)	$^{27}\text{Al}$ , $^{55}\text{Mn}$ , $^{56}\text{Fe}$ , $^{238}\text{U}$ , $^{209}\text{Bi}$ , $^{115}\text{In}$
Optimisation	Multi-element standard containing 10 $\mu\text{g L}^{-1}$ Ba, Be, Bi, Ce, Co, In, Li, Ni, Pb and U.

Samples were diluted to within the calibration range using 2% (v/v) nitric acid. An internal standard solution containing Bi and In was added to all blanks, samples and matrix matched standards to give final concentrations of 0.05  $\mu\text{M}$  and 0.09  $\mu\text{M}$  respectively. Calibration blanks and checks were run after every 10 samples to check for instrument drift; if the drift exceeded 10% samples were re-run.

## 2.3 Results and discussion

**2.3.1 Sediment and water characterisation:** Crediton sediments were dominated by quartz with silicates (chlorite and muscovite), feldspars (albite and microcline) and hematite. Dounreay sediments were composed of quartz, phyllosilicates (orthoclase clinocllore, muscovite). Both Dounreay and Crediton sediments were classified as sandy loam composed of sand (52 % Dounreay, 61 % Sellafeld) with silt (43 % Dounreay, 36 % Sellafeld) and a low clay content (5 % Dounreay, 3 % Sellafeld). These classifications are consistent with the low specific surface areas of Dounreay ( $5.92 \text{ m}^2\text{g}^{-1}$ ) and Crediton ( $6.57 \text{ m}^2\text{g}^{-1}$ ) sediments. The cation exchange capacity of the Dounreay sediment ( $12 \pm 1 \text{ mEq}/100 \text{ g}$ ) was greater than the Crediton sediment ( $9.3 \pm 1 \text{ mEq}/100 \text{ g}$ ), reflecting the higher clay content of Dounreay sediments. Both sediments were acidic in character with a pH of  $4.4 \pm 0.2$  (Dounreay) and  $3.9 \pm 0.3$  (Crediton). The major element composition of the sediments determined following an aqua regia digestion are shown in Table 2.5. The total organic carbon content of the sediments was 4% (Dounreay) and 2% (Crediton) by mass, respectively.

**Table 2.5: Major elemental composition of the sediments determined using an inductively coupled plasma mass spectrometer (ICP-MS) following aqua regia digestion. Means shown (n=3)  $\pm$  1 standard deviation.**

	Dounreay, mmol kg <sup>-1</sup>	Crediton, mmol kg <sup>-1</sup>
Al	300 $\pm$ 9	670 $\pm$ 20
Ca	33 $\pm$ 3	38 $\pm$ 1
Fe	280 $\pm$ 8	420 $\pm$ 6
Mg	140 $\pm$ 4	120 $\pm$ 4
Mn	5.0 $\pm$ 0.3	16 $\pm$ 0.1
Si	25 $\pm$ 1	25 $\pm$ 2
Sr	0.10 $\pm$ 0.01	0.15 $\pm$ 0.01

The mineralogy and particle character in the sediments sourced from Crediton were similar to those sourced 2 km from the Sellafield site (Cumbria, UK) that represent the Quaternary unconsolidated alluvial flood-plain deposits underlying Sellafield (Law *et al.* 2010).

The characteristics of the waters used in the mobilisation experiments are summarised in Table 2.6.

### 2.3.2 Uptake of $^{90}\text{Sr}$ and solid phase associations

During the initial 7 day contamination of the sediments  $^{90}\text{Sr}$  was effectively removed from the groundwater solution and became associated with the sediments. Significantly more ( $p=0.000$ )  $^{90}\text{Sr}$  was associated with Crediton sediments ( $89 \pm 3 \%$ ) compared with Dounreay sediments ( $80 \pm 2 \%$ ).

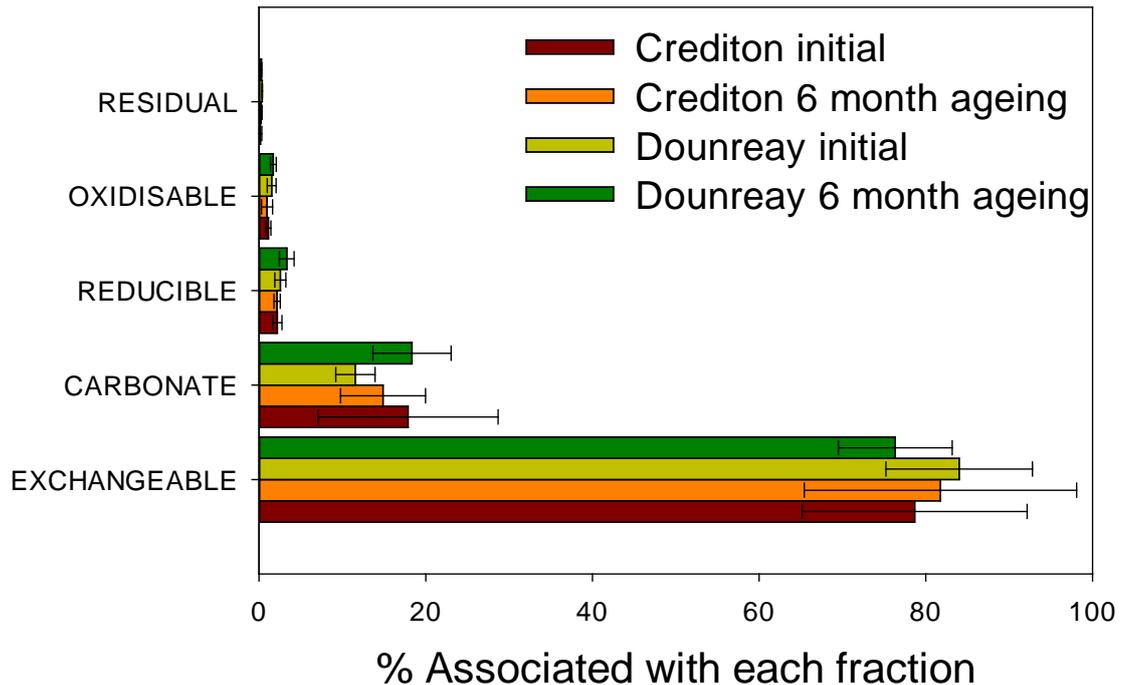
**Table 2.6: Differences in pH, ionic strength, salinity and major cations and anions in groundwater, low salinity water and seawater used in the batch and column experiments**

	groundwater	low salinity water	Seawater
<b>pH</b>	7.35	7.8	7.8
<b>Ionic strength, M</b>	0.045	0.11	0.70
<b>Salinity</b>		4	35
<b>Major cations and anions, mmol L<sup>-1</sup></b>			
Na <sup>+</sup>	0.015	18	460
Mg <sup>2+</sup>	0.0074	2.1	53
Ca <sup>2+</sup>	0.0042	0.42	10
K <sup>+</sup>	0.00017	0.40	10
Sr <sup>2+</sup>	0.0049	0.010	0.15
Cl <sup>-</sup>	0.0010	21	540
SO <sub>4</sub> <sup>2-</sup>	0.0028	0.27	6.8
CO <sub>3</sub> <sup>2-</sup>	0.0039	0.097	2.3

**Solid phase associations:** Sequential extractions were conducted on sediments immediately after the 7 day sorption period and again after a 6 month ageing period (Figure 2.3). The sequential extractions did not identify any significant change ( $p=0.072$ ) in the solid phase association of  $^{90}\text{Sr}$  over this period in either sediment. Strontium was predominately associated with the exchangeable fraction in both Dounreay ( $76 \pm 7.0\%$ ) and Crediton ( $82 \pm 16\%$ ) sediments. A smaller percent of  $^{90}\text{Sr}$  was associated with the carbonate fraction [ $14.9 \pm 5.1\%$  (Crediton);  $18.3 \pm 4.7\%$  (Dounreay)].

The sediments were acidic in character, thus would not be expected to contain significant concentrations of carbonate minerals. Therefore, the 'carbonate fraction' reflected a pH dependent exchangeable fraction, which was mobilised at the lower pH of the second leach step (initially pH 5 compared with pH 7 in the first step). This would presumably be exchangeable at the ambient sediment pH of 3.9 - 4.4. Importantly, only a small amount of  $^{90}\text{Sr}$  was associated with the less exchangeable fractions.

The association of  $^{90}\text{Sr}$  with the exchangeable fraction is consistent with other studies (Jackson and Inch 1983; Standring *et al.* 2002) and suggests that a significant fraction of  $^{90}\text{Sr}$  was reversibly sorbed via ion exchange. Importantly, the 6 month ageing period had no significant ( $p > 0.05$ ) effect on the association of  $^{90}\text{Sr}$  with the sediments which suggests that  $^{90}\text{Sr}$  does not become less exchangeable in these sediments over time, in agreement with previous findings for Mediterranean loamy and loam-sandy soils (Rigol *et al.* 1999).



**Figure 2.3: Changes in the solid phase associations of <sup>90</sup>Sr with Sellafield and Dounreay sediments during a 6 month ageing period. The percentage of <sup>90</sup>Sr in each fraction using a modified Tessier sequential extraction is shown; error bars represent ± 1 standard deviation. Extractants are defined in Table 2.2.**

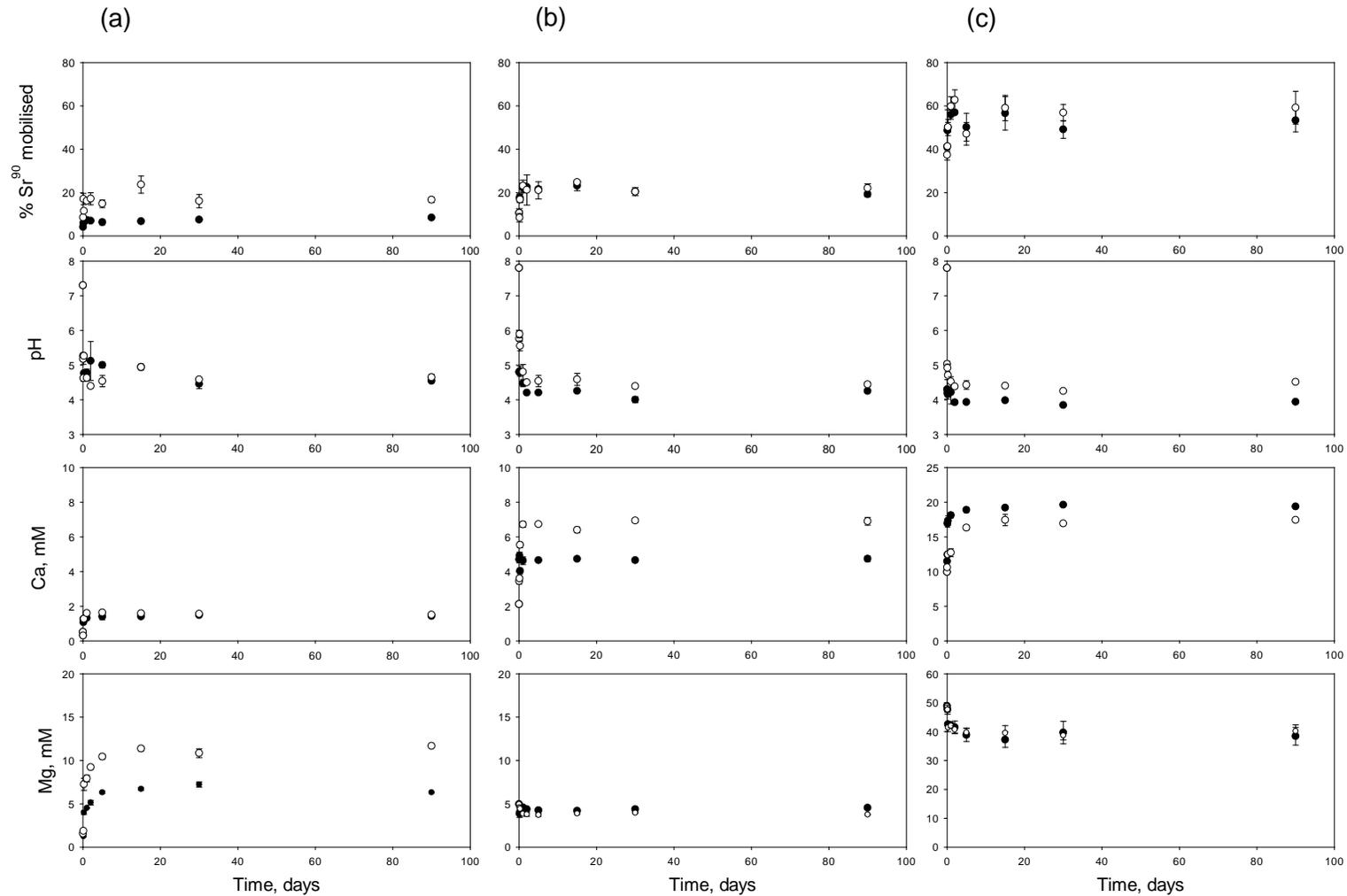
### 2.3.3 Mobilisation during inundation (1:1) scenarios

Batch experiments were conducted in order to investigate the mobilisation of <sup>90</sup>Sr from contaminated sediments during inundation with seawater. Sediments were suspended in groundwater, low salinity water and seawater at high (1:1) sediment to solution ratios over a 90 day period to investigate <sup>90</sup>Sr release with increasing porewater salinity. Results are shown in Figure 2.4.

**Changes in pH during inundation:** The high (1:1) sediment to solution ratio used in these experiments resulted in the pH of the experimental waters decreasing from pH 7.8 to 3.8-5.0 in seawater; pH 7.8 to 4-5.9 in low salinity water and pH 7.35 to 4.4-5.3 in groundwater. Sellafield sediments reduced the pH of each water to a greater extent than Dounreay sediments, due to the lower ambient pH.

**Major cations:** Due to similarities in ionic radii ( $\text{Mg}^{2+}$  65 pm;  $\text{Ca}^{2+}$  99 pm;  $\text{Sr}^{2+}$  113 pm (Mingos 1998)  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  may undergo exchange reactions with sorbed  $\text{Sr}^{2+}$ . Therefore the concentrations of aqueous  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined during the 90 d inundation experiment. In all experiments  $\text{Ca}^{2+}$  was rapidly mobilised from the sediments (Figure 2.4). Release of Ca followed the order groundwater < low salinity water < seawater, reflecting changes in the ionic strength of the water. Magnesium was rapidly mobilised from the sediments when resuspended in groundwater. However in seawater and low salinity water, aqueous  $\text{Mg}^{2+}$  concentrations decreased [seawater (from 49 mM to < 42 mM) and low salinity water (from 5.0 mM to < 4.5 mM)], indicating  $\text{Mg}^{2+}$  sorption onto the sediments.

The reactions taking place reflect the increasing ionic strength of the waters. In groundwater both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were mobilised from the sediments; however as the salinity of the waters increased ion exchange processes dominated. The presence of dissolved  $\text{Mg}^{2+}$  ions in seawater (53.1 mM) competed with  $\text{Ca}^{2+}$  associated with the sediments (33-38 mmol  $\text{kg}^{-1}$ ) to occupy exchangeable sediment surface sites.



**Figure 2.4: Mobilisation of  $^{90}\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  from  $\bullet$ Crediton and  $\circ$ Dounreay sediments and the corresponding changes in pH from during inundation with (a) groundwater, (b) low salinity water and (c) seawater. Sediments were contaminated with  $^{90}\text{Sr}$  ( $200 \text{ Bq g}^{-1}$ ) and aged for 6 months prior to mobilisation experiments. Data show means of 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Note the different scales for Mg and Ca mobilisation in seawater.**

**Inundation with groundwater:** When sediments were inundated with groundwater,  $^{90}\text{Sr}^{2+}$  was rapidly mobilised from both Dounreay and Crediton sediments in the first hour, together with Ca and Mg (Figure 2.4). After 24 h,  $7.3\% \pm 0.6\%$  was mobilised from Crediton and  $16\% \pm 1\%$  from Dounreay sediments. The concentration of  $^{90}\text{Sr}^{2+}$  in the groundwater remained relatively constant for the remainder of the experiment (90 d) [Crediton ( $6.3\% - 8.4\%$ ); Dounreay ( $18\% - 24\%$ )], showing that  $^{90}\text{Sr}^{2+}$  was not re-adsorbed over time.

Sequential extractions did not identify any significant differences in the association of  $^{90}\text{Sr}$  between Crediton and Dounreay sediments (Figure 2.3). However  $^{90}\text{Sr}^{2+}$  was mobilised more rapidly from Dounreay sediments and at the end of the 90 d period significantly more ( $p = 0.002$ )  $^{90}\text{Sr}^{2+}$  was mobilised from the Dounreay ( $17 \pm 1\%$ ) compared with the Crediton ( $8.5 \pm 1\%$ ) sediments.

**Inundation with low salinity water:** Similar to the groundwater incubations in the low salinity water (salinity 4)  $^{90}\text{Sr}^{2+}$  was rapidly mobilised, within the first hour  $\approx 11\%$  of the sediment associated  $^{90}\text{Sr}^{2+}$  released from the sediments (Figure 2.4). After 24 h  $22\% \pm 2\%$  (Crediton) and  $23\% \pm 3\%$  (Dounreay) of  $^{90}\text{Sr}^{2+}$  was released and there was no evidence of  $^{90}\text{Sr}^{2+}$  re-adsorption onto the sediments. However, at this higher salinity (compared with groundwater) there was no significant difference ( $p = 0.112$ ) in the percentage of  $^{90}\text{Sr}^{2+}$  mobilised from Dounreay and Sellafield sediments ( $\approx 25\%$  for both sediments after 90 d), or the initial rate of desorption. Therefore, this relatively low salinity water masked the differences in sediment properties (Section 2.3.1) that resulted in different  $^{90}\text{Sr}^{2+}$  release rates into groundwater for the Dounreay and Crediton sediments.

**Inundation with seawater:** The greatest mobilisation of  $^{90}\text{Sr}^{2+}$  occurred when sediments were inundated with seawater (Figure 2.4). Within 1 h, a significant fraction

(37 -41 %) of  $^{90}\text{Sr}^{2+}$  was released from Crediton and Dounreay sediments. After 24h, this increased to  $56 \% \pm 2 \%$  from Crediton and  $60 \% \pm 4 \%$  from Dounreay sediments respectively. At the end of the experiment (90 d) there was no significant difference ( $p=0.354$ ) in the percentage of  $^{90}\text{Sr}^{2+}$  mobilised from each sediment into seawater. The differences in the sediment properties again had no discernible effect of the mobilisation of  $^{90}\text{Sr}^{2+}$  into seawater. Calcium and  $^{90}\text{Sr}^{2+}$  were mobilised from the sediments and  $\text{Mg}^{2+}$  was removed from the seawater, which suggests that ion exchange at the sediment surface, in particular exchange with  $\text{Mg}^{2+}$ , controlled the  $^{90}\text{Sr}^{2+}$  release observed here.

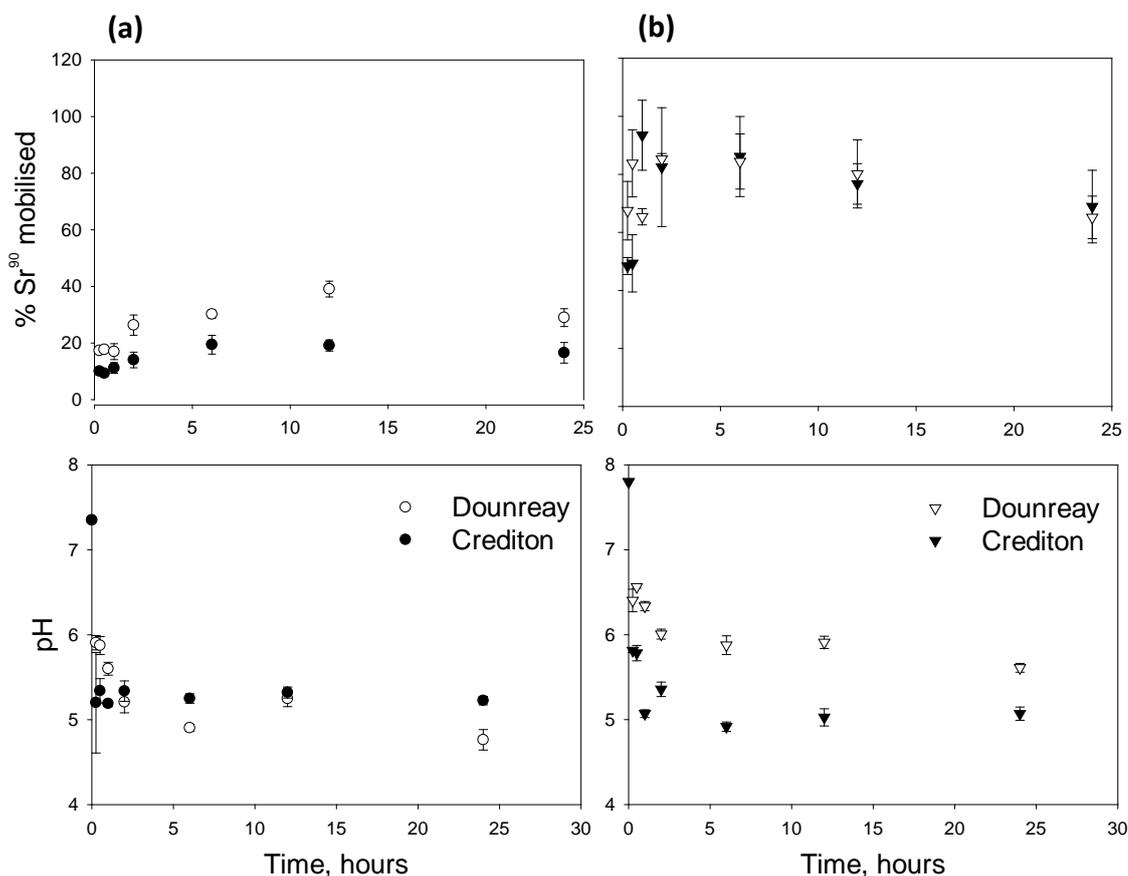
**Release of  $^{90}\text{Sr}$  during inundation (1:1) scenarios:** The percentage of  $^{90}\text{Sr}^{2+}$  released increased with the increasing ionic strength of the matrix, i.e. groundwater  $\leq$  low salinity water  $\ll$  seawater, in accordance with an ion exchange process. This involved  $\text{Mg}^{2+}$  from the saline waters replacing  $^{90}\text{Sr}^{2+}$  associated with exchangeable surface sites. Exchange was facilitated by the similarities in ionic radii of these divalent cations (Ahmad 1995; Jeong *et al.* 1996; Bunde *et al.* 1997; McKinley *et al.* 2007) and the high  $\text{Mg}^{2+}$  concentrations in seawater (Table 2.6). The rapidity of  $^{90}\text{Sr}^{2+}$  desorption was also consistent with an ion exchange process.

The results of the inundation experiments were consistent with the sequential extraction data (Figure 2.3), which showed a large pool of exchangeable  $^{90}\text{Sr}^{2+}$  in both sediments.

### **2.3.4 Mobilisation during erosion (1:10) scenarios**

Sediments were suspended in seawater and groundwater at a lower (1:10) sediment to solution ratio with continuous horizontal shaking at high speed in order to investigate the mobilisation of  $^{90}\text{Sr}$  during erosion of contaminated sediments into seawater.

**Changes in pH during erosion:** The sediments had a significant effect on the pH in both seawater and groundwater (Figure 2.5). After 24 h, the pH had decreased from 7.8 to 5.0 (Crediton) and 5.9 (Dounreay) in the seawater incubations and from 7.3 to 5.3 (Crediton) and 5.2 (Dounreay) in the groundwater incubations (Figure 2.5).



**Figure 2.5: Mobilisation of  $^{90}\text{Sr}^{2+}$  and corresponding changes in pH from Dounreay and Crediton sediments during erosion with (a) groundwater and (b) seawater. Sediments were contaminated with  $^{90}\text{Sr}$  and aged for 6 months prior to mobilisation experiments. Data show means of three separate experiments, error bars represent  $\pm 1$  standard deviation**

**Mobilisation into groundwater:** When suspended in groundwater  $^{90}\text{Sr}^{2+}$  was mobilised more rapidly from Dounreay than Crediton sediments (Figure 2.5). Maximum  $^{90}\text{Sr}^{2+}$  release was observed from Crediton sediments (19 %) after 6 h and from Dounreay sediments (39 %) after 12 h. The concentration of  $^{90}\text{Sr}^{2+}$  mobilised from both sediments then remained constant within experimental uncertainty [18 % (Crediton); 34 % (Dounreay)]. At the end of the 24 h experiment, release from the Dounreay sediments

was significantly higher ( $p=0.001$ ) than from the Crediton sediments which was similar to the trend observed during the inundation experiments.

**Comparison of inundation (1:1) and erosion (1:10) with groundwater:** Strontium was mobilised to a greater extent in the erosion experiments compared with the inundation experiments. For example, after 24 h, significantly (Crediton  $p= 0.035$ ; Dounreay  $p= 0.002$ ) more  $^{90}\text{Sr}^{2+}$  was released during erosion (Crediton 17 %; Dounreay 39 %) compared with inundation (Crediton 7.3 %; Dounreay 16 %).

However, when the sediment to solution ratio is taken into account, the  $K_D$  (Equation 2.2) of the erosion scenario was 4-5 times greater in each case (Table 2.7), i.e. there was a higher association with the sediment relative to the solution.

$$K_D = \frac{{}^{90}\text{Sr activity g}^{-1} \text{ sediment}}{{}^{90}\text{Sr activity mL}^{-1} \text{ solution}} \quad (2.2)$$

This can be explained by the particle concentration effect (EPA 1999), which is widely observed for heavy metal sorption in marine and freshwater environments (Honeyman and Santschi 1988; Benoit *et al.* 1994; Benoit and Rozan 1999) and has been observed previously for Sr in marine and river sediments (Benes and Poliak 1990; Benkdad *et al.* 2008).

**Table 2.7 Differences in  $K_D$  (distribution coefficient) during erosion and inundation with groundwater and seawater after 24 h, means of 3 separate experiments shown.**

	Crediton $K_D$ , mL g <sup>-1</sup>		Dounreay $K_D$ , mL g <sup>-1</sup>	
	Inundation	Erosion	Inundation	Erosion
Groundwater	12.6	50.3	5.17	24.5
Seawater	0.79	4.51	0.67	5.35

**Mobilisation into Seawater:** Strontium was rapidly released from both Crediton and Dounreay sediments (Figure 2.5) into seawater. Maximum release of  $^{90}\text{Sr}^{2+}$  was observed after 1 h from the Crediton sediments ( $93 \pm 12 \%$ ) and after 2h from the Dounreay sediments ( $85 \pm 10 \%$ ). At the end of the experiment, there was no significant difference ( $p=0.337$ ) in the  $^{90}\text{Sr}^{2+}$  concentration released in the two experiments (53-59 %).

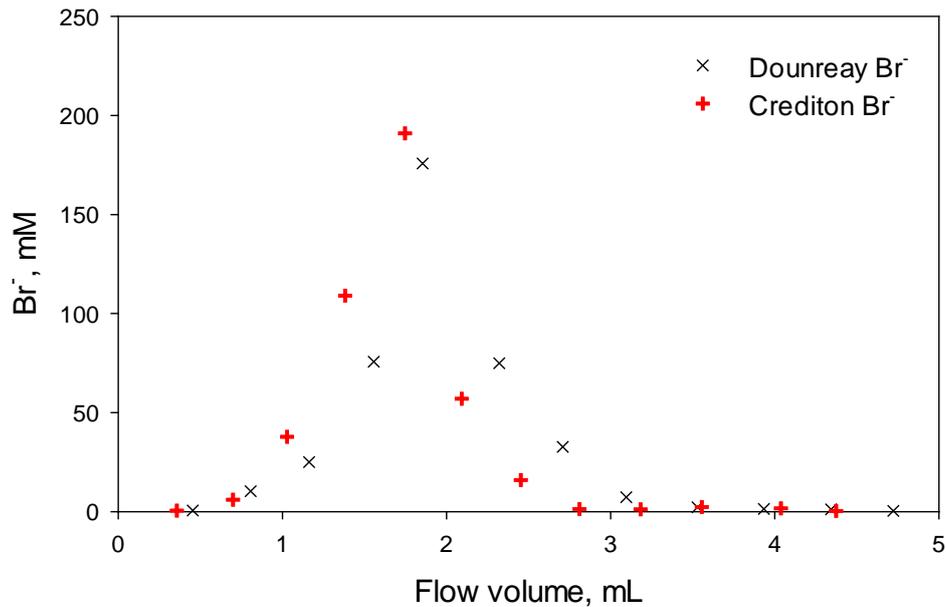
**Comparison of inundation(1:1) and erosion (1:10) with seawater:** Again,  $^{90}\text{Sr}^{2+}$  was initially mobilised more rapidly during erosion than during inundation. However after 24 h similar percentages of  $^{90}\text{Sr}^{2+}$  were released during erosion (65 - 68 %) and inundation (56 - 59%). Similar to groundwater experiments, the  $K_D$  of the erosion scenario was greater than the  $K_D$  of the inundation scenario for both Crediton and Dounreay sediments (Table 2.6). This shows that the release of  $^{90}\text{Sr}^{2+}$  from Dounreay and Crediton sediments are also sensitive to the sediment:solution ratio and therefore changes in suspended matter concentration.

### 2.3.5 Mobilisation of $^{90}\text{Sr}$ into seawater under dynamic flow conditions

Column experiments were used to investigate the mobilisation of  $^{90}\text{Sr}^{2+}$  from Crediton and Dounreay sediments in seawater under more environmentally relevant dynamic flow conditions.

**Column characterisation:** Columns were characterised using a conservative bromide tracer. The breakthrough curves for  $\text{Br}^-$  in both Crediton and Dounreay columns were very similar (Figure 2.6), with narrow peaks, suggesting that there were no preferential flow paths or dead volumes. Maximum  $\text{Br}^-$  concentrations were observed after 1.85 mL of seawater had flowed through the Crediton column and 1.74 mL through the Dounreay column, indicating a small difference in the column porosities.

This can be attributed to differences in the particle size distribution of the sediments, with the Crediton sediments having a greater proportion of sand. The linear flow velocity through the column was calculated as  $253 \text{ m y}^{-1}$  for Crediton and  $240 \text{ m y}^{-1}$  for Dounreay sediments.



**Figure 2.6: The elution profile for the transport of the conservative Br<sup>-</sup> tracer in Crediton (+) and Dounreay (X) column experiments.**

**Changes in pH:** The sediments altered the pH of the inflowing seawater (Figure 2.7) reaching a minimum pH of 3.6-3.8 which was consistent with the batch experiments. The pH then increased steadily to 7.8 after  $\approx 110 \text{ mL}$  of seawater had flowed through the column and then remained constant for the duration of the experiment.

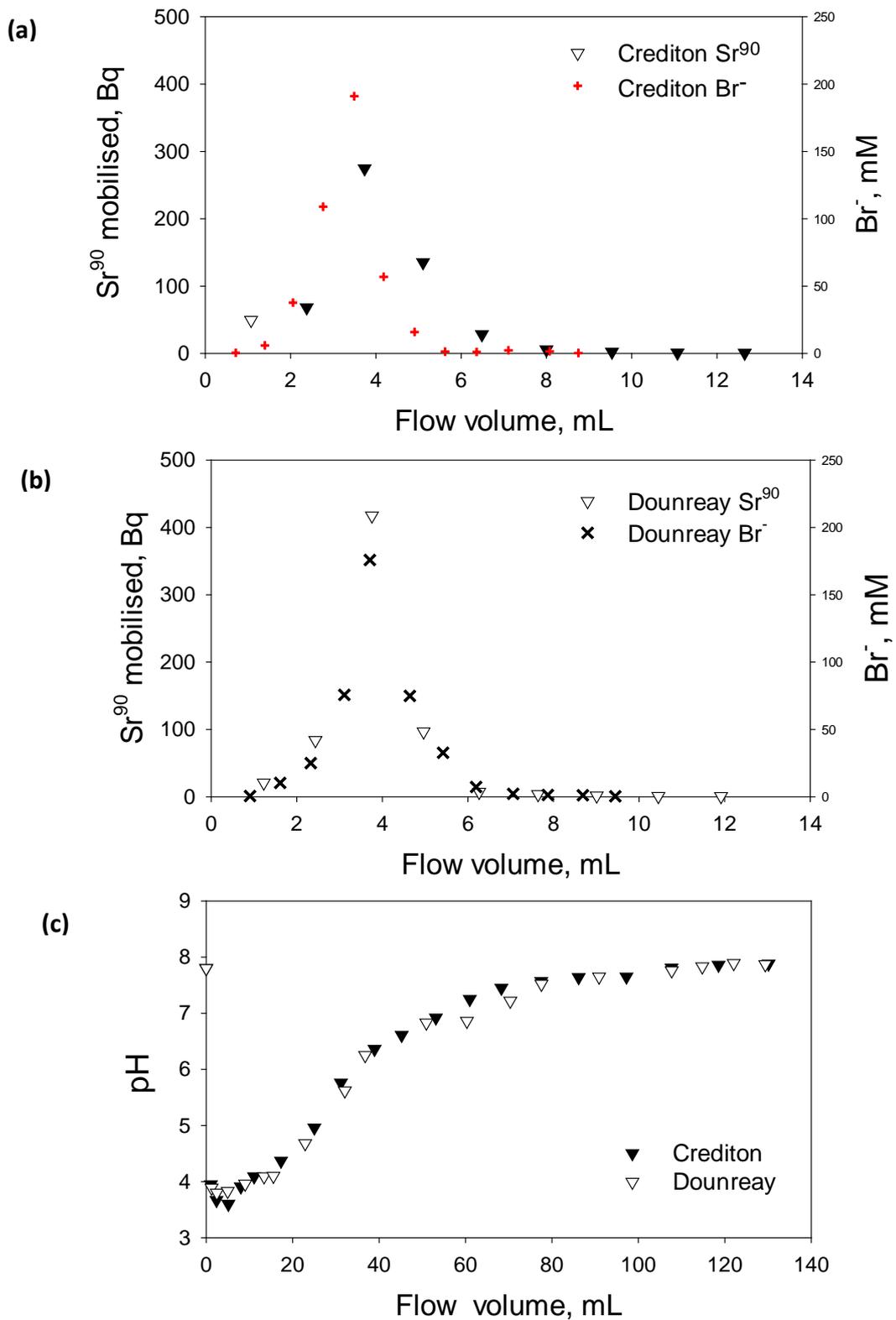
**Mobilisation of <sup>90</sup>Sr:** The release of <sup>90</sup>Sr<sup>2+</sup> closely followed the elution pattern of the conservative Br<sup>-</sup> tracer (Figure 2.7). However, the tracer was injected onto the column in a pulse; therefore <sup>90</sup>Sr transport was slightly delayed with respect to the injected tracer. This is indicative of <sup>90</sup>Sr<sup>2+</sup> having a very low interaction with the sediment (i.e.

low  $K_D$ ), and agrees well with the related batch seawater experimental (inundation)  $K_D$  of  $\approx 0.7-0.8$ .

The release of exchangeable  $\text{Sr}^{2+}$  under dynamic flow through conditions has been observed previously from quartz sand in a high ionic strength (2 mM) eluate containing sodium bicarbonate (0.1 mM) and NaCl (0.2 mM) (Turner *et al.* 2006). Extensive release of  $^{85}\text{Sr}^{2+}$  from a natural silica sand was also observed when KCl (0.1 M) was injected into the column (Solovitch-Vella and Garnier 2006). The symmetrical shape of the elution peak suggests that  $^{90}\text{Sr}^{2+}$  associations with the solid phase are  $K_D$  controlled; i.e.  $^{90}\text{Sr}^{2+}$  is associated with ion exchange sites with rapid exchange kinetics, which was also observed in the sequential extractions (Figure 2.3).

A significant fraction of the sediment associated  $^{90}\text{Sr}^{2+}$  was mobilised from Crediton (80 %) and Dounreay (99 %) sediments. The extensive release of  $^{90}\text{Sr}^{2+}$  from the sediments into seawater confirms that  $^{90}\text{Sr}$  sorption was reversible and release into seawater was promoted via ion exchange processes.

Aqua regia digestion of the sediment following the column experiments confirmed that  $^{90}\text{Sr}$  was extensively mobilised from the sediments. The concentration of  $^{90}\text{Sr}^{2+}$  in the aqua regia digests of Dounreay sediment were below the limit of detection ( $0.4 \text{ Bq mL}^{-1}$ ). A small fraction of  $^{90}\text{Sr}$  ( $\approx 8\%$ ) remained associated with the Crediton sediments. The mass balances were  $99 \pm 9.9 \%$  for Dounreay sediments and  $88 \pm 8.8 \%$  for the Crediton sediments.



**Figure 2.7: Mobilisation of  $^{90}\text{Sr}$  from (a) Crediton and (b) Dounreay sediments relative to the conservative  $\text{Br}^-$  tracer. Also shown are (c) changes in the pH of the eluate during the mobilisation experiments (note the different flow volume scale). Sediments were contaminated with  $^{90}\text{Sr}$  and aged for 6 months prior to the mobilisation experiments.**

## 2.4 Environmental implications

Here we have shown for the first time that the temporary flooding, inundation and erosion of contaminated sediments at legacy sites such as Dounreay and Crediton (UK) with seawater, e.g. as a result of sea level rise, would lead to the rapid mobilisation of  $^{90}\text{Sr}^{2+}$ .

Mobilisation of  $^{90}\text{Sr}$  was relatively rapid ( $< 24$  h) and significant in groundwater (7 - 16 %), low salinity water (23 %) and seawater ( $\approx 60$  %). The percentage of  $^{90}\text{Sr}^{2+}$  released increased with the increasing ionic strength of the matrix; this is consistent with the reversible sorption of  $^{90}\text{Sr}$  to exchangeable binding sites on the sediments. In seawater, release was promoted due to the high concentrations of cations, in particular  $\text{Mg}^{2+}$ . In both seawater and low salinity water  $\text{Mg}^{2+}$  was sorbed onto the sediments concurrent with  $^{90}\text{Sr}$  desorption suggesting an ion exchange process.

A similar fraction of  $^{90}\text{Sr}$  was mobilised from both Crediton and Dounreay sediments ( $\approx 60$  %) during erosion into seawater; however the transfer from a freshwater to a seawater environment had a greater effect on  $^{90}\text{Sr}$  release from Crediton sediments. For example, transfer of Crediton sediments from a freshwater to a seawater environment resulted in an 8 fold increase in  $^{90}\text{Sr}$  release whilst this was 4 fold from Dounreay sediments. Column experiments confirmed the behaviour seen in the batch systems, and further demonstrated that  $^{90}\text{Sr}^{2+}$  will be readily mobilised in seawater regardless of the physical process that occur when sediments are suspended in seawater.

Therefore,  $^{90}\text{Sr}$  mobilisation is expected from both Crediton and Dounreay sediments during inundation and erosion and this has implications for local contamination. Ion exchange processes will likely result in a rapid short term decline in water quality surrounding a nuclear facility following any erosion, inundation and flooding events. Releases of  $^{90}\text{Sr}$  from contaminated sediments may pose a threat to environmental receptors such as shellfish, fish and seaweed (Davidson *et al.* 2005; Morita *et al.* 2010;

SEPA 2011). As  $^{90}\text{Sr}$  dissolved in seawater is considered to have a weak interaction with marine sediments (Lee *et al.* 2005) contamination of local sediments appears less likely.

## **Chapter 3**

### **Mobilisation of U(VI) from contaminated sediments under inundation and erosion scenarios**

### 3.1 Introduction

Uranium is a major and persistent ( $t_{1/2} = 4.5 \times 10^9$  years) radioactive component of contamination at nuclear facilities, mines and waste disposal sites. However the fate of U(VI) associated with oxic sediments following porewater salinization or erosion into seawater remains unclear.

In oxic, circumneutral pH environments sorption to mineral surfaces via surface complexation concentrates U(VI) onto soils and sediments (Curtis *et al.* 2006). In particular, clays (Whicker *et al.* 2007; Rodriguez *et al.* 2008), iron (oxy)hydroxides (Martinez *et al.* 1995; Gómez *et al.* 2006; Duquene *et al.* 2008; Sherman *et al.* 2008) and aluminium and silica oxides (Sylwester *et al.* 2000) are important phases retaining U(VI) in soils and sediments.

Reversible sorption of U(VI) associated with peat and calcareous soils (Braithwaite *et al.* 1997), in sediments with a high silt (41 %) and clay (30 %) fraction (Zheng and Wan 2005) and from pure phases such as goethite (Giammar and Hering 2001) has been reported. Mobilisation is affected by the aqueous and solid phase speciation of U, e.g. both the rate and extent of surface associated U increased with increasing pH and carbonate concentration (Mason *et al.* 1997).

The release and/or transport of U has also been investigated using column experiments (Qafoku *et al.* 2005; Liu *et al.* 2008; Handley-Sidhu *et al.* 2009; Liu *et al.* 2009). For example, the transport of U(VI) in rainwater through dune sand was limited by very slow desorption kinetics from a range of binding sites with different release kinetics (Handley-Sidhu *et al.* 2009). In addition, Qafoku *et al.*, 2005 attributed the slow release of U at mildly alkaline pH from sand textured sediments to diffusion from intraparticle regions prior to mobilisation.

Bicarbonate and carbonate are major components of seawater and U(VI) is known to form strong associations with carbonate. Therefore, during inundation and erosion, the formation of U(VI) carbonate complexes, such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Zhou and Gu 2005; Choy *et al.* 2006) may increase the mobility of surface associated U. Similarly, increased ionic strength promotes the mobilisation of U because dissolved cations compete with U for surface binding sites.

The aim of this Chapter was to investigate the mechanisms controlling the release of U(VI) due to the inundation, temporary flooding and erosion of U(VI) contaminated sediments into seawater during sea level rise scenarios. To allow for more site-relevant results, sediments were aged for 6 months after contamination with U(VI), prior to the mobilisation experiments and changes in the association of U(VI) with the sediments was determined using sequential extractions. The effects of increased porewater salinity on both the extent and kinetics of U(VI) mobilisation during inundation and flooding scenarios was quantified by studying the release into groundwater, low salinity water (salinity 4) and seawater (salinity 35) during long term batch (90 days) experiments. Short term (48 h) batch experiments were conducted to simulate U(VI) release during erosion scenarios into both groundwater and seawater. Finally saturated seawater column experiments were used study U(VI) mobilisation under more environmentally relevant flow conditions.

## **3.2 Experimental**

**3.2.1 Generation of contaminated sediments:** Contaminated sediments (< 2 mm fraction) were generated for use in batch and column mobilisation experiments. Dounreay and Crediton sediments were amended with a simulated groundwater solution containing U (25  $\mu\text{M}$ ) added as a nitrate salt [ $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] AnalaR BDH

Chemicals Ltd (Poole, England) After a 7 d sorption period slurries were centrifuged (4000 g 20 mins). Contaminated sediments were then homogenised and aged in the dark at  $21 \pm 0.5$  °C for 6 months, with periodic opening (every 10-20 days) to re-supply O<sub>2</sub> to the sediments, before use in batch and column mobilisation experiments. To assess if the sediments remained oxic during the ageing period a solid phase acid (0.5 M HCl) extraction procedure was used to extract sedimentary Fe(II) (Lovely and Phillips 1986) prior to spectrophotometric determination of Fe(II) using ferrozine ( $\lambda_{\text{max}} = 562$  nm) (Stookey 1970). Finally changes in the solid state chemical fractionation of U during the ageing period were monitored using a modified Tessier 5 step sequential extraction scheme (Kersten and Förstner 1987; Wallmann 1993) outlined in Section 2.2.9.

**3.2.2 Mobilisation of U from sediments during erosion and inundation:** Batch experiments were used to investigate the mobilisation of U from sediments during inundation and erosion with seawater. Finally column experiments were adopted to investigate U release under more environmentally relevant saturated flow through conditions.

**Inundation experiments:** Sediments were re-suspended into groundwater, low salinity water (salinity 4) and seawater (salinity 35) using a high (1:1) sediment:solution ratio (section) and shaken horizontally for up to 90 d (Section 2.2.7). At pre-determined time points (t= 1 h, 3 h, 6 h, 24 h, 5 d, 15 d, 30 d, 90 d) a 2 mL aliquot of the slurry was removed for immediate determination of pH. The remaining slurry was then centrifuged (4000 g for 30 min) prior to determination of U, Al, Mn, Fe, Si, Ca and Mg (Section 3.2.4).

**Erosion experiments:** Sediments were re-suspended into groundwater and seawater (salinity 35) at a lower (1:100) sediment:solution (m/v) ratio to investigate U mobilisation during erosion. Sediment slurries and shaken horizontally in the dark,

ensuring that the particles were in suspension for up to 48 h. At pre-determined time periods (t=15 min, 30 min, 1 h, 2 h, 6 h, 12 h and 24 h) an aliquot of the slurry was removed for immediate determination of pH. The remaining slurry was then centrifuged (4000 g for 30 min) prior to determination of U, Al, Mn, Fe, Si, Ca and Mg (Section 3.2.4).

**3.2.3 Dynamic flow through seawater column experiments:** Contaminated sediments were packed into a polyetheretherketone (PEEK) self-pack column the method is outlined in Section 2.2.8. The eluate was collected using a fraction collector in 1.2 - 3.6 mL fractions. Flow was stopped for 48 h during the saturated column experiments to assess whether U concentrations in the eluate solutions were in equilibrium with the U sorbed onto the sediments (Qafoku et al., 2005; Yin et al., 2011). The pH of the eluate was measured as soon as possible after collection, and samples were then acidified prior to determination U and Fe (Section 3.2.4). Both columns were characterised using a conservative bromide tracer. The linear flow velocity through the columns was calculated to be 268 m yr<sup>-1</sup> (Crediton) and 229 m yr<sup>-1</sup> (extensively iron reducing), respectively, which is within the range of flow velocities observed in sandy aquifers under natural hydrogeological conditions (Mackay *et al.* 1985). Eluate pH was measured as soon as practicable after elution and Br, Fe and U concentrations were determined by ICP-MS.

**3.2.4 Uranium determination** The U concentration in solution was determined by ICP-MS and the limit of detection, determined by 3 x the standard deviation of the lowest standard, was 0.013-13 nM in all extractants. The highest limit of detection was found in seawater due to the high background concentration of U in seawater ( $\approx$  13 nM). In order to maintain good quality assurance and allow intercomparison of results, a certified reference material TMDA-64 (Ontario lake water, National Research Institute,

Environment Canada) was analysed every time the ICP-MS was used. If the measured value was > 10 % different from the certified value, the standards were re-made and re-run.

### **3.3 Results and discussion**

#### **3.3.1 Uptake of U and solid phase associations**

**Sorption and ageing of U(VI):** Uranium sorbed to both the Dounreay and Crediton sediments within 8 h. After a 7 day sorption period, there was no significant difference ( $p= 0.78$ ) in the extent of U sorption to the Crediton ( $96 \pm 2 \%$ ) and Dounreay ( $99 \pm 4 \%$ ) sediments ( $n= 4$ ) despite differences in the pH determined in Crediton ( $\text{pH}= 4.2$ ) and Dounreay ( $\text{pH}= 4.8$ ) suspensions.

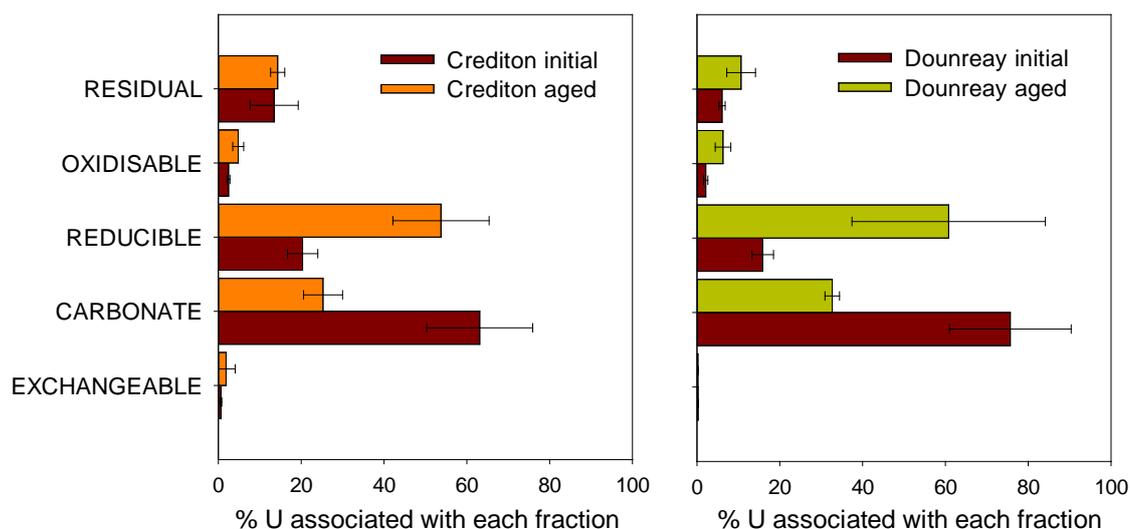
**Sequential extractions:** Sequential extractions were used to identify (1) differences in the solid state chemical fractionation of U in Dounreay and Crediton sediments and (2) changes in the solid state chemical fractionation of U in Dounreay and Crediton sediments during a 6 month ageing period. Uranium was associated with several different binding sites in both Dounreay and Crediton sediments (Figure 3.1).

Initially, U was associated predominately with the carbonate (63 - 76%) fraction.

During the 6 month ageing period there was a significant decrease in the percentage of U associated with the carbonate (to 25 - 33 %) fraction in both Dounreay ( $p= 0.029$ ) and Crediton ( $p= 0.015$ ) sediments. Over the same time period significantly more U became associated with the reducible fraction ( $p= 0.049$  Dounreay;  $p= 0.018$  Crediton) whilst the association of U with other fractions did not change significantly ( $p= 0.069-0.446$ ). Therefore, over time, there was a re-distribution of U and the association of U with

sedimentary Fe(oxy)hydroxides became increasingly important. These results highlight the long-term fixation of U by sediment components, with U being increasingly strongly bound to the sediments over time. Importantly, only a small fraction of the U was associated with the exchangeable fraction (< 0.3 %) and this decreased over time; thus U would not be expected to be readily mobilised on the basis of ion exchange alone during transfer from a freshwater to a seawater environment.

Uranium showed very similar uptake and geochemical associations with the two sediments. This reflects the similarities in the chemical and textural characteristics of the two sediments (Section 2.3.1), and the concentrations of acid extractable Fe (Crediton 420 mmol kg<sup>-1</sup>; Dounreay 280 mmol kg<sup>-1</sup>).



**Figure 3.1: Changes in the solid phase associations of U with; (a) Crediton and (b) Dounreay sediments during a 6 month ageing period. Percentage of U extracted in each fraction using a modified Tessier sequential extraction is shown. Means shown for 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Extractants are described in Table 2.2.**

### 3.3.2 Mobilisation during inundation

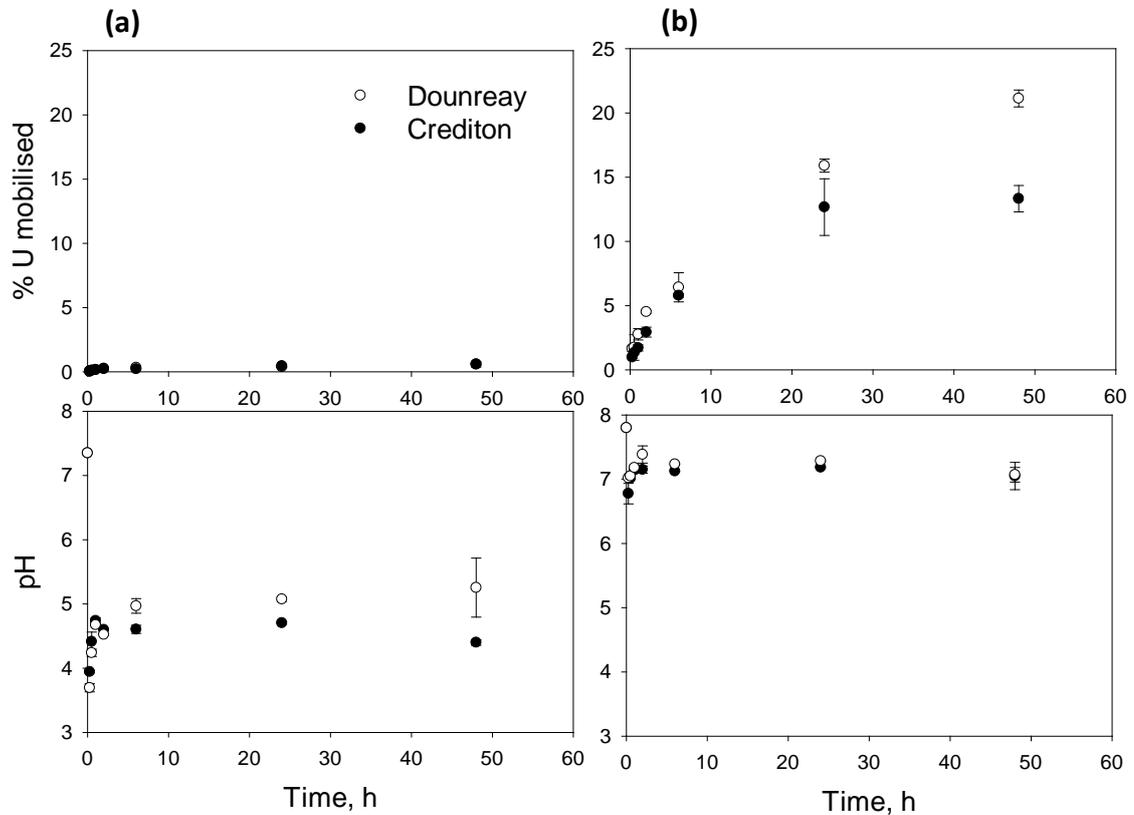
When the aged sediments were inundated with water, there was limited U mobilisation into either the groundwater or low salinity water (< 0.2 %), and the U concentrations in the seawater were less than the concentration of U naturally present in seawater (13 nM). Mobilisation of U(VI) is generally enhanced in the presence of carbonate, via complexation and the formation of aqueous complexes such as  $\text{UO}_2(\text{CO}_3)^{4-}$  and  $\text{UO}_2(\text{CO}_3)_2^{2-}$  (Zhou and Gu 2005; Choy *et al.* 2006). In these experiments, as a result of the high sediment to solution ratio used, the sediments caused a rapid and significant decrease in the pH of the experimental waters (pH 7.8 to 3.9-5.0 in seawater; pH 8.2 to 4.2-5.8 in low salinity water and pH 7.35 to 4.1-5.35 in groundwater). In the pH range measured in these experiments (pH 3.9-5.8) carbonate is not stable, resulting in limited formation of U-carbonate complexes and retention of U(VI) on the sediments (Barnett *et al.* 2000; Zhong *et al.* 2005).

### 3.3.3 Mobilisation during erosion

When U was mobilised from the sediments under the erosion scenario (1:100 sediment:solution ratio), the pH of each water phase was again affected by the sediments (Figure 3.2). However, the alkalinity of the seawater played a significant role, buffering the seawater systems more effectively against changes in pH (pH 6.78-7.39).

**U mobilisation in groundwater:** There was limited release of U into groundwater from both Dounreay and Crediton sediments (Figure 3.2). At the end of the 48 h experiment  $\approx 99$  % of the sediment associated U remained recalcitrant to mobilisation. There was no significant difference ( $p=0.0621$ ) in the release of U from the sediments. This is consistent with the similar geochemical associations of the U in the two sediments

(Figure 3.1), coupled with the limited association of U with the exchangeable fraction (1.8 % Crediton; 0.2 % Dounreay) and the pH of the experiments.



**Figure 3.2: Mobilisation of U and the corresponding changes in pH from Crediton and Dounreay sediments during mobilisation in (a) groundwater and (b) seawater during an erosion scenario. Sediments were contaminated with U in a simulated groundwater solution and aged for 6 months prior to mobilisation experiments. Data show the means of 3 separate extractions, error bars represent  $\pm 1$  standard deviation.**

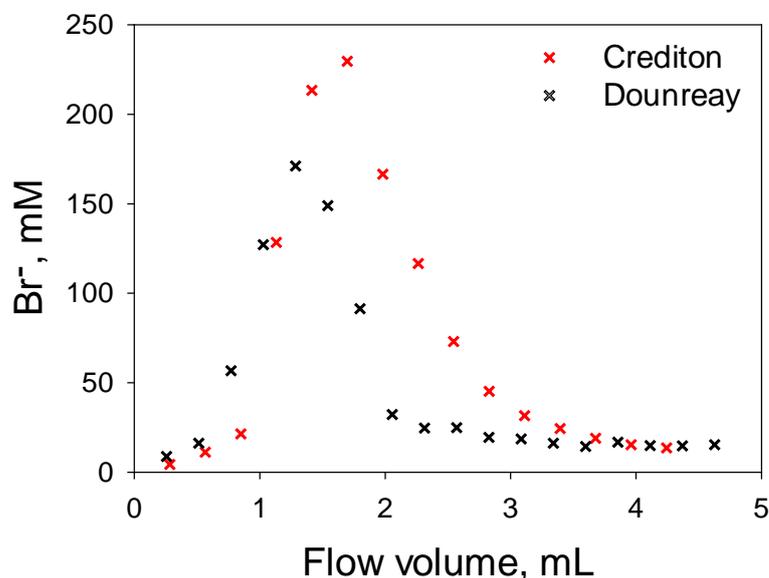
**Uranium mobilisation in seawater:** Significantly more U was mobilised into seawater compared with groundwater (Figure 3.2). Release was kinetically controlled, characterised by a rapid initial release followed by a slower approach to equilibrium. In the first 6 h the rate of release from both of the sediments was similar with 5.8 % mobilised from Crediton and 6.4 % from Dounreay sediments. After 24 h, Crediton sediments reached equilibrium but release was on-going from Dounreay sediments. At

the end of the 48 h experiment significantly ( $p= 0.001$ ) more U was released from the Dounreay sediments ( $21 \pm 0.7$  % compared with  $13 \pm 1.0$  %).

### 3.3.4 Mobilisation of U into seawater under dynamic flow conditions

Column experiments were conducted in order to understand the mobilisation of U from Crediton and Dounreay sediments under environmentally relevant flow conditions. Seawater was pumped vertically up through the column to create fully saturated conditions.

**Column characterisation:** Columns were characterised using a conservative  $\text{Br}^-$  tracer injected as a pulse through the column at the end of the mobilisation experiments. Figure 3.3 shows the  $\text{Br}^-$  elution data from the column experiments. Both profiles exhibited symmetrical peaks with no tailing; therefore there were no preferential flow paths or dead volumes (Schweich and Sardin 1981; Scism 2005).



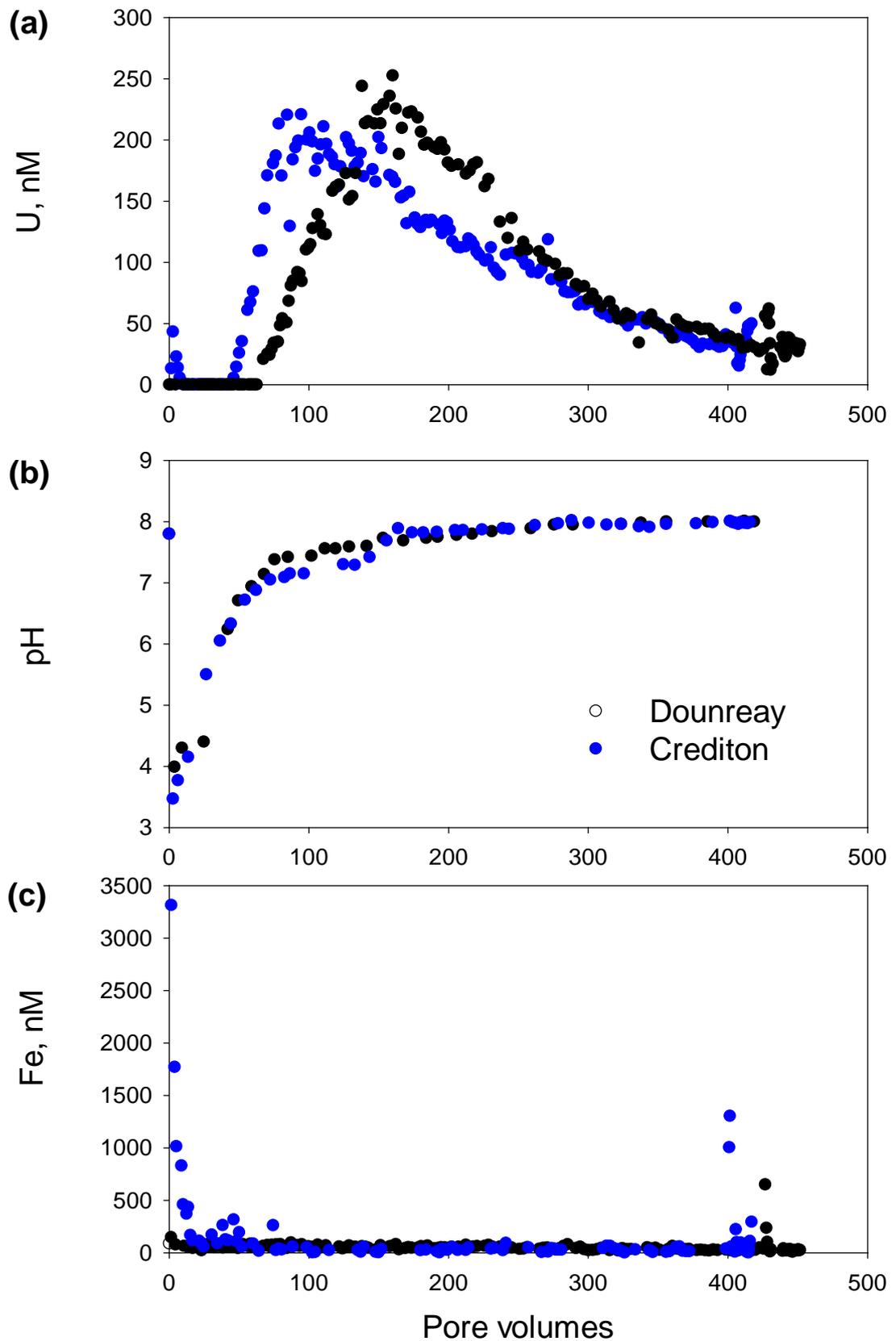
**Figure 3.3: The elution profile for the transport of the conservative  $\text{Br}^-$  tracer used in Crediton (X) and Dounreay (x) column experiments.**

There was some variation in the Br<sup>-</sup> elution profiles in the two columns, which shows that there was some difference between the sediments (e.g. particle size) and packing. The linear flow velocity was 268 m y<sup>-1</sup> (Crediton) and 229 m y<sup>-1</sup> for Dounreay columns respectively, which is within the typical range of 1-1000 m y<sup>-1</sup> for groundwater flow rates in uniform sand and gravel aquifers (Mackay *et al.* 1985).

**Changes in pH:** As seawater flowed through the columns, the sediments initially altered the seawater pH from an inflow of pH 7.8 to an outflow of pH 3.5 (Crediton) and pH 4.0 (Dounreay) (Figure 3.4). This is consistent with the pH changes seen in the inundation batch seawater experiments (pH 3.9 - 5.8), where high sediment to solution ratios were used. The pH in both columns then increased steadily, reaching pH 7 after 60 (Dounreay) and 72 (Crediton) pore volumes, and becoming more representative of seawater (pH 7.8) after 153 (Dounreay) and 155 (Crediton) pore volumes. At this point sediments had no further impact on the pH of the seawater, which remained relatively constant (pH 7.8 - 8.0) over the remainder of the experiment. The stop start event had no discernible effect on the pH.

**Uranium:** The initial mobilisation of U from the two sediments differed (Figure 3.4a). An initial rapid pulse release of U was observed from Crediton sediments which was only slightly retarded with respect to the Br<sup>-</sup> tracer (Figure 3.5). This initial pulse represented a small fraction of the total sediment associated U (0.3 %) and after 10 pore volumes the concentrations of U eluted were significantly lower than the concentration of U in seawater (13 nM).

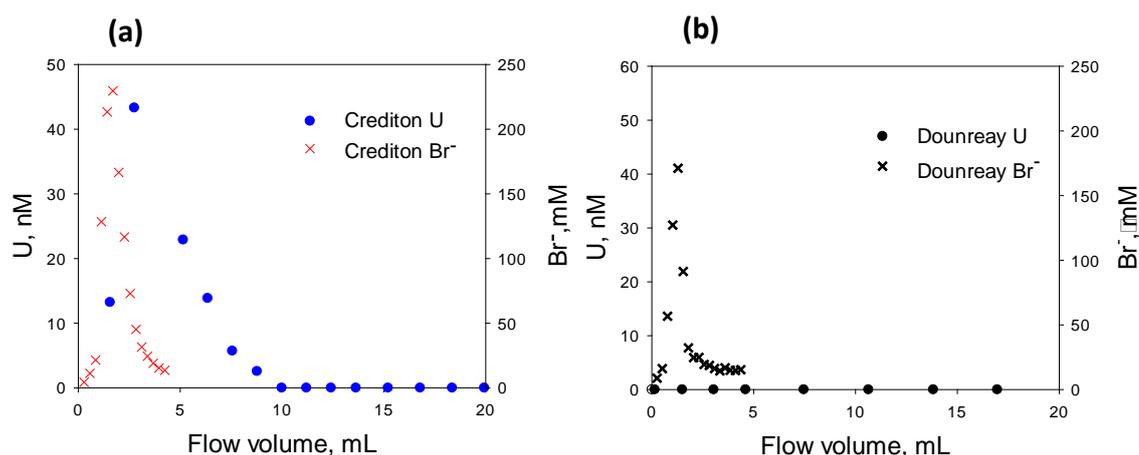
Uranium was predominately associated with the reducible fraction in Crediton sediments (Figure 3.1), presumably complexed with iron(oxy)hydroxides. The initial release of U correlated ( $r= 0.901$ ,  $p= 0.014$ ) with the release of Fe in the first 10 porevolumes.



**Figure 3.4: Mobilisation of (a) U, and (c) Fe coupled with changes in (b) pH from Crediton and Dounreay sediments under saturated dynamic flow through conditions with seawater. Where SSF represents a stop/start flow event.**

Acid (0.5 M HCl) extraction showed that there was no Fe(II) associated with the sediments therefore the sediments has not become iron reducing during the ageing period therefore it seems unlikely that Fe(II) was mobilised during this initial period.

However increasing ionic strength has been shown to displace trace metals and protons adsorbed on sediments, causing an initial decrease in pH, as the pH decreases Fe is more soluble and can become increasingly available for release (Wong *et al.* 2010). Therefore the release of U sorbed to or associated with exchangeable (labile) Fe may have been promoted during initial contact with seawater. After this, U sorption was the dominant on-column process. Neither Fe nor U was released from Dounreay sediments in this initial period.



**Figure 3.5: Mobilisation of U from (a) Crediton and (b) Dounreay sediments relative to the conservative Br<sup>-</sup> tracer during dynamic flow through mobilisation experiments.**

In both Dounreay and Crediton column experiments the sediments reduced the pH of the inflowing seawater and U remained associated with the sediments (Figure 3.4). Uranium mobilisation was only observed when the eluant pH increased, this is consistent with the current understanding of U(VI) mobility, i.e. surface associated U desorption mediated by the formation of soluble U(VI) species such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  and  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  (Duff *et al.* 2002; Dong *et al.* 2005;

Zhong *et al.* 2005; Fox *et al.* 2006). Uranium was mobilised after fewer porevolumes of seawater had flowed through the column from Crediton (46 pore volumes) compared with Dounreay (67 pore volumes) sediments and at a lower pH (Crediton pH 6.5; Dounreay pH 6.9). Maximum concentrations of U in the eluate were similar from Dounreay (252 nmol L<sup>-1</sup>) and Crediton (220 nmol L<sup>-1</sup>) sediments. However, despite the similarities in the associations of U in the two sediments as determined by sequential extractions, maximum concentrations of U(VI) were released more rapidly after reaching the critical pH (Crediton pH 6.5; Dounreay pH 6.9) in the Crediton column (85 pore volumes) than in the Dounreay column (160 pore volumes).

Following this peak, U continued to be released from the sediments. The tailing observed in the U release profiles for both sediments is indicative of kinetically controlled release (Serne *et al.* 2002; Scism 2005), which involves release from sites with slow desorption kinetics and/or a re-distribution between slow and fast reactive sites (Qafoku *et al.* 2005; Liu *et al.* 2008). Sequential extractions conducted prior to mobilisation experiments showed that U was associated with several operationally defined chemical fractions (carbonate, reducible, oxidisable and residual fractions, see Figure 3.1), some of which were more strongly bound to the sediments, which would give rise to a broad distribution of release rates.

The flow was stopped for 48 h during the tailing section of the release profile. After seawater flow was resumed there was an increase in the concentration of U mobilised, with similar concentrations of U mobilised from the two sediments (maximum for Crediton 62 nmol L<sup>-1</sup>; maximum Dounreay 57 nmol L<sup>-1</sup>). During the stop flow period the porewater was in contact with the sediment for a longer period of time (48 h), and the longer equilibration times resulted in higher concentrations of U. This also shows that, even in this reasonably high flow experiment (within the range of groundwater

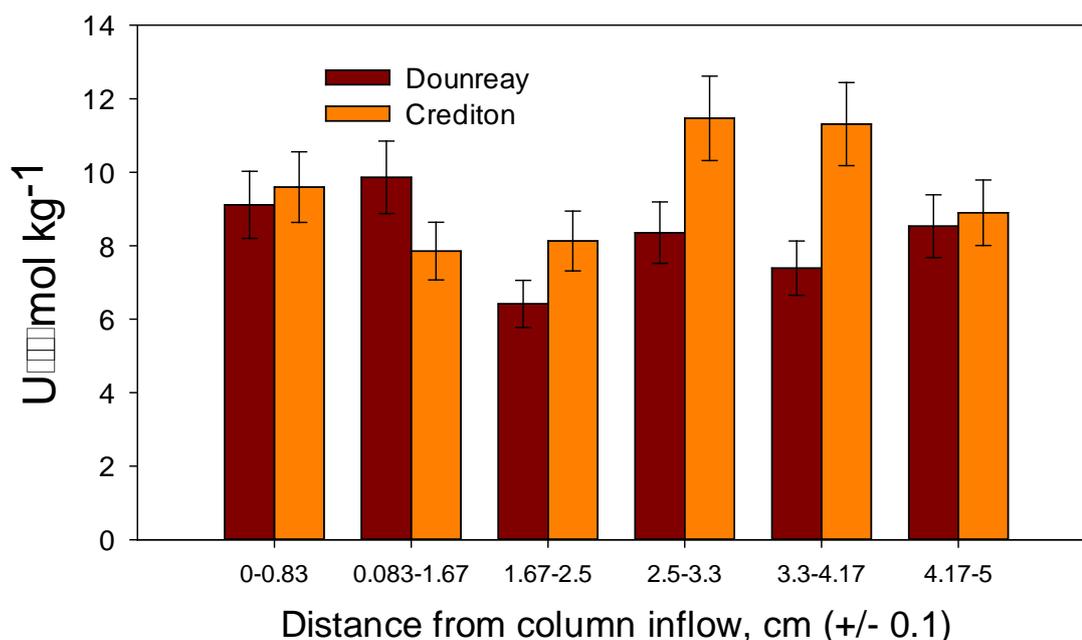
flow), the aqueous U concentrations were not in equilibrium with the solid phase concentrations and U release was kinetically controlled.

Uranium was predominately associated with the reducible fraction in sequential extractions (Figure 3.1) and, although Fe and U release did not correlate strongly after the stop-start ( $r = 0.698$  Crediton;  $r = 0.391$  Dounreay), Fe and U were simultaneously mobilised from both sediments (Dounreay Fe  $650 \text{ nmol L}^{-1}$ ; Crediton Fe  $1300 \text{ nmol L}^{-1}$ ). This again indicates that U associations with Fe(oxy)hydroxides play an important role in controlling U release. Both the U and Fe concentrations then rapidly decreased to similar concentrations prior to the stop/start flow event (Dounreay 6 pore volumes; Crediton 3.5 pore volumes). The stop/start flow event resulted in mobilisation of only a small fraction of the total U associated with the sediments (Dounreay 0.6 %; Crediton 0.1 %).

Overall, mobilisation of U was slow and a different release profile was observed for Crediton and Dounreay sediments (Figure 3.4). Despite differences in the release profiles, a similar fraction of U was mobilised from Crediton 46 % (over 417 pore volumes) and Dounreay 49 % (over 466 pore volumes) sediments. The largest fraction of sediment associated U was mobilised during the tailing period (defined as the U eluted after the peak U concentrations were determined in the eluant and before the stop/start flow event) for both release profiles (Crediton 40 %; Dounreay 39 %) which suggests that relatively slow desorption kinetics will dominate the mobilisation of U in the natural environment.

Aqua regia digestion of the sediments following the column experiments confirmed that a large fraction of U (49 - 63 %) remained associated with the sediments. Mass balance was achieved, with  $109 \pm 13$  % recovered from Crediton and  $98 \pm 12$  % recovered from Dounreay sediments respectively. There was no significant difference (ANOVA

unstacked MINITAB  $p > 0.05$ ) in the distribution of recalcitrant U in Crediton and Dounreay sediments (Figure 3.6), which indicates that U was mobilised evenly throughout the columns and transported with limited interaction with the sediment.



**Figure 3.6: Column digestion results showing the distribution of U along the column. Dounreay and Crediton sediments were contaminated with U, aged for 6 months prior to dynamic seawater column mobilisation experiments under fully saturated flow conditions. Error bars show  $\pm 10\%$  relative standard deviation from combined and analytical uncertainties.**

### 3.4 Environmental Implications

Here we have shown that U(VI) was present in the slow-release pool and exhibited similar behaviour and mobility in both Dounreay and Crediton sediments. Mobilisation of U(VI) from both Dounreay and Crediton sediments was affected by the pH of the system, which was controlled by the sediments themselves in the batch systems and during early elution from the column experiments. The column experiments showed that U(VI) was only mobilised significantly after the pH of the sediment porewaters had

increased, and the pH required was sediment specific. With the intrusion of/inundation by seawater, U release would be delayed with respect to the migrating seawater front. Mobilisation would follow the change in sediment pH, induced by the seawater. After that U release is kinetically controlled and characterised by a slow release from a range of binding sites. Therefore, slow release would be expected during seawater inundation and erosion of Dounreay and Crediton sediments. Uranium mobilised into seawater may become retained in the near surface-sediments associated with salt marshes (Church *et al.* 1981; Church *et al.* 1986; Church *et al.* 1996). Uranium(VI) in seawater may also diffuse into anoxic marine sediments and be reduced to U(IV), precipitating under the sediment-water interface (Anderson 1987).

In terms of erosion, U release would occur when particles are transported through the marine environment. Uranium associated with larger particles would be deposited and accumulate in low energy regions of the tidal system, such as mud banks and estuaries. However U associated with finer sediments would undergo longer range solid phase-associated transport. Sediments in intertidal areas such as estuaries can make a significant contribution to the total radiation exposure of members of the public as these areas are used by the general public (RIFE, 2012).

## **Chapter 4**

# **Uranium mobilisation from reduced sediments under saltwater intrusion scenarios**

## 4.1 Introduction

Uranium ( $t_{1/2} = 4.5 \times 10^9$  years) is a common contaminant found at nuclear facilities and waste disposal sites. In reduced sediments U can be present in both reduced U(IV) and oxidised U(VI) forms (Zhou and Gu 2005; Sharp *et al.* 2011).

U(VI) sorbs to a variety of minerals and related phases including clays (Whicker *et al.* 2007; Rodriguez *et al.* 2008), iron (oxy)hydroxides (Martinez *et al.* 1995; Gómez *et al.* 2006; Duquene *et al.* 2008; Sherman *et al.* 2008) and aluminium and silica oxides (Sylwester *et al.* 2000). Uranium(VI) can also co-precipitate with iron oxyhydroxides and calcium carbonates (Reeder *et al.* 2000; Duff *et al.* 2002) and so its behaviour, at least in some cases, may be influenced by the cycling of other elements in the system. Under reducing conditions, U(IV) species are formed which have a higher affinity for surface binding sites and a lower solubility than U(VI) (Langmuir 1978).

The influence of seawater intrusion on U mobilisation from terrestrial soils or sediments has not been previously investigated. Seawater intrusion causes significant changes in the chemical composition of pore waters such as increased pH, carbonate concentration and ionic strength. Therefore, the formation of U(VI) carbonate complexes, such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , at  $\text{pH} > 6$  (Zhou and Gu 2005; Choy *et al.* 2006) and ternary calcium uranium carbonate complexes including  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$  and  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  (Dong *et al.* 2005; Fox *et al.* 2006; Stewart *et al.* 2010) may enhance U mobilisation. Although thermodynamic data suggests that carbonate does not complex U(IV) or promote  $\text{UO}_2$  dissolution under reducing conditions (Guillaumont *et al.* 2003), the production of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  during microbial respiration has been shown to promote U(IV) release via the formation of stable U-carbonate complexes (Wan *et al.* 2005; Wan *et al.* 2008).

An intruding seawater plume can also introduce oxygen to the sediments and re-oxidise U(IV) to the more soluble U(VI). This has been observed to occur in batch experiments at circumneutral pH where U(IV) was rapidly oxidised to U(VI), followed by mobilisation promoted by bicarbonate complexation (Ulrich *et al.* 2008). When iron rich sediments (representative of Crediton, UK) were re-oxidised in air U(IV) was rapidly reoxidised (within 24 h) and mobilised into solution as U(VI) (Law *et al.* 2011). Reoxidation of sediments does not always lead to the mobilisation of U; for example Zhong *et al.*, (2005) found that U mobilisation from Oak Ridge sediments was limited during reoxidation by sorption of U(VI) to secondary Fe(III) minerals formed during reoxidation. The sediment used was rich in Fe, particularly iron oxides and iron silicates. Additionally, U(IV) may be incorporated into the structure of amorphous ferrihydrite during transformation into a crystalline structure (Payne *et al.* 1994). The products of iron/sulphate reduction such as mackinawite (FeS) have also been shown to partially protect U(IV) from oxidation at circumneutral pH in sandstone sediments with hematite and iron oxyhydroxide coatings (Abdelouas *et al.* 1999). Reoxidation of sorbed Fe(II) on the outer surface of sediments may form an Fe(III) oxide veneer that acts as a diffusional barrier protecting against U(IV) reoxidation (Zhong *et al.* 2005).

Relatively few studies have investigated the mobilisation of U from reduced sediments during reoxidation under more environmentally relevant flow conditions (Abdelouas *et al.* 1999; Moon *et al.* 2007; Komlos *et al.* 2008; Komlos *et al.* 2008; Moon *et al.* 2009) . These studies have shown that secondary products formed during Fe reduction do not protect U(IV) from oxidation and mobilisation under flow conditions (Moon *et al.* 2007; Komlos *et al.* 2008). However iron sulfide precipitates such as mackinawite formed during reduction can act as a buffer to partially prevent U oxidation and/or release under flow conditions from sandstone (Abdelouas *et al.* 1999) and from sediments from a former uranium processing facility (Moon *et al.* 2009). However the ability of Fe phases

to retard U oxidation and/or release into seawater under flow conditions nonetheless remains unclear.

Here the effect of increased porewater salinity on the mobilisation of U from geochemically reduced sediments at different stages of reduction during seawater intrusion is considered. Long term (120 day) batch studies were used to investigate the impact of increased porewater salinity and the introduction of dissolved oxygen on the cycling of U by comparing release into oxygenated groundwater, seawater and degassed seawater. Finally saturated seawater column experiments were used to study U mobilisation under more environmentally relevant flow conditions.

## **4.2 Experimental**

Experiments were conducted using sediments representative of those found at Crediton. An overview of the experimental strategy adopted is outlined in Figure 4.1.

The sediments were contaminated with both U and Tc, and the Tc results are presented in Chapter 5.

### **4.2.1 Reagents and sample preparation**

All glassware and plasticware was immersed in 2 % Decon for at least 24 h, rinsed 5 times in Milli-Q water, transferred to a 10 % (v/v) hydrochloric acid (HCl) bath and soaked for at least 24 h and then rinsed 5 times in Milli-Q water. Plasticware and glassware were then dried under a laminar flow hood and stored double sealed in zip lock plastic bags.

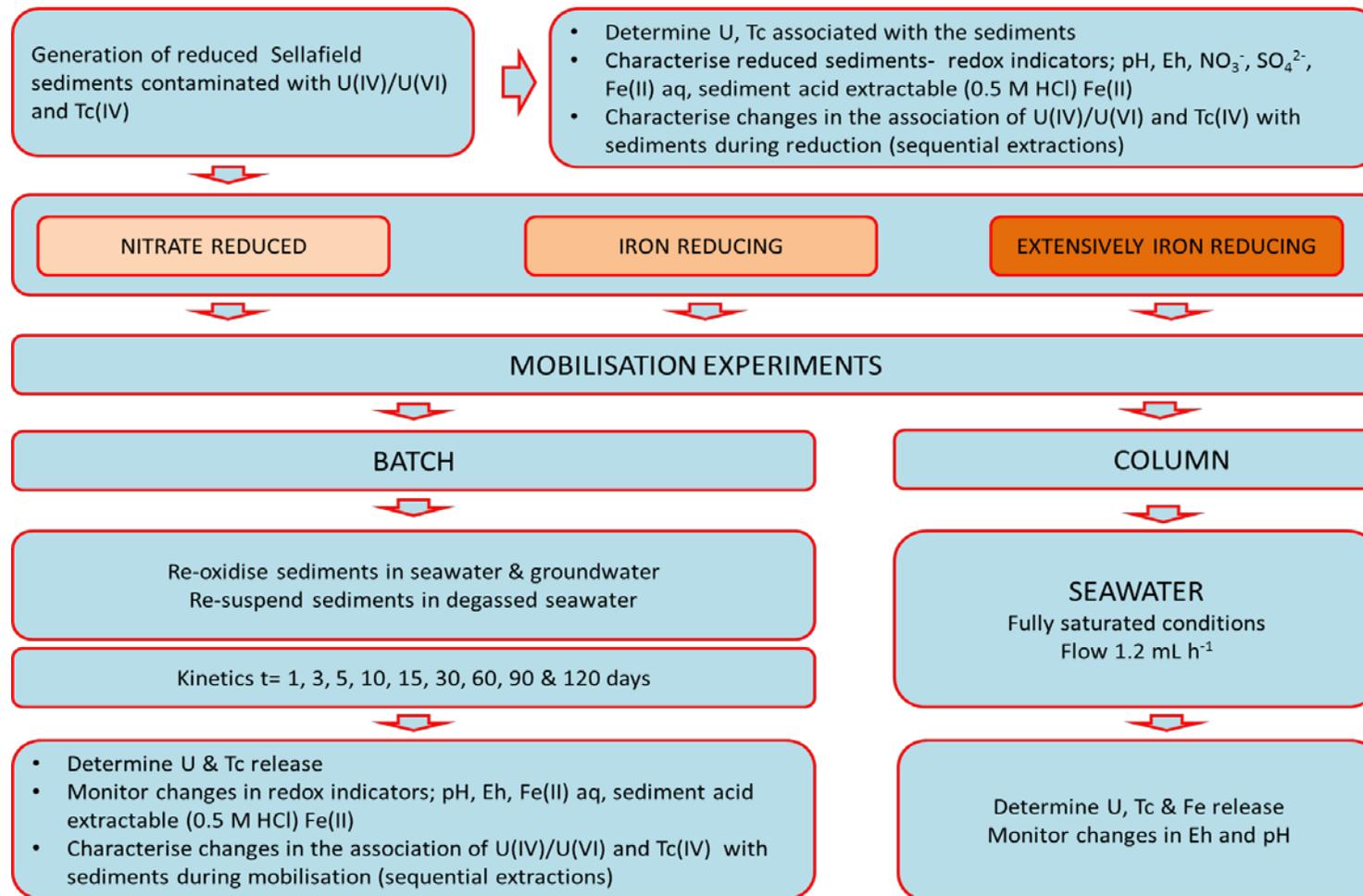


Figure 4.1: Experimental design adopted for Tc and U inundation experiments.

Glass serum bottles (100 mL or 50 mL Wheaton Scientific, New Jersey, USA) were washed as above and then wrapped in aluminium foil and ashed in a muffle furnace at 450 °C for at least 6 h to remove any carbon. When cool, the serum bottles were stored double sealed in zip lock plastic bags until use. All chemicals used in experiments were of analytical grade and obtained from Fisher (Fisher Scientific, Loughborough, UK), AnalaR BDH Chemicals Ltd (Poole, England) or Sigma-Aldrich (Sigma Aldrich Chemicals, Gillingham, Dorset, UK) unless otherwise stated. Milli-Q water (Millipore  $\geq 18 \text{ M}\Omega \text{ cm}^{-1}$ ) was used in standards, groundwater solutions and for all required dilutions. Standards used in ICP-OES and ICP-MS determinations were dilutions of 10 000  $\mu\text{g mL}^{-1}$  emission standards (sourced from Fisher and Romil) in 2%  $\text{HNO}_3$ .

#### **4.2.2 Sediment and water collection, preparation and characterisation**

Sediments representative of those found near the Crediton site, UK were used in this study. The sampling of sediments and water collection are described in Section 2.2.3, sediment characterisation is described in Section 2.2.4.

#### **4.2.3 Generation of reduced U and Tc contaminated sediments**

Uranium nitrate salts [ $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] were dissolved in a synthetic groundwater solution representative of that at the low level waste repository near Drigg (Cumbria, UK). The constituents are shown in Table 2.1. Technetium was added as  $^{99}\text{TcO}_4^-$ , the final concentrations of U and Tc were 25  $\mu\text{M}$  and 1  $\mu\text{M}$  respectively. The pH of the groundwater was 7.35.

Three sets of sealed serum bottles were used to generate ‘bulk’ reduced sediment for the mobilisation experiments; 60 g of sieved (< 2 mm) sediment was placed in each 100 mL

glass serum bottle. In order to reproduce saturated sub-surface conditions, 60 mL of the amended synthetic groundwater (Table 1) was added to give a 1:1 (w/v) moist sediment: solution ratio. The initial water content of the moist sediment was 16 %. The serum bottles were then sealed with a butyl rubber stopper and secured with an aluminium crimp before being transferred to a temperature controlled cabinet and incubated in the dark at a constant  $21 \pm 0.5$  °C until sacrifice after 30 , 60 and 120 days.

#### **4.2.4 Collection of reduced U and Tc contaminated sediments**

After a set of contaminated sediments had been sealed for 30, 60 or 120 days, the serum bottles were removed from the temperature controlled cabinet and mechanically shaken for 20 min at 200 rpm on an orbital shaker to homogenise the sediment and water. In order to preserve anaerobic conditions they were then transferred to a N<sub>2</sub>/H<sub>2</sub> (95:5) flushed anaerobic chamber (COY Laboratory products, MI); all work performed in the anaerobic chamber was undertaken when O<sub>2</sub> concentrations were < 5 ppm. The butyl seals were removed and aliquots of the slurry were pipetted into 7 mL plastic vials for the determination of pH and Eh in each individual serum bottle, and 2 mL of porewater was pipetted into a microcentrifuge tube and centrifuged (10 min 7500 g) to separate the liquid (< 0.45 µm) from the solid fraction. An aliquot of the supernatant was then acidified with HNO<sub>3</sub> and stored for later determination of the aqueous U and Tc. The remaining supernatant was frozen prior to the determination of redox indicators (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and Fe(II) *aq*), and the sediment was stored at -20 °C prior to determination of the acid extractable Fe(II) concentration in each of the serum bottles.

The remaining content of each serum bottle was then transferred into 1 L centrifuge vessels, which were sealed and covered with parafilm before being removed from the anaerobic chamber and centrifuged (20 min, 3500 g). On return to the chamber, the

sediment from each of the replicate serum bottles was transferred to a 1 L plastic screw top pot and homogenised by stirring for 15 min before being sub-sampled for use in further experiments. To validate the homogenisation process, 5 random 1 g subsamples were taken from the bulk sediment; freeze dried and digested using aqua regia, and the total U and Tc concentrations determined. There was no statistically significant difference ( $p = 0.094$ ;  $p = 0.087$ ) between the concentrations of  $^{99}\text{Tc}$  and U in the random sub-samples using a multiple sample ANOVA test (StatGraphics Version 5.1).

Homogenised sediments were then characterised by sequential extraction and used in mobilisation experiments. Sub-samples for the sequential extractions were sealed in plastic vessels, secured with parafilm and double bagged before being frozen ( $-20\text{ }^{\circ}\text{C}$ ) to ensure that anaerobic conditions were maintained during storage.

#### **4.2.5 Progressive mobilisation experiments in seawater and groundwater**

All mobilisation experiments were prepared on the day the serum bottles were opened and were carried out in triplicate for each pre-determined time point. Within the anaerobic chamber, 10 g sediment samples were transferred into 100 mL Erlenmeyer flasks (Fischer Scientific, UK) and amended with 10 mL of synthetic groundwater or seawater. Flasks were then capped with sterile autoclaved porous bungs to allow entry of air and weighed before removal from the chamber. Flasks were then shaken in the dark at 110 rpm and  $21\text{ }^{\circ}\text{C}$  for pre-determined time periods (1, 3, 5, 10, 15, 30, 60, 90 and 120 days). Flasks were reweighed every 1-10 days and an equivalent mass of Milli-Q water was added to replace water lost by evaporation.

At the pre-determined time points, the contents of the flask were transferred to a 50 mL centrifuge tube and 3 mL of slurry was removed for the determination of Eh and pH.

The remaining slurry was centrifuged for 10 min at 7500 g. The supernatant was stored at -20 °C before the determination of geochemical indicators (NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>; Section 4.2.7) or acidified with HNO<sub>3</sub> prior to the determination of dissolved U, Mn, Fe, Al and Si (Section 4.2.10). Total acid (0.5 M HCl) extractable Fe and Fe(II) were determined with and without the addition of hydroxylamine hydrochloride, respectively, followed by a spectrophotometric assay ( $\lambda_{\text{max}} = 562 \text{ nm}$ ) using ferrozine (Stookey 1970; Lovely and Phillips 1986) (Section 4.2.7). The remaining sediments were frozen (-20 °C) and retained for subsequent sequential extractions to compare changes in the solid state chemical fractionation of U before and after the mobilisation experiments (Section 4.2.8).

#### **4.2.6 Mobilisation in degassed seawater**

Reduced sediment samples (10 g) were transferred into 50 mL glass serum bottles inside the anaerobic chamber. Sediments were then amended with 10 mL of seawater that had been degassed with N<sub>2</sub> until the dissolved O<sub>2</sub> concentration was < 0.05 mg L<sup>-1</sup>, determined using a calibrated portable dissolved oxygen meter (YSi-55) . The serum bottles were then sealed with a butyl rubber stopper (Bellco Glass Inc, New Jersey, USA) and aluminium seals (Sigma- Aldrich, Dorset UK). All experiments were incubated in the dark in a temperature controlled cabinet (21 ± 0.5 °C).

On the day of sacrifice, the contents of the serum bottles were homogenised by shaking for 30 min at 200 rpm on an orbital shaker. In order to maintain anaerobic conditions the serum bottles were transferred to the anaerobic chamber opened and a 3 mL aliquot of the slurry was transferred to a polypropylene vial. The Eh and pH were then determined and the sub-sample frozen (-20 °C) on the day of sacrifice. The remaining contents of the serum bottles were transferred to centrifuge tubes, which were secured

with parafilm, centrifuged (7500 g, 20 min) and then returned to the anaerobic chamber before the supernatant was carefully decanted into a polypropylene vial. Determination of the geochemical indicators is described in Section 4.2.7. The remaining sediments were frozen (-20 °C) and retained for subsequent sequential extractions to compare changes in solid state chemical fractionation of Tc and U before and after the mobilisation experiments.

#### **4.2.7 Determination of geochemical indicators**

Changes in biogeochemical conditions were monitored throughout the reduction and mobilisation experiments by the determination of the geochemical indicators Eh, pH, nitrate, nitrite, sulphate and Fe(II) in pore waters and microbially produced Fe(II) in the sediments.

**Determination of Eh, pH and salinity:** The pH of the slurry sub-sampled from each serum bottle and batch experiment was measured within the anaerobic chamber using a calibrated (pH 4.01 and pH 7.01) electrochemical probe (pH 210, Hanna Instruments, Leighton Buzzard, UK). The Eh of the slurry was determined using an electrode that had been corrected (+228 mV) to the standard hydrogen electrode using the experimental Eh reading determined from an Fe(II)/Fe(III) solution (Light 1972). The salinity of the waters was determined using a portable refractometer (DIGIT-100ATC, Medline Ltd, Oxford, UK).

**Determination of anions in porewaters:** At each time point anion ( $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$ ) concentrations in the pore waters were determined by ion chromatography. Within the anaerobic chamber aliquots of the supernatant were filtered (< 0.45  $\mu\text{m}$ , Millex, MF membrane) and pipetted into vials. Porewater  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{SO}_4^{2-}$  were

determined on the day of sacrifice or after storage at -20 °C. To avoid oxidation, frozen samples were defrosted within the anaerobic chamber. Seawater samples were diluted 20 fold in Milli-Q water before analysis (Dionex DX-500, Dionex Co, Camberley, UK). The instrument was calibrated using a calibration series (0 - 2500 µM, 8 point) diluted from a stock solution (10, 000 µM) prepared from salts (NaNO<sub>2</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Sigma Aldrich (Analytical Grade)). Standards were regularly re-run (after every 10 samples) and if instrumental drift was > 10 % samples were rerun. All calibrations gave R<sup>2</sup> values > 0.99. Instrument parameters are shown in Table 4.1.

**Determination of microbially produced Fe(II) in sediments:** Iron reduction has been reported to occur in sediments between 10 and 20 days before being observed in sediment pore waters (Islam *et al.* 2004; Burke *et al.* 2005). Therefore a solid phase extraction scheme was adopted to provide more detailed information on changing redox conditions in the reduction and mobilisation experiments.

**Table 4.1: Instrument Parameters for Dionex DX-500 for the determination of anions in solution.**

<i>Instrument</i>	<i>Dionex DX-500</i>
Eluant	1.9 mM sodium carbonate
Column	Dionex IonPac AG9-HC, IonPac AS9-HC
Flow rate	1.0 mL min <sup>-1</sup>
Detection	100 mA current
System backpressure	≈ 2200 psi
Background conductance	≈ 30 µS
Software	PeakNet 6

Extraction with 0.5 M HCl has been shown to specifically extract microbially produced Fe(II), although small amounts of mineral derived Fe(II) may also be measured (Lovely and Phillips 1986). Acid (0.5 M) extractable Fe(II) was therefore determined using the spectrophotometric ferrozine assay (Stookey 1970).

Sealed vials containing 0.1 g of reduced sediments were stored in the freezer (-20 °C) until Fe(II) was determined. Sediments were defrosted within the anaerobic chamber in order to maintain anaerobic conditions. An aliquot of 5 mL of 0.5 M HCl was pipetted into each vial; vials were then sealed and shaken horizontally for 1 h at 21 °C. After extraction, samples were filtered [0.45 µm, Millex, MF membrane (mixed cellulose esters)] and 100 µL of the extract was added to 5 mL of ferrozine solution (1 g L<sup>-1</sup>) prepared in 50 mM HEPES buffer (Fisher Bioreagents, Leicestershire, UK; pH 7.3 ± 0.1). Samples were mixed for 15 s and the absorbance measured at 562 nm (UV/VIS, Diode Array, Hewlett Packard, 8453, Germany). Total bioavailable iron was also determined by adding 100 µL of 6.25 M hydroxylamine hydrochloride to the acid extraction mixture prior to digestion and the ferrozine assay (McBeth *et al.* 2007). A 5 point calibration was performed using Fe(II) standards prepared in 0.5 M HCl, and samples were analysed as described above. Calibrations gave R<sup>2</sup> values > 0.99 with a limit of detection of 0.10 µM (calculated as 3 times the standard deviation of the lowest standard). Standards were rerun after every 10 samples and if instrumental drift was greater than 10 % samples were re-run.

#### **4.2.8 Solid phase associations of U and Tc**

The operationally defined chemical associations of U and Tc were determined in the nitrate, iron and extensively iron reducing sediments before use in the mobilisation experiments, and at selected times (5, 30 and 90 days) during the mobilisation experiments.

**Sequential extractions:** The sequential extraction procedure adopted was a 5 step scheme (Tessier *et al.* 1979) modified for use with anoxic sediments (Kersten and Förstner 1987; Wallmann 1993). Sequential extractions were carried out in triplicate and an outline of the sequential extraction procedure is given in Table 2.2 and a detailed description of the method in Section 2.2.9. In order to maintain anaerobic conditions, approximately 1.00 g of reduced sediment was accurately weighed into each centrifuge tube within the anaerobic chamber. To prevent oxidation of samples, all manipulations during steps 1-3 (i.e. those prior to the oxidising leach) were also carried out in the anaerobic chamber. Leachate solutions for these steps were degassed with N<sub>2</sub> and the centrifuge tubes were sealed with parafilm and double bagged during shaking and centrifugation to prevent entry of air.

#### **4.2.9 Dynamic seawater column experiments**

Column experiments were conducted under fully saturated seawater flow conditions to investigate the mobilisation of U from nitrate reduced (day 30) and extensively iron reducing (day 120) sediments during sea water intrusion. Under anaerobic conditions contaminated sediments were packed into a polyetheretherketone (PEEK) self-pack column. Columns were then removed from the anaerobic chamber and saturated with seawater (Section 2.2.8). An upward flow direction was used to ensure saturated conditions and prevent the formation of preferential flow channels. The eluate was fractions using a fraction collector and uncertainty associated with the flow rate was < 5%.

Flow was stopped for 2 weeks during the saturated column experiments, at approximately 760 pore volumes to assess whether uranium concentrations in the eluate solutions were in equilibrium with sorbed uranium in the sediments (Qafoku *et al.* 2005;

Yin *et al.* 2011). A second stop flow event lasting for 2 weeks was carried out in columns packed with extensively iron reducing sediments at 1050 pore volumes.

The linear flow velocity through the columns was calculated as 235 m yr<sup>-1</sup> (nitrate reduced) and 262 m yr<sup>-1</sup> (extensively iron reducing), respectively. This falls within the range of flow velocities observed in sandy aquifers under natural hydrogeological conditions (Mackay *et al.* 1985). During the experiment, 1450 mL (nitrate reducing) and 1610 mL (extensively iron reducing) of seawater flowed through the column, corresponding to 993 (nitrate) and 1070 (extensively iron reducing) pore volumes respectively. After completing the mobilisation experiments, a conservative tracer (200 µL of 75 mM Br<sup>-</sup>) was injected into each column, Br<sup>-</sup> was determined by ICP-MS.

Throughout the experiment, the pH and Eh were measured as soon as practicable after elution and aliquots were removed for the determination of Fe(II) by a spectrophotometric assay ( $\lambda_{\text{max}} = 562 \text{ nm}$ ) using ferrozine (Section 4.2.7). The samples were then acidified with HNO<sub>3</sub> for the determination of U, Fe, Mn and Al concentrations by ICP-MS.

After each run the column was opened the sediment was separated into fractions (Section 2.2.8) and total U was determined by ICP-MS (Section 3.2.4) after aqua-regia digestion (outlined in Section 2.2.9).

## **4.3 Results and discussion**

### **4.3.1 Sediment reduction and solid phase associations of U**

The sediments became progressively anoxic over time, as shown in Table 4.3. The time points shown are those at which the sediments were used immediately in remobilisation experiments or frozen for subsequent characterisation.

The Eh decreased over time from an initial value of  $424 \pm 36$  mV to  $173 \pm 11$  mV after 30 days and  $25.3 \pm 8.3$  mV after 60 days. The Eh then remained relatively constant from 60 days to 120 days ( $15.2 \pm 5.0$ ). The sediments had a significant impact on the experimental pH; the pH of the groundwater decreased from 7.35 to  $\approx 4.76$ . However during nitrate reduction the pH increased significantly (from  $4.76 \pm 0.6$  to  $6.35 \pm 0.6$ ). This trend of increasing pH has been observed previously in microcosm experiments and is consistent with the production of  $\text{HCO}_3^-$  and  $\text{OH}^-$  during microbial respiration (Chang *et al.* 2005; Law *et al.* 2010).

**Table 4.2: Conditions in the sediments and pore waters. Data show means (n=10)  $\pm$  1 standard deviation. LOD is the limit of detection- shown in brackets.**

	Original conditions	Nitrate reduced	Iron reducing	Extensively iron reducing
Reduction time	1 h	30 d	60 d	120 d
Eh, mV	$420 \pm 36$	$170 \pm 1$	$25 \pm 8$	$15 \pm 5$
pH	$4.8 \pm 0.6$	$6.4 \pm 0.6$	$6.9 \pm 0.3$	$7.0 \pm 0.5$
U, associated with sediments, $\mu\text{mol kg}^{-1}$	< LOD (0.013)	$25.6 \pm 0.1$	$25.4 \pm 0.1$	$25.3 \pm 0.1$
% U associated with sediments		99	98	98
$\text{NO}_3^-$ , $\mu\text{M}$	$4700 \pm 200$	$4.4 \pm 0.6$	<LOD (2.5)	< LOD (2.5)
Acid extractable Fe (II), $\text{mmol kg}^{-1}$	< LOD (0.55)	< LOD (0.55)	$8.3 \pm 0.8$	$16.0 \pm 1.0$
$\text{SO}_4^{2-}$ , $\mu\text{M}$	$3.60 \pm 0.36$	$4.20 \pm 0.9$	$4.8 \pm 0.9$	$4.8 \pm 0.1$

After 30 days, porewater nitrate concentrations had decreased by three orders of magnitude, from  $4.7 \pm 0.3$  mM to  $4.36 \pm 1.6$   $\mu$ M, indicating that nitrate reduction had been the dominant respiration process, and was now complete. After 60 days the nitrate concentration was below the limit of detection (2.5  $\mu$ M), although no accumulation of nitrite was observed. Iron reduction had initiated, as indicated by ingrowth of 0.5 M HCl extractable Fe(II) ( $8.3 \pm 0.8$  mmol kg<sup>-1</sup>). By day 120, significantly more Fe(II) was observed in the sediments ( $16 \pm 1$  mmol kg<sup>-1</sup>). Porewater SO<sub>4</sub><sup>2-</sup> concentrations also increased over the 120 day reduction period, possibly as a result of desorption of SO<sub>4</sub><sup>2-</sup> or organic sulphur mineralisation (Nevell and Wainwright 1986). There was no blackening of the sediments which provided supporting evidence that sulphate reduction did not occur in the sediments.

The geochemical conditions followed the classical redox cascade of NO<sub>3</sub><sup>-</sup> followed by Fe(III) reduction. Sediments were classified operationally by the geochemical processes occurring in the sediments at the point when they were used in the mobilisation experiments; nitrate reducing conditions were defined as sediments where extensive nitrate reduction had occurred and ingrowth of 0.5 N HCl extractable Fe(II) was not detected; iron reducing conditions were defined as systems with ingrowth of sediment associated 0.5 M HCl extractable Fe(II) had occurred, and extensively Fe reducing conditions were defined as when Fe(II) ingrowth was high and sulphate reduction had not initiated.

**Behaviour of uranium:** During nitrate reduction, 99 % of U(VI) was removed from solution. In general U(VI) reduction does not occur alongside nitrate reduction (Finneran *et al.* 2002), and it is likely that U remains in the oxidised form, as U(VI), and is sorbed to the nitrate reduced sediments ;(Martinez *et al.* 1995; Sylwester *et al.* 2000;

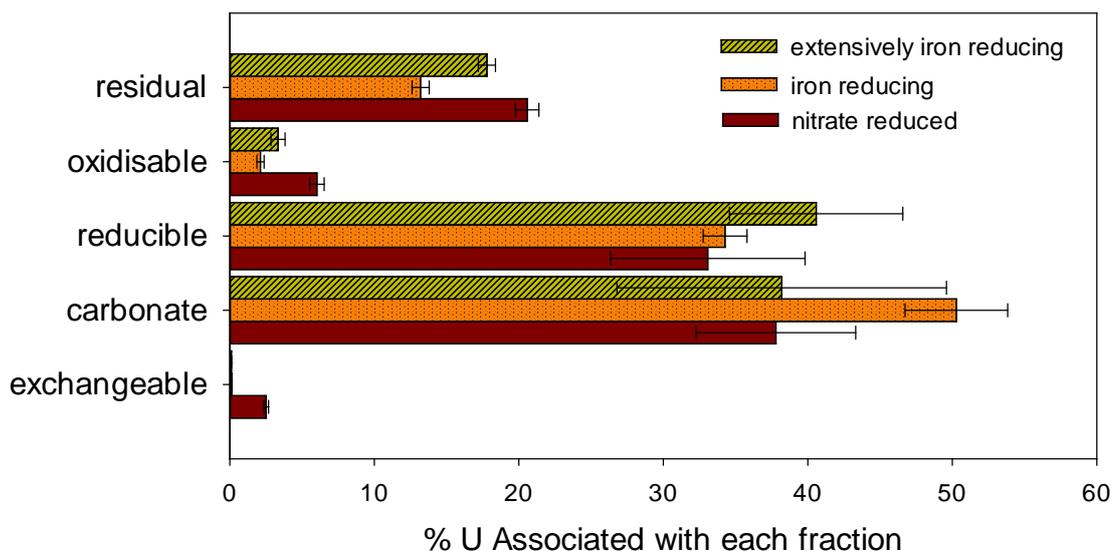
Gómez *et al.* 2006; Duquene *et al.* 2008; Sherman *et al.* 2008) or co-precipitated with iron oxyhydroxides and calcium carbonates (Reeder *et al.* 2000; Duff *et al.* 2002). Abiotic or microbial reduction of U(VI) to U(IV) is generally observed in soils and sediments alongside Fe(III) reduction (Finneran *et al.* 2002; Senko *et al.* 2002). Therefore, concurrent with Fe(III) reduction, U(VI) (sorbed to the sediment surface) may have been reduced to insoluble U(IV) phases (Gu *et al.* 2005; Begg *et al.* 2011). The product of U(VI) reduction is often uraninite (UO<sub>2</sub>) (Ginder-Vogel *et al.* 2006; Campbell *et al.* 2011). However the formation of non-crystalline (monomeric) adsorbed U(VI) species has also been reported (Fletcher *et al.* 2010; Boyanov *et al.* 2011; Campbell *et al.* 2011; Sharp *et al.* 2011).

Therefore removal of U from solution as conditions became increasingly reducing can be attributed to (i) sorption of U(VI) species, (ii) reduction of sorbed U(VI) or (iii) the presence of several U species (U(VI)/U(IV)/ monomeric U).

**Solid phase associations:** Sequential extractions were used to identify changes in the solid state chemical fractionation of U as reducing conditions developed (Figure 4.2).

Uranium was associated with several different binding sites in the reduced sediments. Its association with the carbonate (38 – 50 %) and reducible (33 – 41 %) fractions suggest that U is present co-precipitated with/sorbed to CaCO<sub>3</sub> (Serne *et al.* 2002) and iron and/or manganese oxyhydroxides (Martinez *et al.* 1995; Duff *et al.* 2002; Sherman *et al.* 2008). A significant fraction of U was associated with the residual fraction (13-20 %) which has been attributed to immobilisation by trapping within clay interlayers (Braithwaite *et al.* 1997) and becoming bound in crystalline mineral sites such as silicates (McKinley *et al.* 1995; Turner *et al.* 1996; Sylwester *et al.* 2000). Importantly, only a small fraction of U was associated with the exchangeable fraction (< 2.5 %), and this decreased over time, suggesting that U was re-distributed from weak surface sites to

stronger binding sites as the sediments became increasingly reducing and/or as U(IV) was formed during reduction. Uranium(IV) would be expected to be less prone to mobilisation as reducing conditions developed compared with U(VI) sorbed to the nitrate reduced sediments.



**Figure 4.2: Solid phase association of U with reduced sediments. Percent of U extracted in each fraction using a modified Tessier sequential extraction scheme for use in anaerobic environments. Sediments were contaminated with Tc and U in a simulated groundwater solution and allowed to become progressively more reducing over time. Data show means of 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Extractants are described in Table 2.2.**

#### 4.3.2 Mobilisation of U during intrusion

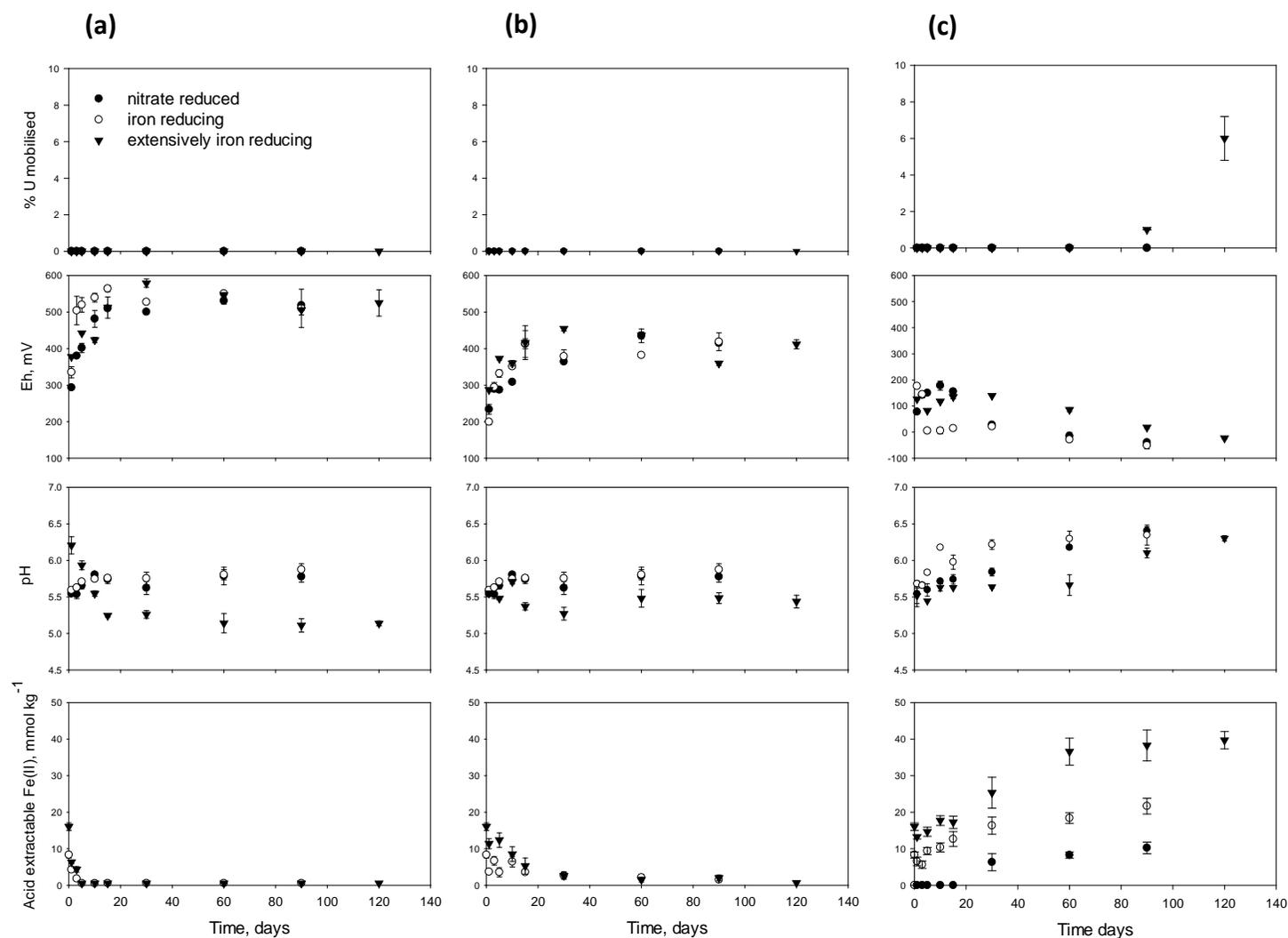
Reduced sediments were suspended in groundwater and seawater to investigate the impact of increased pore water salinity on U mobilisation during the reoxidation of reduced sediments. The processes controlling U release were investigated further by comparing the mobilisation of U into seawater and degassed seawater. Changes in the

association of U with reduced sediments during reoxidation were monitored using sequential extractions. Changes in the geochemical conditions over the mobilisation period are shown in Figure 4.3.

**Groundwater:** When the sediments were reoxidised in groundwater, the Eh increased more rapidly in the iron-reducing sediments than the nitrate-reducing sediments. However, there was no significant difference in the Eh in any system once equilibrium had been established, by day 60. The addition of groundwater initially decreased the pH of both sediments. The pH then varied in all systems, with significant ( $p < 0.05$ ) differences between extensively iron reducing compared with nitrate reduced and iron reducing sediments.

**Seawater:** The Eh data showed that the sediments were reoxidised more slowly in seawater than groundwater, and reached a lower equilibrium Eh (Figure 4.3). Again, the initial rate of Eh increase was significantly faster ( $p < 0.05$ ) for the iron reducing sediments and there was no significant ( $p > 0.05$ ) difference in the Eh by day 90. The sediments used in these experiments decreased the pH of the seawater from 8.2 to  $< 5.3$ . Similar changes were seen for the nitrate reduced and iron reducing sediments, but the pH was significantly lower in the extensively iron reducing sediments.

**Degassed seawater:** In these systems, conditions became increasingly reducing, as shown by the Eh data. By day 30, there was no significant difference in the Eh of the three sediments. The decrease in Eh observed in these microcosms corresponded with an increase in pH, which is consistent with the production of  $\text{HCO}_3^-$  and  $\text{OH}^-$  during microbial respiration (Chang *et al.* 2005; Wan *et al.* 2005; Law *et al.* 2010). It is interesting to note that, despite the addition of seawater to previously freshwater environments, at least a part of the anaerobic microbial population was viable



**Figure 4.3: Mobilisation of U and corresponding changes in geochemical indicators (Eh and pH) from initially nitrate reduced, iron and extensively iron reducing sediments when suspended in (a) groundwater, (b) seawater and (c) degassed seawater over increasingly long timescales. Sediments were contaminated with U and Tc in a simulated groundwater solution. Data show means of 3 separate extractions  $\pm$  1 standard deviation. Note the different scales for Eh in the degassed seawater experiments (c).**

**Mobilisation of U from reduced sediments during re-oxidation:** When the sediments were suspended in oxic groundwater and seawater, U remained recalcitrant to mobilisation, and the release of U into solution was below the limit of detection [groundwater (0.21 nM) and seawater (1.3 nM)]. The addition of seawater might be expected to enhance U mobility through carbonate complexation (Zhou and Gu 2005), but the sediments lowered the pH of both the seawater (from 7.8 to 5.7) and groundwater (from 7.4 to 5.0), thereby removing carbonate from solution. The data suggest that ionic strength alone does not have a significant effect on U(VI) or U(IV) mobility in these systems.

**Mobilisation of U from reduced sediments in degassed seawater:** A small fraction of U (6 %) was mobilised from extensively iron reducing sediments between 90 days and 120 d of reduction in seawater. In this set of experiments, there was an increase in pH as reduction progressed, consistent with the production of  $\text{CO}_3^{2-}$ , and  $\text{HCO}_3^-$  during microbial respiration. Carbonates have previously been seen to promote U(VI) release via the formation of stable U-carbonate complexes even when U is present as U(IV) (Wan *et al.* 2005; Wan *et al.* 2008). However, the Fe data provides evidence of an alternative or concurrent mechanism of U release. The sequential extractions (Figure 4.2) identified that iron hydroxides are an important binding phase for U in these sediments and ingrowth of Fe(II) in pore waters (12 mM) during on-going reduction was observed to the greatest extent in the extensively Fe-reducing mobilisation experiment. Therefore U release may also be related to the reduction of Fe(III) minerals to more soluble Fe(II) species (Fredrickson *et al.* 2000).

**Uranium mobilisation during intrusion:** Uranium was not released from the sediments even though they were effectively reoxidised over time in both groundwater

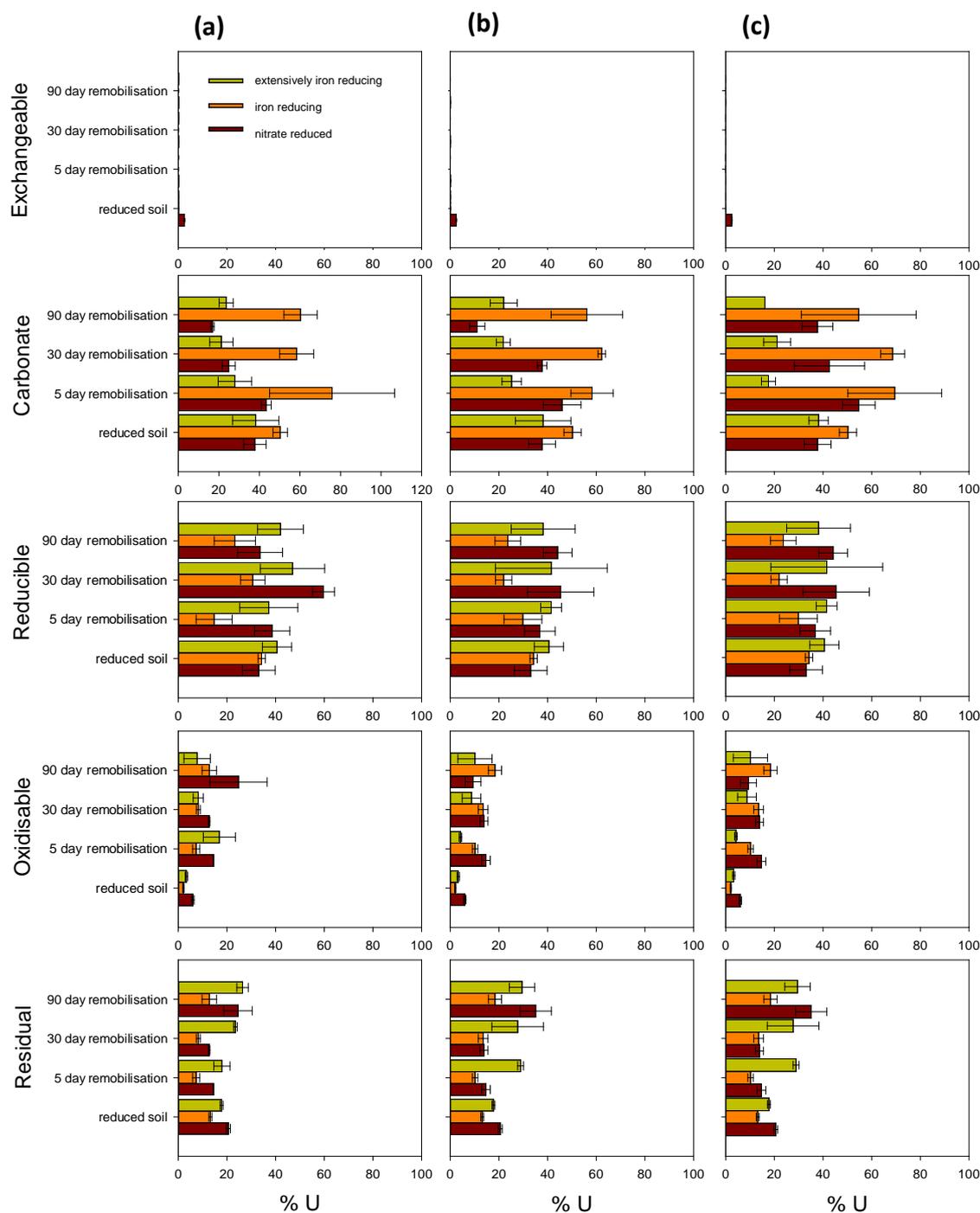
and seawater. Therefore, the recalcitrance to mobilisation appears to be independent of salinity at the experimental pH. The natural capacity of these sediments to lower the pH of the water phase has limited the release of U. However the reductive dissolution of Fe(III) oxides and the increased alkalinity produced during microbial respiration could potentially influence the long term stability of both U(VI) and U(IV) if conditions become increasingly reducing during seawater intrusion.

#### **4.3.4 Changes in solid phase associations of U during mobilisation**

Conducting sequential extractions at selected time points during the mobilisation experiments allowed the behaviour of U to be related to changes in solid phase associations under specific redox conditions and pore water salinity. Results of the sequential extractions are shown in Figure 4.4. In all experiments U remained predominately associated with the carbonate (11-76 %) and reducible (33-60 %) fractions and there is an indication from the nitrate reduced- and significantly iron reducing sediments that U is moving from the carbonate fraction into the oxidisable fraction over time, i.e. becoming less available for mobilisation. The limited association of U with the exchangeable fraction (< 2.5 %) observed in these experiments may explain the recalcitrance of U to mobilisation.

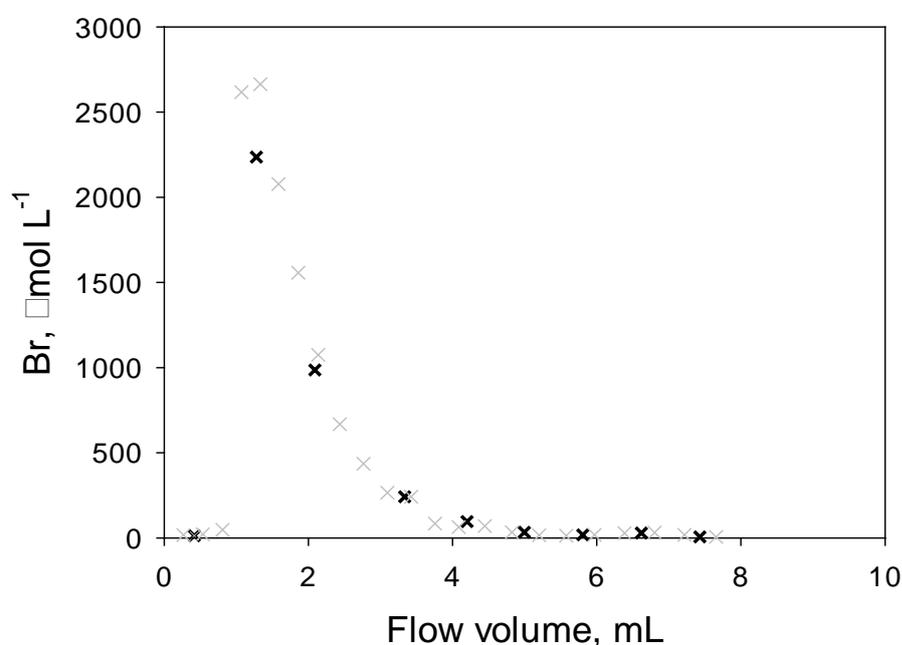
#### **4.3.4 Mobilisation of U into seawater under dynamic flow conditions**

Column experiments were conducted in order to investigate the mobilisation of U from nitrate reduced and extensively iron reducing sediments under more environmentally relevant conditions. Seawater was pumped up through the vertically mounted column to create fully saturated conditions.



**Figure 4.4: Changes in the solid phase associations of sediment bound U with nitrate reduced, iron reducing and extensively iron reducing sediments during mobilisation in (a) groundwater, (b) seawater and (c) degassed seawater. The percentage of U associated with each fraction of a modified sequential extraction scheme adapted for use in anaerobic environments is shown. Results show the association of U with reduced sediments prior to mobilisation (reduced sediment) and after mobilisation for 5, 30 and 90 days respectively. Means are calculated from 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Extractants are explained in Table 2.2.**

**Column characterisation:** Columns were characterised using a conservative  $\text{Br}^-$  tracer (200  $\mu\text{L}$  of 75 mM  $\text{Br}^-$ ) injected as a pulse through the column at the end of the mobilisation experiments. Figure 4.5 shows the  $\text{Br}^-$  elution data from the column experiments. Both profiles exhibited narrow peaks, suggesting that there were no preferential flow paths, and were similar. There was some variation in  $\text{Br}^-$  breakthrough, i.e. column porosity, which indicates that there were some minor inconsistencies in packing the columns and/or heterogeneity in the sediment (e.g. variable particle size). The linear flow velocity was 235  $\text{m y}^{-1}$  (nitrate reduced) and 262  $\text{m y}^{-1}$  for extensively iron reducing columns respectively.



**Figure 4.5: Elution profile for the transport of the bromide tracer used in the nitrate reduced (x) and extensively iron reducing (X) column experiments.**

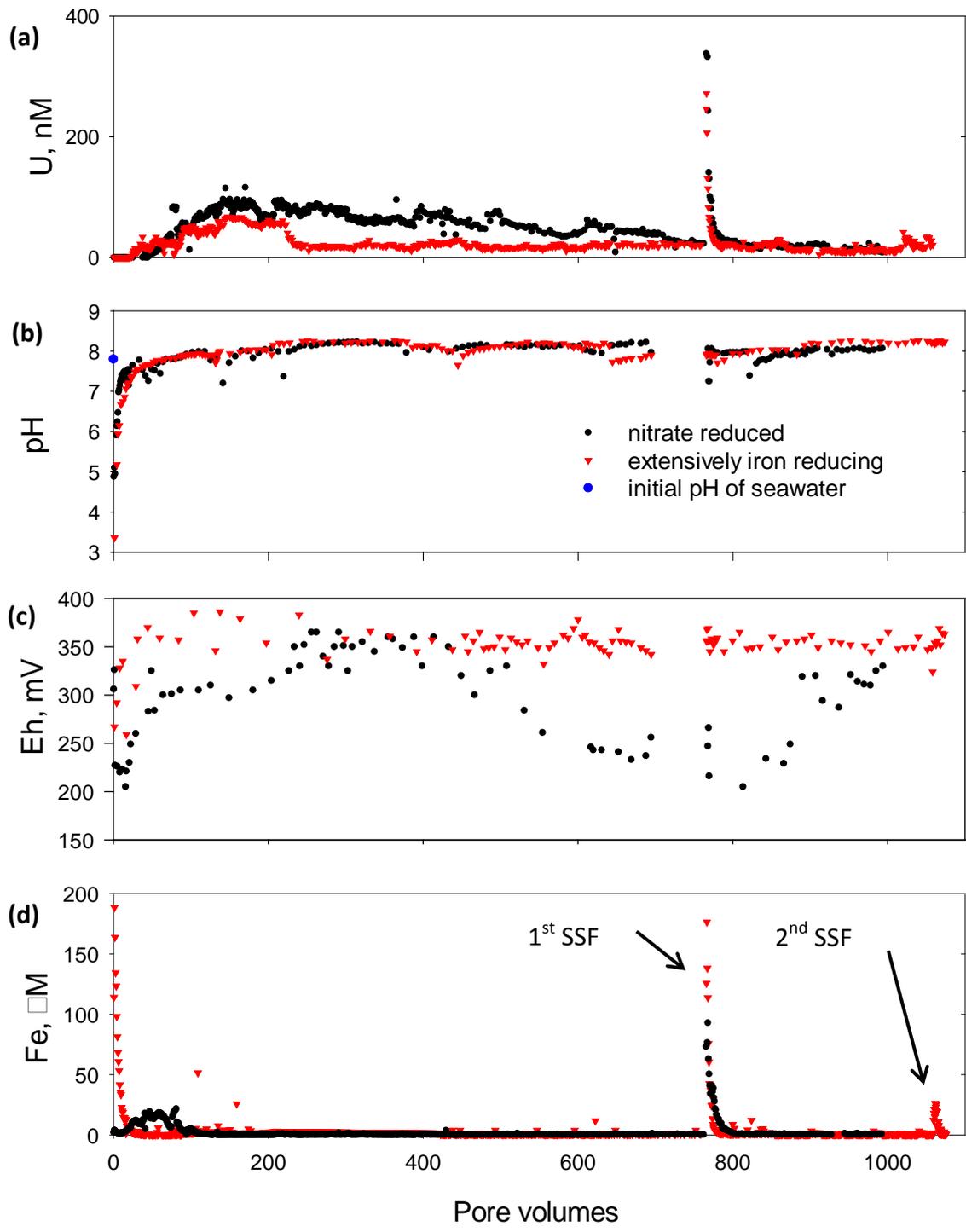
**Changing geochemical conditions in the column:** The pH of the inflowing seawater (7.8) initially fell during transport through both sediments Figure 4.6. The initial pH was significantly lower in the outflow of the extensively iron reducing sediments (pH 3.4) compared with 4.9 in the nitrate reduced columns. The pH in both columns then increased steadily, reaching the pH of the inflow after 33 (nitrate reduced) and 51 (extensively iron reducing) pore volumes. At this point, the sediments no longer

affected the pH of the seawater, which remained relatively constant (7.2 - 8.2) over the remainder of the experiment. The stop/start flow event had no discernible effect on the pH. The pH of the outflow from the extensively iron reducing sediments was lower than that of the nitrate reduced sediments in the initial phase, which may be due to hydrolysis of Fe during oxidative precipitation of Fe(III) phases [Equation 4.1.] (Stumm and Morgan 1996; INAP 2009).



The Eh of the outflow from the columns increased as the sediments were re-oxidised (Figure 4.6), ranging from 203 to 386 mV in both columns. These Eh values are lower than those observed after 10 days in the batch experiments, reflecting the flow-controlled input of oxygen. Extensively iron reducing sediments were reoxidised faster than nitrate reduced sediments, which is consistent with the results from the batch experiments, and they also showed less variation in Eh over time.

**Mobilisation of U:** The sediments were reoxidised as seawater flowed through the column; however, there was an extended period when the pH of the inflowing seawater was lowered by the sediments from 7.8 to < 7.3. During this period, U remained associated with the sediments (Figure 4.6). Uranium mobilisation was initiated after 22 pore volumes (extensively iron reducing; pH 7.4) and 38 pore volumes (nitrate reduced; pH 7.5) of seawater had flowed through the column.



**Figure 4.6: Mobilisation of (a) U and (d) Fe from sediments with corresponding changes in (b) Eh and (c) pH in the leachate during saturated flow through column experiments. Columns were packed with initially nitrate reduced and extensively iron reducing sediments. Stop/start flow events (SSF) are shown; the second stop/start event was only carried out for the extensively iron reducing sediment column**

The data again show that the increased ionic strength and resultant competition between seawater cations (e.g.  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and sorbed U species did not drive U mobilisation. The initial mobilisation of U from the reduced sediments was only promoted at a higher pH (7.4–7.5). Therefore, the increase in carbonate concentration with pH and the formation of soluble U(VI)-carbonate species such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ ,  $\text{CaUO}_2(\text{CO}_3)_3^{2-}$  and  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ . (Dong *et al.* 2005; Zhong *et al.* 2005; Fox *et al.* 2006) enhanced desorption of surface associated U(VI). Additionally, in extensively iron reducing sediments, reduced U(IV) species were re-oxidised and released as oxic seawater flowed through the column, in agreement with the previously reported re-oxidation of U(IV) in sediments by air (Begg *et al.* 2011; Law *et al.* 2011). After the initial breakthrough, U concentrations in the eluant increased steadily over time. The eluate U concentration reached a maximum of  $115 \text{ nmol L}^{-1}$  after 140 pore volumes from nitrate reduced and  $72 \text{ nmol L}^{-1}$  after 150 pore volumes from extensively iron reducing columns.

Significant ‘tailing’ was observed after the peak in both U elution profiles. This type of behaviour has previously been explained by U association with different sorption sites with a distribution of desorption rates and/or thermodynamic properties (Serne *et al.* 2002; Scism 2005; Handley-Sidhu *et al.* 2009). The sequential extractions (Figure 4.2) indicated that U associations defined by the operationally defined chemical fractions were similar in the two sediments; however a more pronounced tail was observed in nitrate reduced compared with extensively iron reducing columns. Therefore column experiments provide evidence of different binding and release mechanisms that the sequential extractions did not reveal.

Flow was stopped for 2 weeks during the tailing period of the saturated column experiment (1<sup>st</sup> at 765 and 2<sup>nd</sup> (extensively iron reducing sediments only) at 1060 pore volumes) to assess whether solution phase concentrations of species were in equilibrium

with the sediment concentrations (Qafoku *et al.* 2005). Dissolved U concentrations increased 15 and 12 fold from the nitrate reducing and extensively iron reducing sediments, respectively, during the stop/start flow events. There was then a period of  $\approx$  10 pore volumes where U concentrations decreased rapidly. Only a small percentage of the total U associated with the sediments was mobilised during this stop-start event, for example, after 10 pore volumes 1.4 and 0.9 % of the sediment associated U was mobilised from the nitrate reduced and extensively iron reducing sediments, respectively. Increased U mobilisation during the start/stop flow events suggests that U release was kinetically controlled, and may be attributed to the re-distribution of U from less exchangeable to more exchangeable sites and/or that U is held in a chemical fraction with slow desorption kinetics (Mason *et al.* 1997; Qafoku *et al.* 2005; Ilton *et al.* 2008; Liu *et al.* 2008). The concentration of U mobilised from extensively iron reducing sediments during a second stop/start flow (of comparable duration to the first) was significantly lower; U concentrations increased 2 fold and a limited fraction (0.08 %) of the U originally associated with the sediments mobilised, suggesting that the U mobilised was part of a limited pool.

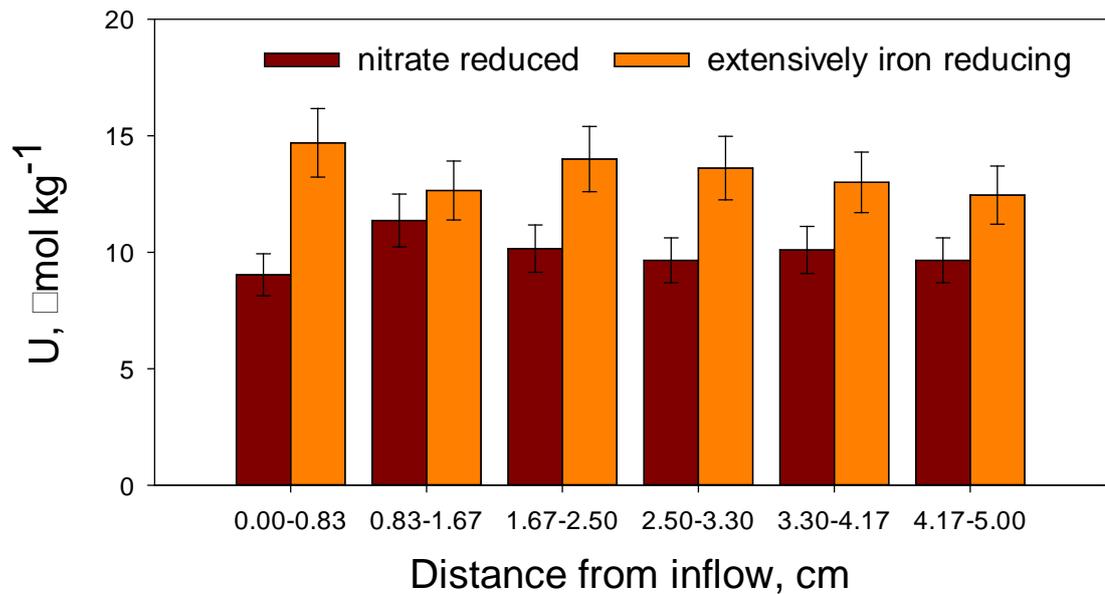
Sequential extractions showed that a considerable fraction (33-41 %) of U was initially associated with the reducible fraction (including iron oxides). The initial pulse release of Fe from extensively iron reducing sediments and the period of elevated Fe release observed in nitrate reduced columns (at 20 -70 pore volumes) did not promote U mobilisation (Figure 4.6), however this may have been affected by the pH of the systems during these periods. After this, there was a low concentration of Fe in the column eluant that increased during the stop flow events, showing that the on-going mobilisation of Fe is kinetically controlled. The observed mobilisation of U during the stop flow event correlated with the release of Fe from both nitrate ( $r= 0.888$ ,  $p= 0.000$ ) and extensively iron reducing ( $r= 0.977$ ,  $p= 0.000$ ) sediments, therefore U release is

linked to Fe cycling, and the slow release from the sediments may reflect hindrance by Fe phases.

The on-going release of U was observed over the duration of the 1 month long experiment. At the end of the experiment,  $53 \pm 7$  % of U had been mobilised from the nitrate reduced sediment and  $38 \pm 5$  % from the extensively iron reducing sediment. Even under flow conditions, with the pH reaching that of the inflowing seawater, the slow and incomplete release of U was observed. The release profiles of U suggest that relatively slow desorption kinetics will dominate the mobilisation of U in the environment.

Acid digestion of the sediments following the column experiments confirmed that U was mobilised uniformly throughout the column (Figure 4.7). The fraction of U (40-54 %) remaining on the sediment at this point (as determined by acid extraction) was far greater than the fraction of U associated with the residual fraction in sequential extractions ( $\approx 20\%$ ). A mass balance established that  $93 \pm 10$  % (nitrate reduced) and  $92 \pm 11$  % (extensively iron reducing) of the U has been accounted for.

Over the month long experimental period the sediments exhibited different release profiles and 15 % more of the total U was mobilised from the nitrate reduced sediments compared with the significantly iron reducing sediments. Since the sequential extractions identified limited differences in the association of U with the geochemically different sediments (Figure 4.2), changes in the sediment character during reoxidation may have been responsible for the differences in the release behaviour of U.



**Figure 4.7: Column digestion results showing the distribution of U remaining in the nitrate reduced and extensively iron reducing sediments after dynamic seawater mobilisation experiments were conducted under fully saturated flow conditions. Error bars show  $\pm 10\%$  relative standard deviation from combined analytical and method uncertainties.**

The reoxidation of Fe(II) may have retarded U(VI) release from extensively iron reducing sediments compared with nitrate reduced sediments (where no Fe(II) ingrowth was detected). During reoxidation, U(VI) may have been sorbed onto, incorporated into, or trapped by newly formed crystalline and amorphous Fe(III) oxides (Ohnuki *et al.* 1997; Sato *et al.* 1997; Stewart *et al.* 2009). Additionally, freshly precipitated Fe(III) oxides may have acted as a veneer that prevented the ingress of oxygen and hence the re-oxidation of U(IV), thereby retarding U release.

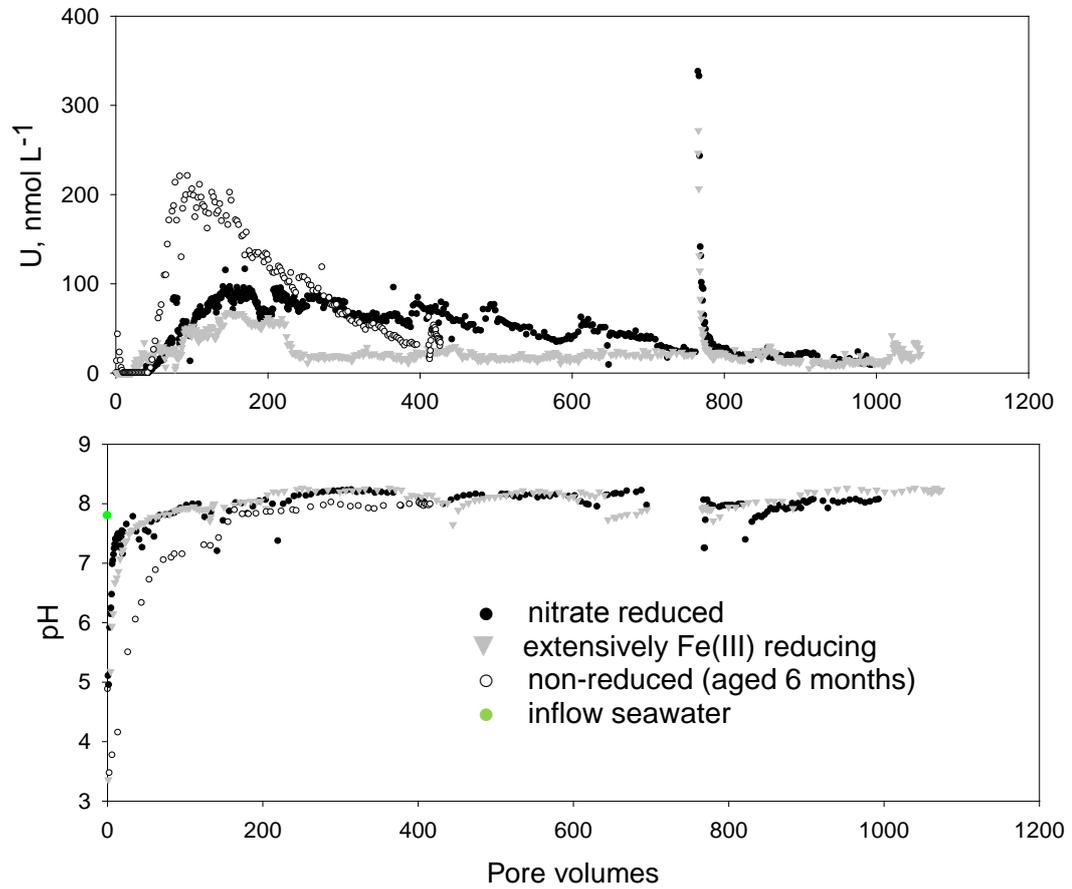
#### 4.4 Environmental Implications

In these experiments U(VI) was sorbed to the sediments during nitrate reduction and as iron reduction progressed U was association with the sediments as (a) sorbed U(VI) species, (b) U(IV) [monomeric and/or UO<sub>2</sub>] or (c) as several species including

U(IV)/U(VI). There was no mobilisation of U from reduced sediments in the batch systems or during early elution from the column experiments into oxic seawater. The column experiments showed U release would be delayed with respect to the migrating seawater front. Mobilisation would follow the change in sediment pH, induced by the seawater. After that time U release was kinetically controlled and characterised by a slow release from a range of binding sites. As nitrate reducing and extensively iron reducing sediments were re-oxidised in seawater, U release was pH dependent, promoted via the formation of U(VI)-(Ca)-CO<sub>3</sub> complexes and characterised by slow release from kinetically hindered binding sites over time. Under flow conditions, release was more extensive from initially nitrate reducing sediments (53 %) compared with extensively iron reducing sediments (38 %). Sequential extractions showed that there was no significant difference in the initial associations of U with the sediments; therefore the less extensive release from extensively iron reducing sediments may be due to changes in the sediments themselves during reduction or delayed due to the oxidation of U(IV) to U(VI) prior to release. Importantly, the re-oxidation of Fe(II) to Fe(III) appears to be able to retard U release by providing sorption sites for U(VI) and/or incorporation of U into the precipitating Fe(III) oxy-hydroxides or by forming a veneer preventing U(IV) reoxidation and release.

When the data from the aged, oxic sediment column experiment are compared with those from the reducing sediment columns (Figure 4.8), it is clear that mobilisation profiles of U from the oxic sediment was different from the reduced sediments and that the release of U was more rapid (46 % after 417 pore volumes). The pH at which U mobilisation started from the initially oxic sediments (pH 6.5) was sufficiently high for the formation of U carbonate complexes. Therefore, in the reduced sediments, the formation and release of U carbonate complexes is hindered over the pH range 6.0 - 7.3. Therefore, changes in the sediments during reduction and/or during re-oxidation in

seawater hinder U mobilisation from reduced sediments and increase the pH required for mobilisation. Reduced sediments will therefore act as a long term source of pollution to marine environments as a result of intrusion with oxidic seawater.



**Figure 4.8: Mobilisation of U from oxic sediment, nitrate reduced sediment and extensively iron reducing sediment into seawater during column experiments.**

## **Chapter 5**

# **Technetium mobilisation from reduced sediments under saltwater intrusion scenarios**

## 1.1 Introduction

Sea level rise predictions associated with climate change suggest that coastal areas, where many of the UK's nuclear sites are located, are threatened by seawater inundation and intrusion (Choudhury *et al.* 2001), leading to salinisation of previously freshwater aquifers, soils and sediments. Changes in the salinity of the contaminated sediments may trigger ion exchange and dissolution-precipitation reactions and impact on the stability of radionuclides associated with sub-surface sediments. Additionally, the inflow of oxygenated water may move sub-surface redox boundaries, enhancing the mobilisation of redox sensitive radionuclides through reoxidation.

The long lived ( $t_{1/2} = 2.1 \times 10^5$  years), high yield fission product  $^{99}\text{Tc}$  is of particular concern at contaminated nuclear sites due to its abundance in radioactive waste and relatively high environmental mobility under oxic conditions as the pertechnetate anion,  $\text{Tc(VII)O}_4^-$ . However, under anoxic conditions  $\text{Tc(VII)O}_4^-$  is reduced to Tc(IV) and is retained in soils and sediments as hydrous  $\text{Tc(IV).nH}_2\text{O}$  phases (Burke *et al.* 2004; Fredrickson *et al.* 2004; Maes *et al.* 2004; Wildung *et al.* 2004; McBeth *et al.* 2007) and by adsorption to aluminium and iron oxides (Lloyd *et al.* 2000; Wildung *et al.* 2000; Abdelouas *et al.* 2005) and/or organic matter (Tagami and Uchida 1996; Keith-Roach *et al.* 2003). The formation of soluble Tc(IV) carbonate complexes and colloids may facilitate technetium migration in reducing geochemical environments (Paquette and Lawrence 1985; Wildung *et al.* 2000; Alliot *et al.* 2009) e.g. during intrusion with seawater.

The oxidative mobilisation of Tc(IV) has been studied extensively using batch experiments (Finneran *et al.* 2002; Burke *et al.* 2006; McBeth *et al.* 2007). Technetium(IV) can be oxidised by  $\text{O}_2$  (Senko *et al.* 2002; McBeth *et al.* 2007; Komlos *et al.* 2008; Morris *et al.* 2008) but re-oxidation and mobilisation is often incomplete (McBeth *et al.* 2007; Begg *et al.* 2008; Moon *et al.* 2009). Oxidation resistant Tc has

been found to be associated with iron containing particles such as Fe-phyllosilicates, micas and clay minerals (Zachara *et al.* 2007; Fredrickson *et al.* 2009; Jaisi *et al.* 2009). Technetium incorporated into the lattice of iron oxides such as goethite [ $\alpha$ -Fe(III)O(OH)] has also been found to be resistant to re-oxidation and less prone to mobilisation compared with Tc sorbed onto iron oxides or existing as discrete  $\text{TcO}_2 \cdot 2\text{H}_2\text{O}_{(s)}$  crystals (Lukens *et al.* 2005; Um *et al.* 2011). Equally, when incorporated into less stable, poorly ordered iron phases, including green rust and ferrihydrite, Tc was not oxidised or released when these phases were transformed into goethite (Pepper *et al.* 2003; Zachara *et al.* 2007). Therefore, iron(III) oxides produced during re-oxidation may be able to 'vener' Tc, protecting it from, or limiting, re-oxidation (Menager *et al.* 1994; Payne *et al.* 1994; Zachara *et al.* 2007; Peretyazhko *et al.* 2008; Jaisi *et al.* 2009). These studies examined the oxidation of Tc using static (no flow) batch experiments but there is a lack of knowledge regarding Tc re-oxidation under more environmentally relevant flow conditions, in particular the ability of these secondary phases to protect Tc release under oxic flow conditions.

Since reducing subsurface soils are sinks for Tc, it is important to understand and predict the behaviour of Tc during intrusion with seawater. Therefore the focus of this study was to investigate the mobilisation of Tc(IV) from geochemically reduced sediments, at different stages of reduction, during seawater inundation and intrusion. The effect of increased porewater salinity and the re-introduction of dissolved oxygen on the mobilization of Tc was studied using batch experiments to compare release into groundwater, degassed seawater and oxic seawater over time. Column experiments were then used to investigate Tc release into seawater under more environmentally relevant, dynamic, flow through conditions

## 5.2 Experimental

**5.2.1 Sediment reduction** Sediments were amended with a synthetic groundwater solution representative of those found at the low level waste repository at Drigg (Cumbria UK) containing Tc and U. Technetium was added as  $^{99}\text{TcO}_4^-$  (Amersham) to give a final concentration of 1  $\mu\text{M}$ . The experimental strategy adopted is outlined in Figure 4.1. Amended synthetic groundwater was added to the sediments to give a 1:1 (m/v) sediment:solution ratio and incubated anaerobically in 250 mL serum bottles in the dark at 21 °C (Section 4.2.3). At selected time intervals serum bottles were transferred to an anaerobic chamber and the geochemical conditions determined. Sediment slurries were analysed for pH and Eh using calibrated electrodes prior to centrifuging (10 min at 7500 g). The supernatant was then analysed for  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  (Section 4.2.7); aqueous Tc and  $\text{Fe}_{[\text{total}]}$  concentrations were determined by ICP-MS. Total acid (0.5 M HCl) extractable sedimentary Fe(II) was determined spectrophotometrically using ferrozine ( $\lambda_{\text{max}} = 562 \text{ nm}$ ) (Stookey 1970; Lovely and Phillips 1986). Reducing conditions were allowed to develop until nitrate reduced (30 days), iron reducing (60 days) and extensively iron reducing (120 days) conditions dominated. The operationally defined solid phase associations of Tc with the reduced sediments used in the mobilisation experiments were determined using a modified sequential extraction procedure (Section 4.2.8)

**5.2.2 Mobilisation of Tc:** At the pre-determined time points the Tc contaminated sediments were homogenised and then sub-sampled for use in the mobilization experiments. Samples were transferred into 100 mL Erlenmeyer flasks (Fischer Scientific, UK) for re-oxidation experiments and amended with synthetic groundwater or seawater to give a 1:1 (m/v) sediment:solution ratio. Flasks were then capped with

sterile autoclaved porous bungs to allow entry of air and shaken in the dark at 110 rpm and 21 °C for pre-determined time periods, up 120 days (Section 4.2.5).

To investigate the mobilization of Tc in seawater under reducing conditions, reduced sediments were amended with degassed seawater ( $N_2$ ;  $O_2 < 0.05 \text{ mg L}^{-1}$ ) in serum bottles and incubated in the dark (see Section 4.2.6). At pre-determined time intervals the contents of the Erlenmeyer flasks and serum bottles were transferred to centrifuge tubes in the anaerobic chamber. Sediment slurries were analysed for pH and Eh using calibrated electrodes prior to centrifuging. The supernatant was then analysed for  $NO_3^-$ ,  $SO_4^{2-}$ , aqueous Tc,  $Fe_{[total]}$  and total acid (0.5 M HCl) extractable sedimentary Fe(II) as described above.

**5.2.3 Column design and operation.** Column experiments were conducted to investigate the mobilization of Tc from nitrate reducing and extensively iron reducing sediments under fully saturated seawater flow conditions, representative of sea water intrusion. Under anaerobic conditions contaminated sediments were packed into a polyetheretherketone (PEEK) self-pack column (Section 4.2.9) Columns were then removed from the anaerobic chamber and a high-performance liquid chromatography (HPLC) pump was used to saturate the column at a constant flow rate ( $1.2 \text{ mL h}^{-1}$ ). The eluate was collected in 1.2 - 3.6 mL fractions using a fraction collector (Section 4.2.9). Flow was stopped for 2 weeks (SSF 1) during the saturated column experiments, after approximately 765 (nitrate reduced) and 760 (extensively iron reducing) pore volumes. A second stop flow event (SSF2) lasting 2 weeks was carried out in columns packed with extensively iron reducing sediments at 1050 pore volumes. Columns were characterised using a bromide tracer. Both pH and Eh were measured as soon as practicable after elution. Technetium,  $Br^-$  and  $Fe_{[total]}$  concentrations were determined by ICP-MS. After each run the column was opened and the packed sediment pushed out

using a clean polypropylene rod. The sediment was separated into fractions at approximately  $0.8 \pm 0.2$  cm intervals and total Tc determined by ICP-MS after aqua regia digestion.

**5.2.4 Determination of Tc.** Technetium was determined by ICP-MS. The limit of detection of Tc was 30- 300 pM in all extractants, determined by 3 x the standard deviation of the lowest standard. Ruthenium (Ru) has an isotope of mass 99 which can interfere in the ICP-MS analysis of Tc. Therefore, contaminated sediments were digested in aqua regia and the extract analysed for a signal at m/z 99. It was found that background Ru was negligible in these sediments and would not cause interferences.

## **5.3 Results and discussion**

### **5.3.1 Sediment reduction and solid phase associations of Tc**

**Changes in biogeochemical conditions during progressive reduction:** The sediments became progressively anoxic over time. Table 5.1 shows the sediment conditions at the time points when the sediments were sub-sampled for immediate use in mobilisation experiments and for storage ( $-20$  °C) for subsequent characterisation. The evolution of the biogeochemical conditions is explained in detail in Section 4.3.1. In brief, the Eh decreased over time as the sediments became increasingly reducing. Nitrate reduction was complete after 30 days, and iron reduction had initiated after 60 days (indicated by ingrowth of 0.5 M HCl extractable Fe(II)). After 120 days conditions were extensively iron reducing.

**Behaviour of technetium:** As conditions became increasingly reducing, Tc(VII) was presumably reduced to Tc(IV) and became associated with the sediments (Table 5.1). Although nitrate has been shown to inhibit the reduction of metals under reducing

conditions in sediments (Dichristina 1992; McBeth *et al.* 2007), in these experiments extensive Tc removal from solution (87 %) occurred alongside nitrate and early metal reduction.-

**Table 5.1: Conditions in the sediments and pore waters. Sediments were homogenised for use in mobilisation experiments and sequential extractions. Data show means (n=10)  $\pm$  1 standard deviation. LOD is the limit of detection- shown in brackets.**

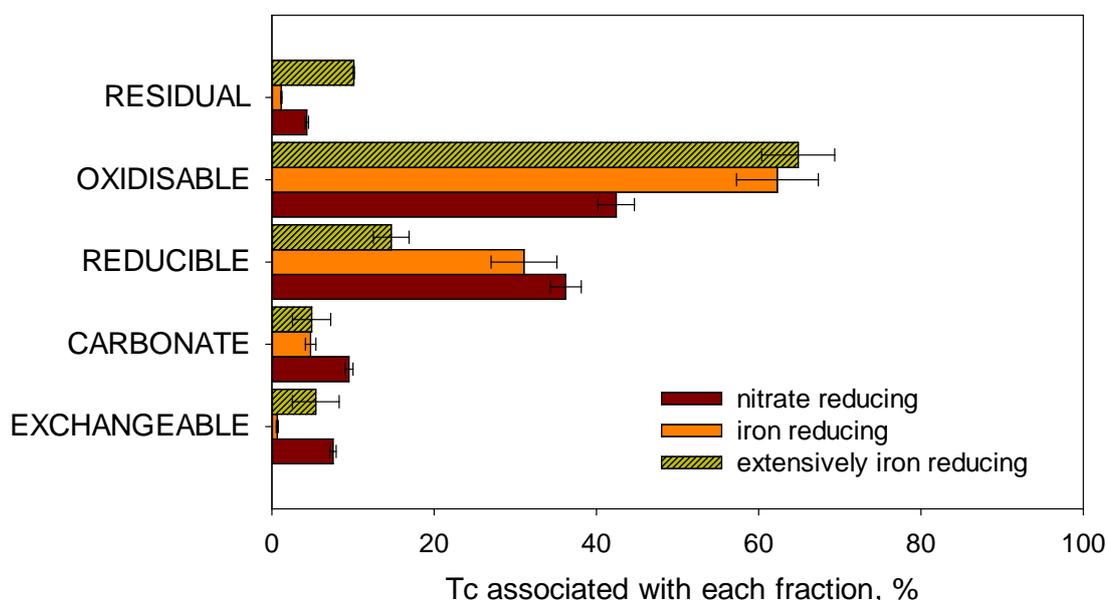
	<b>Original conditions</b>	<b>Nitrate reduced</b>	<b>Iron reducing</b>	<b>Extensively iron reducing</b>
Reduction time	1 h	30 d	60 d	120 d
Eh, mV	424 $\pm$ 36	170 $\pm$ 1	25 $\pm$ 8	15 $\pm$ 5
pH	4.8 $\pm$ 0.6	6.4 $\pm$ 0.6	6.9 $\pm$ 0.3	7.0 $\pm$ 0.5
Tc, $\mu\text{mol kg}^{-1}$ (dry mass)	< LOD	0.916 $\pm$ 0.04	1.03 $\pm$ 0.002	1.04 $\pm$ 0.006
% Tc associated with sediments	-	87	98	99
NO <sub>3</sub> <sup>-</sup> , $\mu\text{M}$	4700 $\pm$ 200	4.36 $\pm$ 0.6	<LOD (2.5)	< LOD (2.5)
Acid extractable Fe (II), $\text{mmol kg}^{-1}$	< LOD (0.55)	< LOD (0.55)	8.3 $\pm$ 0.8	16 $\pm$ 1
SO <sub>4</sub> <sup>2-</sup> , $\mu\text{M}$	3.60 $\pm$ 0.4	4.20 $\pm$ 1	4.8 $\pm$ 1	4.8 $\pm$ 0.1

This has been observed previously in microcosm experiments (Maset *et al.* 2006), under field conditions in a nitrate co-contaminated aquifer (Istok *et al.* 2004) and in estuarine sediments, when a significant fraction (90 %) of the nitrate was removed from solution (Burke *et al.* 2005).

By day 60, when active in-growth of Fe(II) was observed in the sediments, significantly more ( 98 %) of the Tc was reduced and removed from solution, which increased to 99 % as Fe(III) reduction progressed. Technetium reduction has been observed as Fe(III) reducing conditions develop in many environmental matrices including; Fe(III)-oxide containing sediments from Oak ridge USA (Fredrickson *et al.* 2004), from a shallow

sandy coastal plain sediments (Wildung *et al.* 2004), organic matter rich soils (Abdelouas *et al.* 2005), estuarine sediment (Burke *et al.* 2005), Dounreay sediments (Begg *et al.* 2008). Although conditions in the microcosms became extensively iron(III) reducing over time, a small fraction (1 %) of the Tc remained in solution.

**Changes in solid phase associations during reduction:** Sequential extractions were conducted to investigate changes in the solid phase associations of Tc as the sediments became increasingly reducing (Figure 5.1). For ease of reference the descriptive names for the different chemical leaches will be used (Keith-Roach *et al.* 2003).



**Figure 5.1: Solid phase associations of Tc with reduced Crediton sediments.** Percentage of Tc extracted in each fraction using a modified Tessier sequential extraction adapted for use in anaerobic environments. Sediments were contaminated with Tc in a simulated groundwater solution and allowed to become progressively more reducing over time. Data show means of 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Extractants are described in Table 2.2.

In reduced sediments, Tc was predominately associated with the oxidisable (42-64 %) and reducible (14-36 %) fractions. This association with the oxidisable fraction is consistent with other studies [e.g. reduced estuarine sediments (70 %) (Burke *et al.*

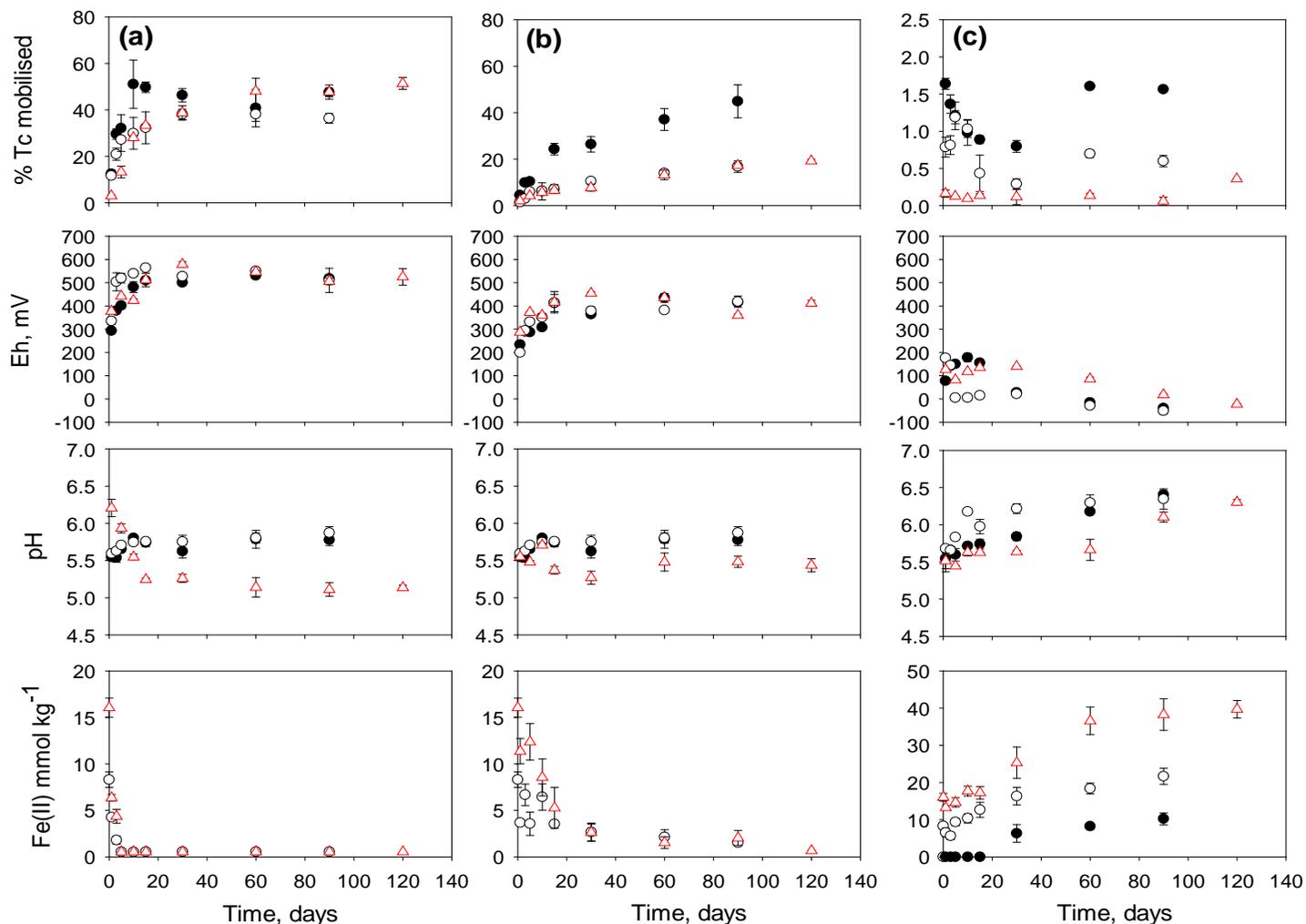
2010) ; reduced organic matter rich soils (60-66 %) (Abdelouas *et al.* 2005); reduced marine sediments (79-83 %) (Keith-Roach *et al.* 2003) and river sediments (80-85 %) (Standring *et al.* 2002).

As conditions changed from nitrate reducing to iron reducing and extensively iron reducing, significantly ( $p= 0.007$ ) more Tc became associated with the oxidisable fraction. Since this increase exceeded the amount of Tc(VII) that was reduced in this period, Tc appears to undergo structural rearrangement between the geochemical fractions. The oxidisable extractant is generally considered to leach metals associated with sediment organic matter (Tessier *et al.* 1979; Wallmann 1993; Keith-Roach *et al.* 2003), and Tc binding with particle associated organic matter has been shown to restrict Tc mobility (Stalmans *et al.* 1986; Wolfrumm and Bunzl 1986). Burke *et al.*, (2010) suggest that this extraction may provide an over-estimation of the association of Tc with organic matter and is more indicative of the ability of  $H_2O_2$  to oxidise Tc(IV)O<sub>2</sub> to Tc(VII) (German *et al.* 2003). These results provide evidence that Tc(IV) becomes more strongly associated with the sediments as reduction progresses and hence would be less prone to mobilisation under changing geochemical conditions.

### **5.3.2 Mobilisation of Tc during intrusion**

Reduced sediments were suspended in groundwater and seawater to investigate the impact of salinity on Tc mobilisation during the oxidation of reduced sediments. The effects of salinity and oxidation were decoupled by comparing Tc mobilisation into air-equilibrated and degassed seawater. Changes in the solid phase associations of Tc during mobilisation experiments were monitored using sequential extractions

**Changes in geochemical conditions:** Changes in the geochemical conditions over the mobilisation period are shown in Figure 5.2.



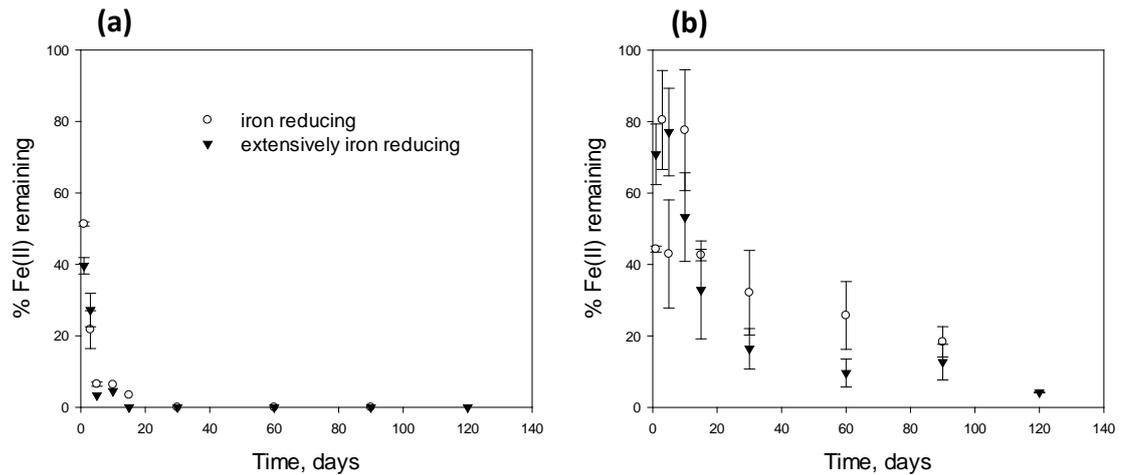
**Figure 5.2: Mobilisation of Tc from reduced sediments and the corresponding changes in the geochemical indicators Eh, pH and acid (0.5 M HCl) extractable Fe(II) during mobilisation of ● nitrate reduced, ○ iron reducing and △ extensively iron reducing sediments in (a) groundwater, (b) seawater and (c) degassed seawater respectively. Sediments were contaminated with Tc ( $\approx 1 \mu\text{M}$ ) in a simulated groundwater solution. Data show means of 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Note the different scales for %Tc mobilised, Eh and acid extractable Fe(II) in degassed seawater experiments.**

**Groundwater:** When the sediments were re-oxidised in groundwater, the Eh initially increased most rapidly in the iron-reducing sediments. However, there was no significant difference between the Eh of the three systems once equilibrium had been established by day 60. In all cases, the addition of groundwater immediately decreased the sediment pH. The pH then varied in all systems, with significant ( $p < 0.05$ ) differences between extensively iron reducing sediments and both nitrate and iron reducing sediments.

**Seawater:** The Eh data showed that the sediments were re-oxidised more slowly in seawater than groundwater, and reached a lower equilibrium Eh (Figure 5.2). Again the addition of seawater to the sediments had a significant effect on the pH; both the pH of the sediments (originally pH 6.4-7.0) and the seawater (pH 7.8) decreased to  $< 5.3$ . The pH variations were again similar in the nitrate reduced and iron reducing sediments, but significantly ( $p = 0.013$ ) lower in the extensively iron reducing sediments.

**Degassed seawater:** In these systems, conditions became increasingly reducing, as shown by the Eh data. By day 30, there was no significant difference between the Eh of all three sediments. The decrease in Eh observed in these microcosms corresponded with an increase in pH, which is consistent with the production of  $\text{HCO}_3^-$  and  $\text{OH}^-$  during microbial respiration (Law *et al.* 2010).

**Changes in acid extractable Fe(II):** The concentration of acid (0.5 M HCl) extractable Fe(II) associated with the iron reducing and extensively iron reducing sediments declined rapidly during re-oxidation (Figure 5.3). Approximately 40-50 % of the original sediment-associated Fe(II) persisted after the sediments had been suspended in groundwater for 1 day, which decreased to 3-5 % after 10 days.



**Figure 5.3: Percentage of acid extractable Fe(II) retained in initially iron reducing and extensively iron reducing sediments during reoxidation; reduced sediments were suspended in (a) groundwater and (b) seawater. Data show means (n=3) ± 1 standard deviation. Concentrations of Fe(II) were below the limit of detection in nitrate reducing sediments.**

Re-oxidation of Fe(II) was slower in seawater; there was no significant oxidation of sedimentary Fe(II) over the first 10 days (50-80 % remaining associated with the solid phase). Re-oxidation of aqueous Fe(II) has previously been shown to be retarded in seawater compared with freshwater (Gonzalez *et al.* 2010). After 90 days, concentrations of acid extractable Fe(II) were lower than the limit of detection in the groundwater systems whilst in seawater 13-18 % remained.

**Cycling of Tc in degassed seawater:** Limited (< 2%) Tc mobilisation was observed into degassed seawater. Over time, as conditions became increasingly reducing, Tc continued to be reduced this shows that cation-exchange or formation of soluble Tc(IV) carbonate or chloride complexes are of negligible importance in Tc mobility in comparison with re-oxidation.

**Mobilisation of Tc in groundwater:** There was a rapid initial mobilisation of Tc into groundwater from all three sediment types, 3 - 12 % of Tc was mobilised after 1 day,

increasing to 28 - 51 % after 10 days (Figure 5.2). Technetium was initially mobilised more rapidly from nitrate reduced sediments compared with iron and extensively iron reducing sediments despite the slower increase in Eh. After 90 days, similar concentrations of Tc (36 - 48 %) were mobilised from all sediments. Release of Tc correlated with increasing Eh over the course of the experiment (nitrate reducing  $r=0.927$ ,  $p=0.001$ ; iron reducing  $r=0.814$ ,  $p=0.014$ ; extensively iron reducing  $r=0.833$ ,  $p=0.019$ ). Therefore mobilisation was dependent on the oxidation of Tc(IV) prior to Tc(VII) prior to mobilisation. At the end of the experiment, despite the oxidising conditions (Eh= +506 - 518 mV) and differences in the association of Tc with the sediments identified in the initial sequential extractions (Figure 5.1), 52 - 64 % of Tc remained associated with the sediments. Therefore a fraction of Tc remains recalcitrant to mobilisation in groundwater, which is consistent with other reoxidation studies where Tc also remained associated with Oak Ridge sediments (20 %) (McBeth *et al.* 2007), estuarine sediments (50 %) (Burke *et al.* 2006), Dounreay sediments (42 %) (Begg *et al.* 2008).

**Mobilisation of Tc in seawater** Technetium was mobilised from all of the sediments in oxic seawater but more slowly than in groundwater (Figure 5.2). The initial redox conditions effected the release of Tc, with Tc mobilised significantly faster from initially nitrate reduced sediments compared with sediments with ingrowth of Fe(II) (both iron reducing and extensively iron reducing sediments). For example, after 5 days, 10 % of Tc was released from nitrate reduced sediments compared with iron reducing (4 %) and extensively iron reducing (6 %) sediments, despite the Eh initially increasing more rapidly in iron reducing sediments. After the 90 d experimental period, significantly more ( $p<0.016$ ) Tc was mobilised from nitrate reduced sediments ( $45 \pm 7$  %) than from iron reduced and extensively iron reducing sediments ( $17 \pm 2.5$  %). The Eh measured over the course of the experiment was lower in seawater compared to

groundwater, however the Eh was sufficiently high ( $< + 360$  mV) that the formation of Tc(VII) would be expected from thermodynamic calculations. Therefore, there is a difference between the groundwater and seawater release mechanisms that cannot be explained by the Eh of system alone.

**Release of Tc during intrusion:** The results show that a fraction of the Tc(IV) was weakly sorbed to or associated with ‘unprotected’ sediment surfaces that was readily re-oxidised and released when in contact both oxygenated seawater (17 – 45 %) or groundwater (36 - 48 %). A second fraction of Tc was less available for re-oxidation and release and remained immobile. The combination of Fe(II) in-growth in the sediments and seawater resulted in a smaller “available” Tc fraction than in all other situations. However, the extent of Fe(II) ingrowth had no effect on the release of Tc into seawater. These results suggest that the association of Tc(IV) with sedimentary Fe(II) can influence both the rate and extent of Tc re-oxidation and release in seawater. In these experiments sedimentary Fe(II) was re-oxidised faster than Tc was released; therefore Tc may be protected from re-oxidation and mobilisation by incorporation into the structure of, or become *veneered* by, freshly precipitated iron(III)oxides (Zachara *et al.* 2007; Peretyazhko *et al.* 2008; Jaisi *et al.* 2009). The slower re-oxidation of sedimentary Fe(II) observed in the seawater (compared with groundwater), coupled with the presence of increased concentrations of complexing cations and anions, may have resulted in the formation of a different iron re-oxidation product with a different structure (Sung and Morgan 1980; Charette and Sholkovitz 2002) which acted as a more effective veneer; thereby preventing the diffusion of oxygen and hindering the release of Tc(VII).

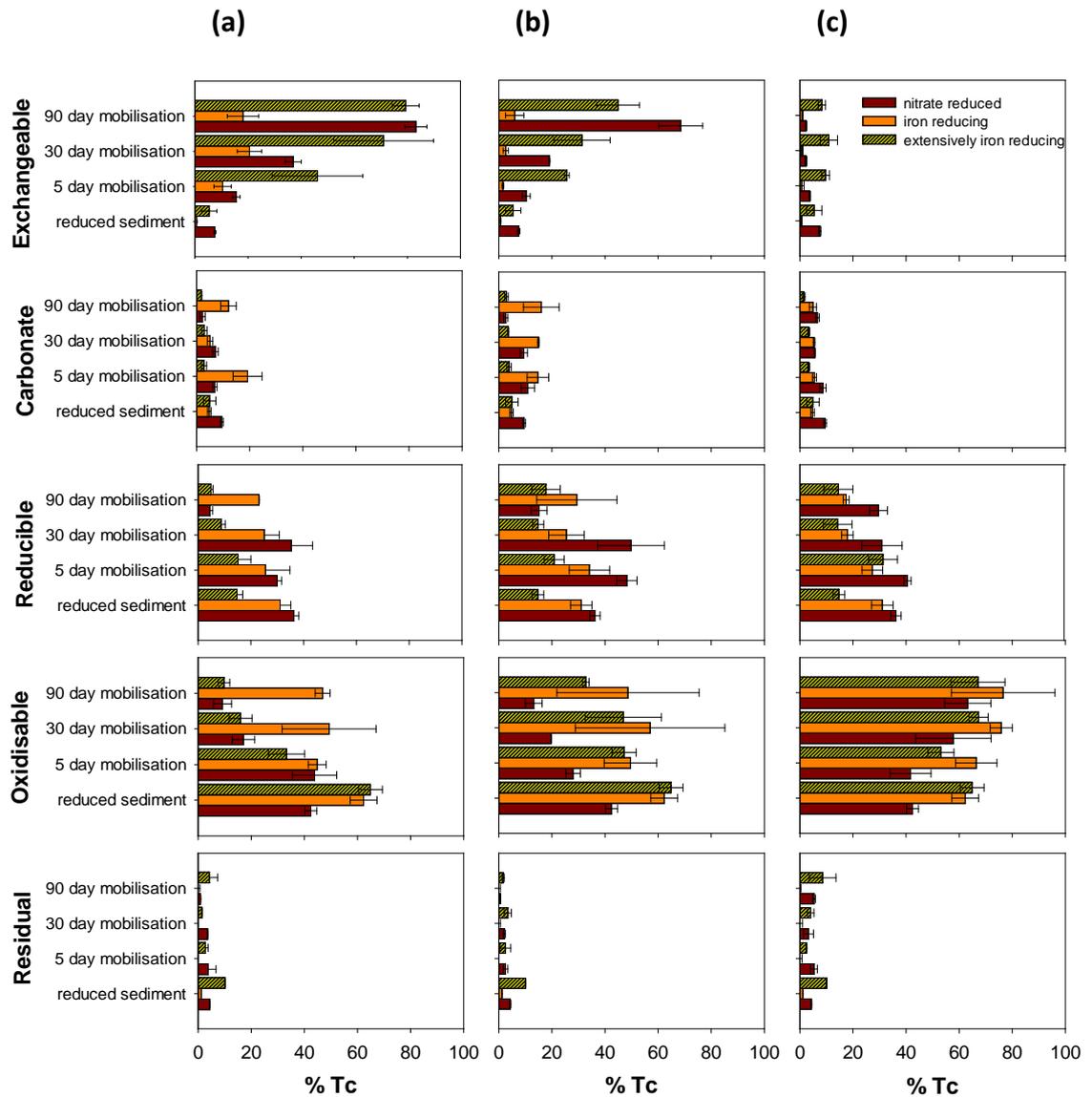
Additionally, if Tc became incorporated into the lattice of sediment associated iron phases during reduction, then during re-oxidation these phases may have been able to

prevent Tc re-oxidation and release (Pepper *et al.* 2003; Lukens *et al.* 2005; Zachara *et al.* 2007; Fredrickson *et al.* 2009). It was not possible to identify subtle changes in these phases and detect newly formed Fe(III) phases due to a lack of sensitivity of bulk solid phase analytical techniques such as XRD and SEM and the complex nature of the matrix.

### **5.3.3 Changes in solid phase associations of Tc during mobilisation**

A further series of sequential extractions was conducted to assess any changes in the solid phase association of Tc during the batch mobilisation experiments. Figure 5.4 shows the associations of Tc with the initial reduced sediments and after 5, 30 and 90 day mobilisation periods in groundwater, seawater and degassed seawater. Whilst Tc remained predominately associated with the oxidisable and reducible fractions, there was evidence of changes in the association of Tc during re-oxidation.

The most notable re-distribution of Tc involved transfer into the exchangeable fraction during re-oxidation in both seawater and groundwater. It was clear that Tc became associated with the exchangeable fraction at a greater rate and to a greater extent in groundwater compared with seawater, and the most significant changes were seen in the nitrate reduced and extensively iron reducing sediments. Although the same trend was observed in iron reducing sediments, the concentration of Tc associated with the exchangeable fraction was significantly lower in these experiments and the reason for this is unclear. Technetium became increasingly exchangeable during re-oxidation however Tc mobilisation was limited which suggests that Tc may have been trapped by an exchangeable veneer which prevented Tc release.



**Figure 5.4: Changes in the solid phase associations of the sediment bound Tc with nitrate reduced, iron and extensively iron reducing conditions during mobilisation in (a) groundwater, (b) seawater and (c) degassed seawater. The percentage of Tc extracted in each fraction using a modified sequential extraction scheme adapted for use in anaerobic environments is shown. Sediments were contaminated with Tc in simulated groundwater solution and allowed to become progressively more reducing over time. Results show association of Tc with sediments prior to mobilisation (reduced sediment) and after 5, 30 and 90 days of mobilisation respectively. Means are calculated from 3 separate extractions, error bars represent  $\pm 1$  standard deviation. Extractants are described in Table 2.2**

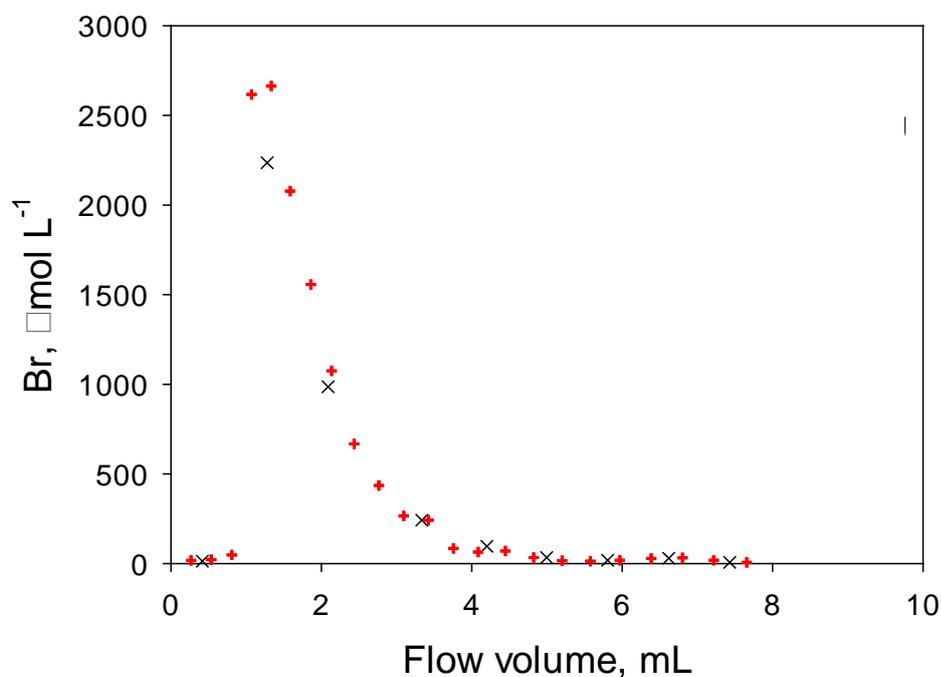
In degassed seawater, where conditions became increasingly anaerobic over time, only a small fraction of the Tc was associated with the exchangeable fraction (< 5 %). In these experiments Tc remained recalcitrant to mobilisation.

A large fraction of Tc remained associated with the oxidisable fraction (Figure 5.4) when sediments were re-oxidised in groundwater (9 – 47 %) and seawater (13 – 49 %). The percent of Tc associated with this fraction in initially nitrate reducing sediments decreased during re-oxidation (from 42 % to between 9 and 13 %). However when initially iron and extensively iron reducing sediments were re-oxidised in seawater, a larger percent of Tc remained associated with the oxidisable fraction (33 - 49 %). The oxidisable extraction conditions have the capacity to leach metals associated with sediment associated organic matter (Tessier *et al.* 1979; Wallmann 1993). Although the organic content of the sediments was low (2 % by mass), salt induced contraction of these organic coatings may have enhanced veneering during Fe(II) oxidation, making Tc less accessible.

#### **5.3.4 Mobilisation of Tc into seawater during dynamic seawater intrusion**

Column experiments were conducted in order to understand the mobilisation of Tc from nitrate reduced and extensively iron reducing sediments under environmentally relevant flow conditions. Seawater was pumped up through the vertically mounted column to create fully saturated conditions.

**Column characterisation:** Columns were characterised using a conservative Br<sup>-</sup> tracer (200 µL of 75 mM Br<sup>-</sup>) injected as a pulse through the column at the end of the mobilisation experiments. Figure 5.5 shows the Br<sup>-</sup> elution data from the column experiments.



**Figure 5.5: Elution profile for the transport of the bromide tracer used in nitrate (X) reduced and extensively (+) iron reducing column experiments.**

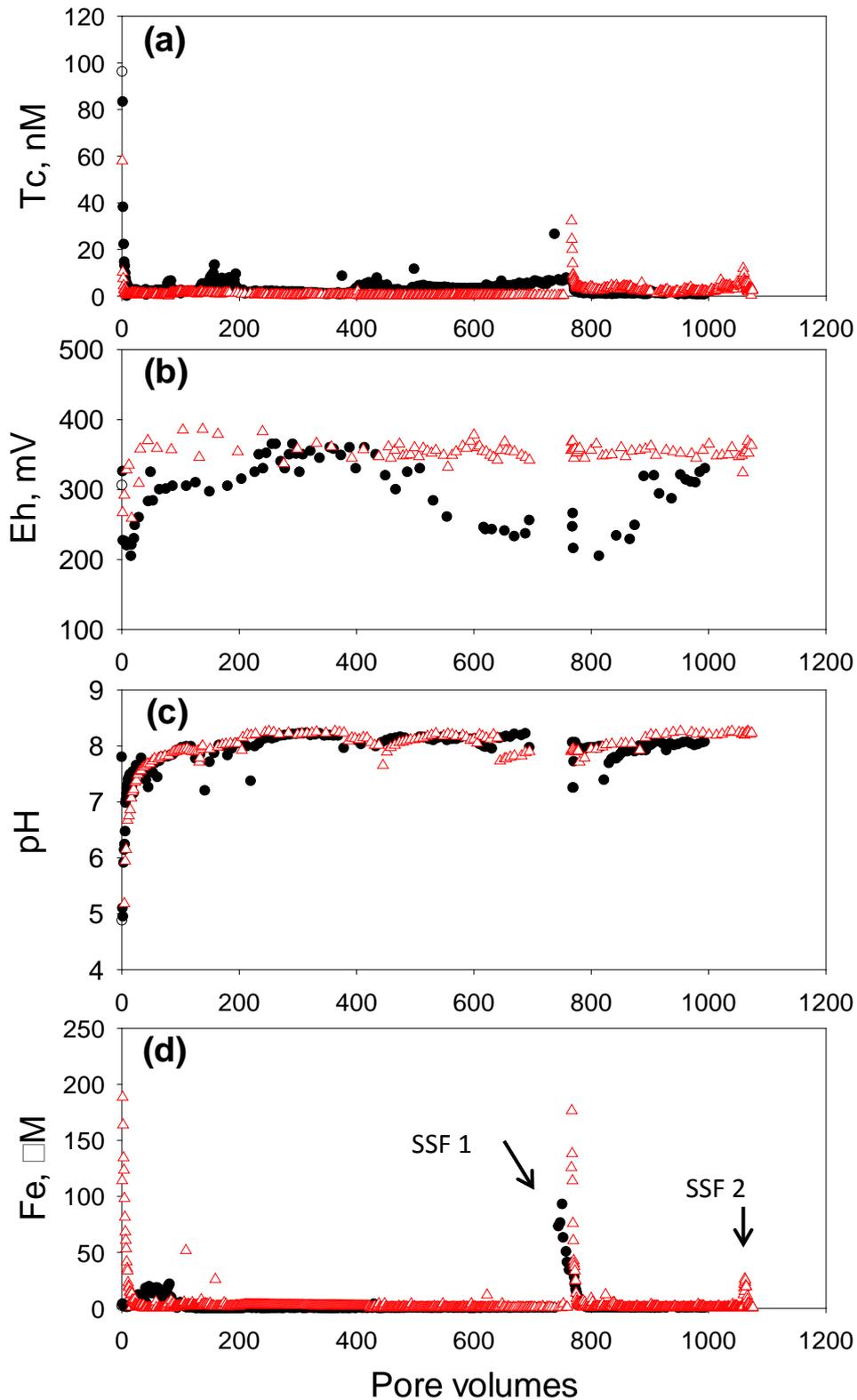
Both profiles exhibited similar, narrow peaks suggesting that there were no preferential flow paths and that the columns were packed consistently. The linear flow velocity was  $235 \text{ m y}^{-1}$  (nitrate reduced) and  $262 \text{ m y}^{-1}$  for extensively iron reducing columns respectively.

**Changing geochemical conditions in the column:** The Eh of the columns increased as the sediments were re-oxidised (Figure 5.6). The Eh of the leachate in both columns remained  $> +200 \text{ mV}$ , and ranged from  $+203$  to  $+386 \text{ mV}$ . These values are lower than the Eh observed after 10 days in the batch experiments, reflecting the flow-controlled input of oxygen. Extensively iron reducing sediments were re-oxidised faster than nitrate reduced sediments which is consistent with the batch experiments. The Eh in the extensively iron reducing columns then remained relatively constant over the 1 month experimental period whereas the Eh in the nitrate reducing was not constant over time.

The pH of the outflow seawater (3.4 - 4.9) was initially lower than the inflow seawater (7.8) in both column experiments (Figure 5.6). The pH was significantly lower in the outflow of the extensively iron reducing sediments (3.4) compared with 4.9 in the nitrate reduced columns. The pH in both columns then increased steadily reaching a pH (7.8) more representative of seawater after 60 (nitrate reducing) and 44 (iron reducing) pore volumes. Beyond this point sediments had no further influence on the pH of the seawater, which remained between pH 7.2 - 8.2 over the remainder of the experiment. The stop-start event had no discernible effect on the pH.

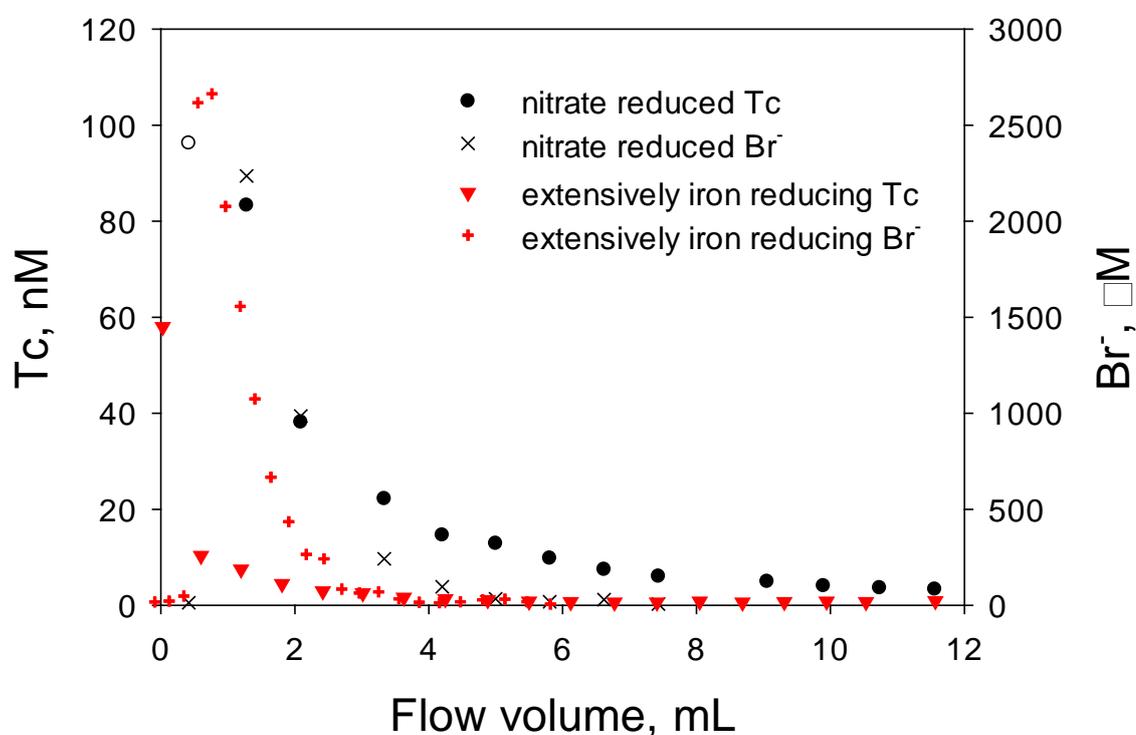
Initially, significantly more Fe was eluted from the extensively iron reducing ( $190 \mu\text{mol L}^{-1}$ ) compared with nitrate reduced ( $3.8 \mu\text{mol L}^{-1}$ ) sediment, which is consistent with their reduced status. In the extensively iron reducing sediments, the concentration of Fe mobilised then decreased over time as Fe(II) was oxidised to poorly soluble Fe(III). There was also a distinct period of Fe release from the initially nitrate reduced sediments between 20 and 120 pore volumes.

Flow was stopped for 2 weeks during the tailing period of the saturated column experiments at approximately 765 (both columns) and 1060 (extensively iron reducing) pore volumes to assess whether concentrations of species in the water were in equilibrium with the sediment concentrations. (Qafoku *et al.* 2005; Yin *et al.* 2011). After the first stop start event, there was a pulse release of Fe from both the nitrate reduced ( $93 \mu\text{mol L}^{-1}$ ) and extensively iron reducing sediments ( $176 \mu\text{mol L}^{-1}$ ). Significantly less Fe was released from the extensively iron reducing sediments ( $26 \mu\text{mol L}^{-1}$ ) after the second stop/start event. This suggests that the pool of readily exchangeable iron was becoming depleted over time.



**Figure 5.6:** Concentration of (a) Tc and (d) Fe mobilised from sediments with corresponding changes in (b) Eh and (c) pH in the leachate during saturated flow through column experiments. Columns were packed with ● nitrate reduced and Δ extensively iron reducing sediments with seawater as the mobile phase. Note the different scales for Fe mobilisation ( $0\text{-}100\ \mu\text{mol L}^{-1}$ ) and Tc mobilisation ( $0\text{-}40\ \text{nmol L}^{-1}$ ). Stop/start flow events (SSF) are shown on the figure.

**Technetium:** A near instantaneous, high concentration pulse release of Tc was observed from both sediments (Figure 5.7), similar to the transport behaviour of the conservative Br<sup>-</sup> tracer. This was followed by a decrease in Tc concentration, which was more rapid in the iron reducing columns. After 12 (nitrate reduced) and 7 (iron reducing sediments) pore volumes the rate of release slowed considerably, concentrations of Tc released then remained constant until approximately 133 pore volumes of seawater had eluted. The Eh observed in both columns was above the theoretical Tc(VII)/Tc(IV) couple of 100-200 mV at pH 7 (Burke *et al.* 2006; Icenhower *et al.* 2010).



**Figure 5.7: Mobilisation of Tc relative to the conservative Br tracer from nitrate reduced and extensively iron reducing sediments during dynamic flow through column experiments with seawater as the mobile phase.**

Whilst rapid, only a small fraction of the total Tc associated with the sediments was mobilised. In the first 12 pore volumes more Tc was released from nitrate reduced sediments (7 %) compared with iron reducing sediments (5 %), which corresponds to the percentage of Tc associated with the exchangeable fraction in the sequential

extractions (7.5 % nitrate and 5.4 % iron reducing). The data strongly supports the previous conclusion that a fraction of the Tc(IV) is weakly sorbed or associated with unprotected surfaces and is readily re-oxidised and released when the sediment comes into contact with the seawater solution. Technetium was mobilised faster from nitrate reduced compared with to iron reducing sediments in seawater which was also seen in the batch experiments.

Release of Tc from nitrate reduced sediments did not remain constant over time (Figure 5.6). Two discrete periods of elevated Tc release were observed; a smaller event between 134 and 194 pore volumes (where 11 % of the total Tc was released), followed by a larger event between 398 and 732 pore volumes which resulted in 41 % of the total Tc being released from the nitrate reduced sediment. Although these periods of enhanced Tc mobility did not correspond with significant changes in pH, they reflect periods of lower Eh. Flow-path modifications caused by oxidative dissolution of minerals, coupled with secondary mineral precipitation, can result in variations in the Eh of the eluate. These channels may enable oxygen to be transported further into the pore spaces and also create pockets of reduced sediment which would be slower to oxidise due to mass transfer restrictions (Moon *et al.* 2009).

The initial 'pulse' release of Tc from the extensively iron reducing sediments was followed by a slower sustained release that continued throughout the month-long experiment, with the majority of the Tc associated with a chemical fraction that was slowly released over time. Release of Tc from iron reducing columns remained relatively constant (0.45 - 2.1 nmol L<sup>-1</sup>) over the experimental period with 51 % of the total Tc mobilised before the first stop/start event.

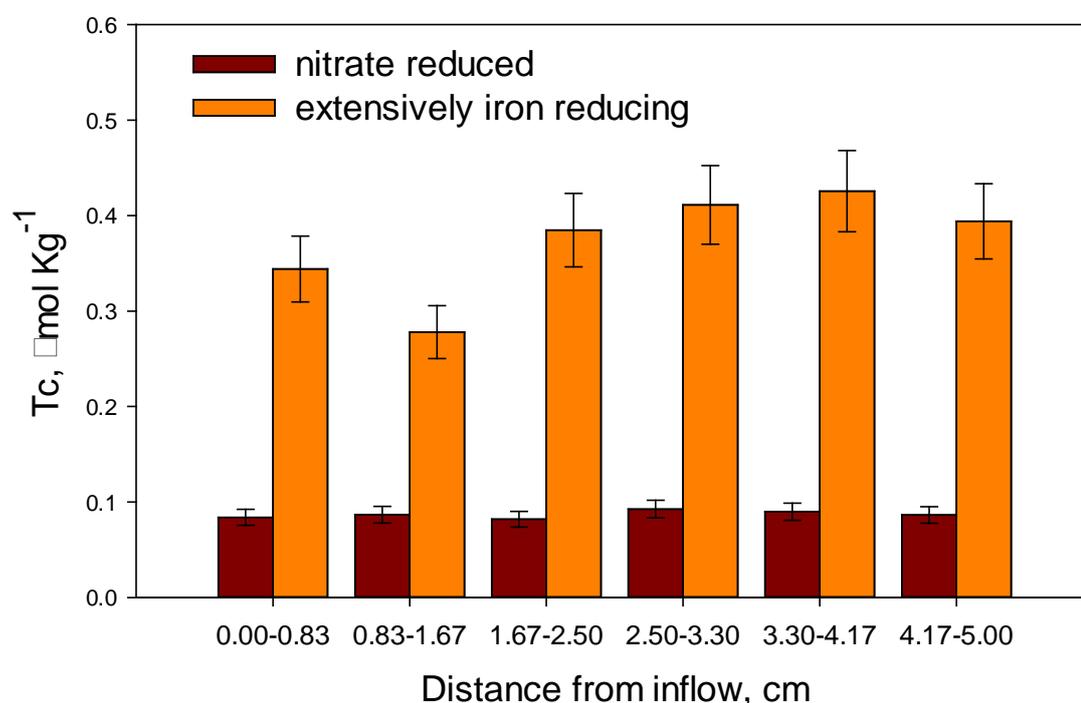
After the 2 week stop period, there was an immediate increase in the concentration of Tc eluted from both columns (Figure 5.6). Similar concentrations of Tc were released

from nitrate reduced ( $27 \text{ nmol L}^{-1}$ ) and extensively iron reducing ( $32 \text{ nmol L}^{-1}$ ) sediments. Technetium concentrations then quickly decreased, but after 10 pore volumes 6 % (nitrate reduced columns) and 8 % (extensively iron reducing columns) of the Tc originally associated with the sediments had been mobilised. The second stop-start flow event was conducted on the iron reducing sediments and this resulted in a smaller pulse release of Tc.

The stop-start events show that Tc release from the sediments is kinetically controlled with Tc re-distributed from less exchangeable to more exchangeable binding sites. Additionally the correlation between Tc and Fe release (nitrate reduced  $r= 0.695$ ,  $p= 0.000$ ; extensively iron reducing  $r= 0.912$ ,  $p= 0.000$ ) suggests that Tc incorporated into iron minerals was released as Fe(II) or Fe(III) phases dissolved. Alternatively, the mobilisation of surface associated Fe may have 'exposed' sediment associated Tc(IV), leading in re-oxidation and ultimately release.

At the end of each of the experiments more Tc was released from the nitrate reduced columns (93 %) compared with 79 % in the iron reducing columns, despite the additional stop-start flow event and the extended experimental period for the iron reducing columns. Release of Tc was more extensive under dynamic flow conditions (79 - 93 %) compared with the batch experiments (20 - 47 %). The higher concentration of Tc mobilised in the column experiments compared with the batch may be attributed to the continual re-supply of oxygenated seawater promoting the dissolution and/or desorption of surface associated phases. As Tc release is coupled with reoxidation, removal of the veneer protecting Tc or dissolution of Fe phases will enhance Tc release. Moon *et al.*, (2007) found that secondary Fe phases formed during Fe reduction were unable to protect U(IV) from oxidation and release under flow conditions, however this has not been reported previously for Tc.

At the end of the experiments the column was digested and each 0.8 cm length was digested with aqua regia and analysed to investigate the spatial distribution of Tc in the sediments. In both nitrate reduced and extensively iron reducing columns Tc was relatively evenly distributed throughout the column (Figure 5.8); therefore Tc(VII) was mobilised throughout the column which confirms that once mobilised, Tc(VII) was not re-adsorbed onto the sediments. The fraction of Tc that was recalcitrant to mobilisation at the end of the column experiments (nitrate reducing 3 %; extensively iron reducing 15 %) was similar to the percentage of Tc associated with the residual fraction of the reduced sediments (nitrate reduced 4 %; extensively iron reducing 10 %) observed in sequential extractions prior to use in the column experiments (Figure 5.1). Technetium was mobilised at a slower rate in the extensively iron reducing columns compared with nitrate reduced columns and release was on-going at the end of the  $\approx 50$  day flow period.



**Figure 5.8: Column digestion results showing the distribution of Tc remaining in the nitrate reduced and extensively iron reducing columns after dynamic seawater mobilisation experiments were conducted under fully saturated flow conditions. Error bars show 10 % relative standard deviation from combined analytical and method uncertainties.**

#### 5.4 Environmental implications and impact of Tc cycling

Here we have shown for the first time that Tc will be mobilised from reduced sub-surface sediments if inundated with oxic seawater. When sediments were re-oxidised in seawater, a fraction of the Tc(IV) that was weakly sorbed or associated with unprotected surfaces was readily re-oxidised and released from the sediments. A second fraction was less available for re-oxidation and was released slowly over time. The readily oxidisable/mobilisable fraction was larger (45 % versus 17 %) in the nitrate reducing sediments; therefore the sediment conditions at the time of intrusion will have a significant impact on the mobilisation Tc. Iron cycling in the sediments and the impact of this on Tc mobilisation are affected by the water chemistry. The slower re-oxidation of sedimentary Fe(II) in seawater compared with groundwater resulted in the incorporation of Tc into the structure of, or the veneering of Tc with, freshly precipitating Fe(III) (oxy)hydroxides. Under flow conditions more Tc was mobilised from nitrate reduced compared with extensively iron reducing sediments, providing further evidence of an important Fe-cycling control process or mechanism.

Importantly, the release of Tc from the nitrate-reduced and extensively iron-reducing sediments was more extensive under dynamic seawater flow conditions. For example, in batch experiments, 45 % of the sediment associated Tc was mobilised from nitrate reduced sediments and 17 % from extensively iron reducing sediments into seawater. In the column experiments 93 % was mobilised from nitrate reduced and 79 % from extensively iron reducing sediments. The mobilisation of Tc from reduced sediments has been studied wholly using a batch approach (Burke *et al.* 2006; McBeth *et al.* 2007; Begg *et al.* 2008). These experiments have shown that the batch approach may underestimate the release of Tc and over-estimate the importance of Fe in retarding Tc release in these systems. This has important implications for the adoption of bioreduction

approaches to the remediation of radioactive wastes, especially in dynamic environments.

Technetium accidentally released into the marine environment as a result of seawater intrusion will exist as the pertechnetate ( $\text{Tc(VII)O}_4^-$ ) anion in seawater (McCubbin *et al.* 2006). Pertechnetate is mobile in seawater and historical discharges from nuclear facilities such as Sellafield and La Hague have been traced as far away as the Arctic (Dahlgard *et al.* 1995) therefore Tc mobilised due to the impact of sea level rise from nuclear facilities such as Sellafield may also be expected to undergo long-range transport. Discharges of  $^{99}\text{Tc}$  into the Irish Sea from Sellafield (Cumbria) have resulted in increased  $^{99}\text{Tc}$  activity concentrations in a number of marine species including seaweed and crustaceans (in particular lobster) (Coppstone *et al.* 2004; Nawakowski *et al.* 2004) and health concerns may arise where individuals with a high consumption of locally caught seafood and seaweed.

Reduced marine sediments may act as a sink for Tc in marine environments, for example the accumulation of Tc(IV) has been observed in anoxic fiords (Keith-Roach *et al.* 2003) Therefore the uptake of Tc by marine sediments will be variable and depend on local biogeochemical conditions. Although the overlying water column in the Irish sea remains well-oxygenated throughout the year (Kershaw *et al.*, 1992) sediments in the Irish Sea can be reducing, and studies have shown that  $^{99}\text{Tc}$  can accumulate in Irish Sea sub-tidal sediments and may therefore act as a temporary sink for Tc with Tc release governed by re-oxidation and the rate and extent of re-dissolution processes.

# **Chapter 6**

## **Conclusions and future work**

## 6.1 Conclusions

The main aim of this project was to test the hypothesis that radionuclides (Sr, Tc and U) would be mobilised from contaminated sediments during inundation, erosion and inundation scenarios resulting from future sea level rise. This study has shown, for the first time, that during predicted sea level rise (inundation, erosion and intrusion), radionuclides will be released from contaminated sediments into local marine environments. Mobilisation from contaminated sediments therefore poses a potential hazard to marine environmental receptors. The main aim of this study has therefore been achieved.

This study has shown contrasting behaviour between Sr, Tc and U when mobilised into seawater and demonstrated that both the rate and extent of release is radionuclide specific. Strontium was rapidly mobilised; in contrast Tc and U were released more slowly over time, reflecting the different processes driving their release. The sediment matrix also plays an important role in controlling radionuclide release. The sediments used in this study were iron rich and this work has highlighted the importance of Fe oxides (and the cycling of these phases) in controlling the release of both U and Tc. This may not be the same for other sediments, for example, with a low iron content, high organic and/or clay content, especially as clays can have sites with permanent fixed charged sites (Coppin *et al.* 2002). Additionally carbonates and other mineral phases may well be important in controlling the release of radionuclides.

In this study sediments contaminated with  $^{90}\text{Sr}$  and U were aged for 6 months prior to use in the inundation, flooding and erosion scenarios. Sequential extractions showed that ageing had no significant effect on the solid phase association of Sr with the sediments (Chapter 2). However sequential extractions showed that there was a significant re-distribution of U during the 6 month ageing period, with U becoming

increasingly strongly bound to the sediments over time (Chapter 3). The large scale use of nuclear power in the USA, UK, Russia and Canada since the 1950's has resulted in a significant legacy of contaminated land and up to  $\approx 60$  years of ageing in the field will undoubtedly affect the release of radionuclides. This highlights the importance of knowing the history of the site and taking into account the "ageing" effect.

The hypothesis underlying the  $^{90}\text{Sr}$  work (Chapter 2) was that the release of  $^{90}\text{Sr}$  from oxic sediments will be promoted by cation exchange under seawater inundation and erosion scenarios. In this study  $^{90}\text{Sr}$  was rapidly mobilised from the sediments. Both the rate and extent of release increased with increasing ionic strength, with seawater > low salinity water  $\geq$  groundwater. This is consistent with the reversible sorption of  $^{90}\text{Sr}$  associated with exchangeable binding sites on the sediments. Even at low salinity,  $\text{Mg}^{2+}$  was sorbed to the sediments whilst  $^{90}\text{Sr}$  was released into solution, which is evidence that exchange reactions promoted  $^{90}\text{Sr}$  release. Results from column experiments confirmed that  $^{90}\text{Sr}$  was rapidly mobilised under flow conditions and travelled quickly through the column due to a low interaction with the sediment.

Chapter 3 tested the hypothesis that the release of U(VI) from oxic sediments would be promoted by the formation of U(VI) carbonate complexes under seawater inundation and erosion scenarios. Mobilisation of U(VI) from both sediments was controlled by the system pH in the batch experiments and during early elution in the column experiments. Uranium was only released from the sediments at circumneutral pH ( $> 6.5$ ). Uranium mobilisation was kinetically controlled, characterised by a slow release from a range of binding sites, with U release promoted by the formation of U-carbonate complexes (e.g.  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ) into seawater.

In Chapter 4 experiments were designed to test the hypothesis that the intrusion of oxic seawater into reduced sediments would lead to the mobilisation of uranium. Initially

U(VI) was sorbed to the sediments (during nitrate reduction). However as conditions became increasingly reducing U was associated with the sediments via (i) sorption of U(VI) species, (ii) reduction of sorbed U(VI) to U(IV) species ( $\text{UO}_2$  or monomeric U(IV)) or (iii) the presence of several U(VI)/U(IV) species. Similar to the oxic experiments described in Chapter 3, there was no mobilisation of U in the batch experiments and during early elution from the column experiments into oxic seawater, suggesting that U release would be delayed with respect to the migrating seawater front. Uranium release was promoted by the formation of U-carbonate complexes and was slower from reduced sediments compared with oxic sediments (Chapter 3). Therefore reduced sediments would act as a longer term secondary source of U to marine environments. Release was more extensive from initially nitrate reducing sediments (53 %) compared with extensively iron reducing sediments (38 %). The difference in release could be explained by the longer contact period of U(VI) with the iron reducing sediment relative to the nitrate reducing sediment, which would lead to slower desorption. Additionally U(IV) species would be released more slowly compared with U(VI) species sorbed to the sediments.

The hypothesis underlying the work in Chapter 5 was that the intrusion of oxic seawater into reduced sediments will lead to the re-oxidation of Tc(IV) to Tc(VII). The release of Tc was dependent on sediment re-oxidation coupled with the oxidation of Tc(IV) to Tc(VII). Batch experiments showed that only a small proportion of Tc was rapidly (within 5 days) released from the sediments into seawater and groundwater, which suggests that the majority of any Tc(IV) contamination will be released slowly as the seawater plume migrates through the sediments. Technetium release was slowest and ultimately limited to the greatest extent (17%) in initially Fe-reducing sediments, when they were re-oxidised in seawater. Therefore seawater appears to enhance the formation

of an effective Fe veneer. Thus the cycling of iron and the impact of the water chemistry on iron mineralogy were important for hindering Tc release. Column experiments showed that iron minerals were less effective at retarding Tc release under flow-through conditions. Kinetically controlled and solubility limited Fe dissolution led to on-going Tc release from the sediments, i.e. the retarding effect of iron phases was temporary and significantly more Tc was mobilized (79-93%) compared with the batch experiments (17-45%). Therefore, if sea level rise-driven intrusion and inundation increases the delivery of oxygenated water to the subsurface environment, the net effect would be predicted to involve Tc release.

**Experimental approach:** This study has shown the value of using column experiments to complement traditional batch approaches when investigating the mobilisation of radionuclides. For example, the columns allowed the interactions of the sediments and seawater to be observed as a function of flow, and showed how the porewater characteristics, such as pH, varied and affected the release of uranium. Although pH was not the dominant controlling factor for Tc release, Tc was mobilised to a greater extent under flow conditions, which shows the importance of simulating the most relevant field conditions in the laboratory. Column experiments are particularly useful for studying the release of radionuclides when the release is not controlled by  $K_D$  alone, i.e. when the radionuclide is more tightly bound. This was demonstrated in this study, with the column experiments being more important and informative for Tc and U compared with Sr.

Sequential extractions give information on the operationally defined chemical leachability of metals and were applied here to identify the initial associations of the radionuclides and how they changed over time in the batch experiments. The

radionuclides extracted in the exchangeable fraction relate reasonably well with the readily mobilisable fraction seen in the batch and column experiments. This was seen clearly for Sr, where the sequential extraction data were consistent with the experimental results. The progressive sequential extractions examining changes in Tc associations showed a clear trend of Tc becoming increasingly associated with the exchangeable fraction over time. This was a compelling visualisation of the process of Tc moving from tightly bound binding sites to exchangeable sites prior to mobilisation and made a valuable contribution to understanding the behaviour of Tc. The information on U mobilisation gained from the sequential extractions was limited with the batch approach, but it was clear that the U associations changed during reoxidation and the degree of change depended on the initial sediment conditions. Therefore, by adopting the same extraction scheme throughout a study, one can enhance the understanding of radionuclide associations with sediments prior to and during mobilisation, which aids the interpretation of results from batch experiments.

## **6.2 Future work**

The holistic approach adopted in this study has proved suitable for investigating the mobilisation of radionuclides from reduced sediments in static (batch) and dynamic (column) environments during sea level rise processes. The study has identified some important questions with respect to U and Tc mobilisation and thus the recommendations for future work are as follows:

- The results from this study suggest that the association of U and Tc with Fe minerals is important in controlling their release in both oxic and reduced environments (Chapters 3-5). In order to investigate this relationship in more detail bulk analytical techniques such as Mössbauer spectroscopy, X-ray diffraction (XRD) and scanning

electron microscopy (SEM) should be used to identify the key reactive phases. Once identified, their formation mechanisms, stability, transformations under oxidation/reduction, and ultimately their ability to control radionuclide release under transient conditions, need to be explored further under both static and flow conditions in order to predict radionuclide release to the aquatic environment more accurately.

- The use of pure culture and/or pure mineral experiments can be used to provide important insights into the binding of radionuclides with sediments. Additionally the use of molecular environmental science tools including XANES and EXFAS can be used to investigate the oxidation state and binding of radionuclides with solid matrices.
- The mobilisation of Tc from reduced sediments was studied using batch and column experiments (Chapter 5). In the batch experiments, a significant fraction of Tc remained recalcitrant to mobilisation during reoxidation into seawater and groundwater. One of the significant findings of this work is that Tc release is more extensive under continuous flow conditions. In-situ bioremediation processes are being considered to remediate sites contaminated with nuclear waste. These results have important implications for bio-reduction schemes where oxidants may be introduced to the bio-stimulation zone under flow conditions. Therefore future studies should explore re-oxidation scenarios under flow conditions.
- In keeping with previous studies, this thesis has shown that U is associated with a range of binding sites with different release kinetics and this variability in desorption rates may ultimately control the long term behaviour of U in the environment. Therefore models based on column experiments, rather than simple  $K_D$  values obtained from batch experiments, should be used in risk and performance assessments concerned with the long term transport of contaminants.

- If sediments become inundated with seawater for extended periods, conditions may become increasingly reducing over time. Therefore experiments should be conducted in order to investigate the mobilisation of radionuclides alongside redox sensitive species such as Fe (oxy)hydroxides during reduction.

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