

STUDENT SUMMER INTERNSHIP TECHNICAL REPORT

**Plutonium Migration from Estuary Sediments
(Ravenglass, UK)**

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ABSTRACT

In 1952, Sellafield (a nuclear reprocessing plant in the UK) authorized the discharge of low-level radioactive effluents via pipeline into the Irish Sea. These effluents consisted of radionuclides such as Am, Cs, Pu, Tc, U and Np. Overtime, the radionuclides mobilized and accumulated onto a nearby fine-grained Mud-patch in the Irish Sea. The radionuclides then re-dispersed via sedimentary deposition from the Mud Patch along the coast including a nearby saltmarsh, Ravenglass, which is located 10 km from Sellafield. Overtime, the radionuclides have accumulated onto the soils of the saltmarsh due to the tidal currents. The long-term vertical distribution and retention of radionuclides in the soils of Ravenglass saltmarsh remains unknown. Therefore, batch desorption experiments were conducted to better understand the desorption behavior of plutonium from solution overtime under anoxic and oxic conditions. Preliminary conclusions suggest that plutonium mobility increases under anoxic conditions.

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1. INTRODUCTION

The Sellafield site on the northwest coast of England was established in 1947 to support the UK nuclear weapons program. Since 1952, Sellafield authorized the continual discharge of low-level radioactive liquid effluents into the northeast Irish Sea. The liquid effluents (purge waters from spent fuel reprocessing) consisted of various actinides and fission products such as americium (Am), plutonium (Pu), uranium (U) and neptunium (Np) cesium (Cs), and technetium (Tc) (Carborn *et al.*, 2016). The discharge histories suggested that in the 1970s, the activity concentrations for radionuclides for ^{137}Cs , Pu isotopes (^{238}Pu and $^{239/240}\text{Pu}$) and ^{241}Am reached a maximum and later declined (Gray *et al.*, 1995, Carborn *et al.*, 2016).

In the Eastern Irish Sea the majority of the transuranic activity has settled into an area of sediments (“mud patch”) off the Cumbrian coast. The radionuclides from the mud-patch have been re-dispersed via particulate transport in fine-grained estuarine and intertidal sediments in the North-East Irish sea (Hamilton and Clarke, 1984; Kershaw *et al.*, 1995; Mackenzie *et al.*, 1994) including the Ravenglass estuary (Burton and Yarnold, 1988; Caborn *et al.*, 2016; Lucey *et al.*, 2004; Mackenzie and Scott, 1993; Mackenzie *et al.*, 1994).

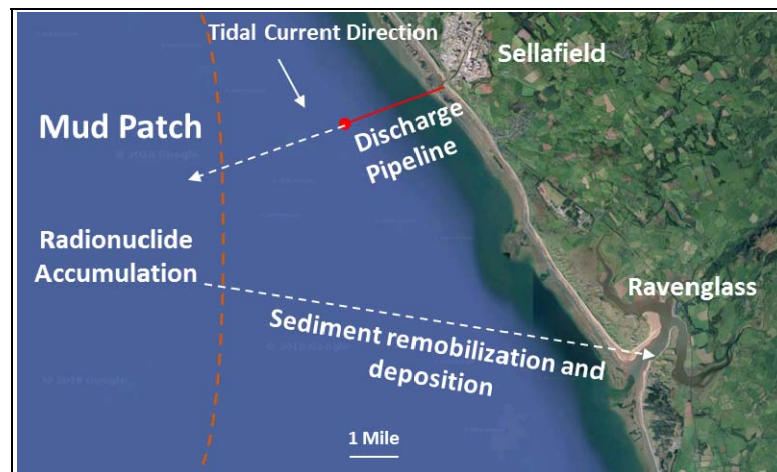


Figure 1: General schematic of radionuclide transport from the Sellafield site.

The Ravenglass saltmarsh is located 10 km south of the Sellafield site, U.K. The Ravenglass saltmarsh is a low energy, intertidal region that accumulates Sellafield-derived contamination (Hamilton and Clarke, 1984). Salt marshes like Ravenglass are highly dynamic systems which are vulnerable to external agents (Adam, 2002) (sea level changes, erosion, sediment supply and fresh water inputs), and there are uncertainties about their survival under current sea level rises and possible increases in storm activity (Leonardi *et al.*, 2016; Temmerman *et al.*, 2004). Salt marshes erosion has been observed along the western English coastal waters, and is also associated with the risk or dispersal of contaminated sedimentary deposits, which can become a source of pollution for surrounding area (Rahman *et al.*, 2013). A recent study has demonstrated that salt marsh erosion and loss of areal extent at the Ribble estuary (50 miles south of Ravenglass) intensifies tidally induced fluctuations in suspended

sediment, which suggests an increase of potential movement of sediments within the estuary and with a possible increase in transport of contaminants, including actinides(Li et al., 2018).

Despite periodic study over the past several decades, understanding of the biogeochemical controls on long-term radionuclide distribution and retention at Ravenglass remains limited (Aston and Stanners, 1981; Caborn et al., 2016; Lindahl et al., 2011; Lucey et al., 2004; Marsden et al., 2006; Morris et al., 2000). Thus, far, studies on Sellafield impacted sediments in the Ravenglass saltmarsh have focused on sediment concentration measurements with little detailed study of processes impacting radionuclide distributions. Recent work has indicated redox conditions shift from aerobic at the very top of the core, to Fe(III) reducing within 12 cm of the surface, and sulfate reducing between 18-28 cm.(Daisy, 2013, 2018 (submitted)). Changing redox profiles together with changing hydrological regimes have the potential to impact the speciation and mobility of the redox active elements, such as, Pu, Np and U (Begg et al., 2011; Behrends and Van Cappellen, 2005; Latta et al., 2012; Law et al., 2010; Lloyd, 2003).

In this study the goal is to examine the factors affecting the mobility of Pu in estuarine, redox stratified soils by conducting sorption/desorption experiments of contaminated Ravenglass sediments under both oxic and anoxic conditions. The overall goal of this work is to determine the behavior of radionuclide in:

- Ravenglass sediment cores under anoxic conditions;
- Ravenglass sediment cores under oxic condition;

The results will provide detailed information on the potential mobilization of actinides in estuary sediments due to changing climatic conditions.

2. EXECUTIVE SUMMARY

This research work has been supported by the DOE-FIU Science & Technology Workforce Initiative, an innovative program developed by the US Department of Energy's Environmental Management (DOE-EM) and Florida International University's Applied Research Center (FIU-ARC). During the summer of 2019, a DOE Fellow intern Frances Zengotita spent 10 weeks doing a summer internship at the Glenn T. Seaborg Institute in Lawrence Livermore National Laboratory (LLNL) under the supervision and guidance of Dr. Enrica Balboni (Staff Scientist). The intern's project was initiated on June 3, 2019, and continued through August 10, 2019 with the objective to investigate the desorption behavior of risk-driving contaminants such as Pu under both anoxic and oxic conditions from estuary sediments.

3. RESEARCH DESCRIPTION

Soil sampling

The team at Lawrence Livermore National Laboratory sampled a sediment core (up to 30 cm in depth) from the Ravensglass saltmarsh. The general schematic of a sediment core can be observed in **Figure 2**. The sediment core was divided into six different layers, from 0-5 cm up to 25-30 cm in depth. Reducing conditions are expected in respect to depth. The soil samples were shipped frozen, to the LLNL where solid characterization and batch desorption experiments were conducted.

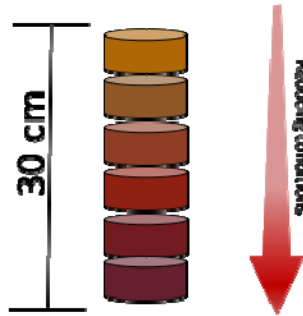


Figure 2: General schematic of a sediment core.

Soil characterization

A spatial distribution of radioactivity found in Ravensglass soils by autoradiography can be found in **Figure 3**. The autoradiography essentially is a thermal map and suggest that there is some radioactivity found in the soils.

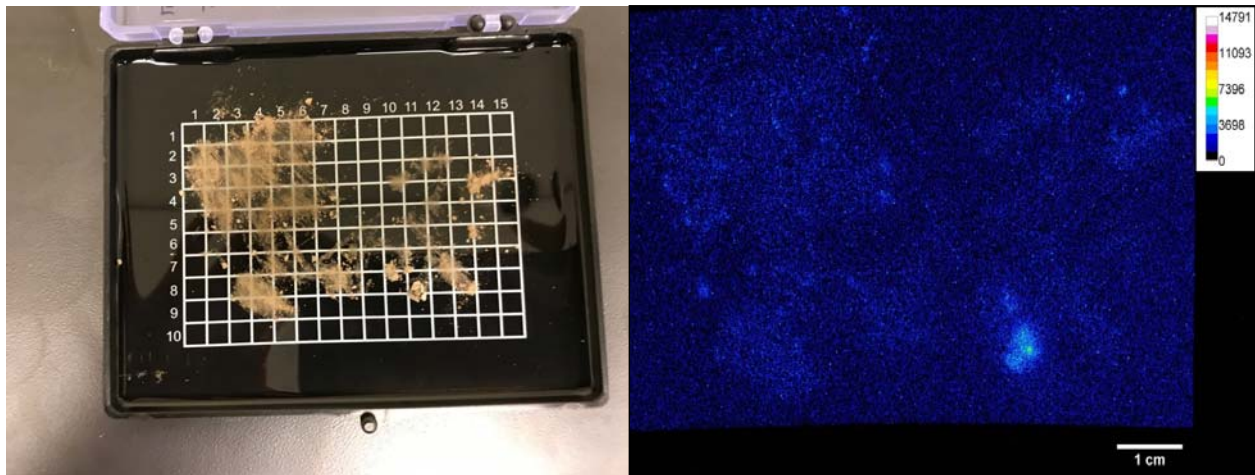


Figure 3: Spatial distribution of radioactivity found in Ravensglass soils by autoradiography imaged by autoradiography. Soil samples in GelPack boxes (on left) and corresponding autoradiographs (on right).

Total Pu characterization

Approximately 0.2 g of each sediment section was digested via total acid dissolution and prepared for analysis via multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). **Figure 4** represents the total Pu concentration (pg/g) found in the Ravenglass soils as a function of depth. The data shows that the highest concentration of Pu found in the soils was between 0-20 cm in depth. For the 10-week summer research project, we analyzed Pu concentration in desorption solution from 0-20cm, since the shallow layers had a higher concentration of Pu.

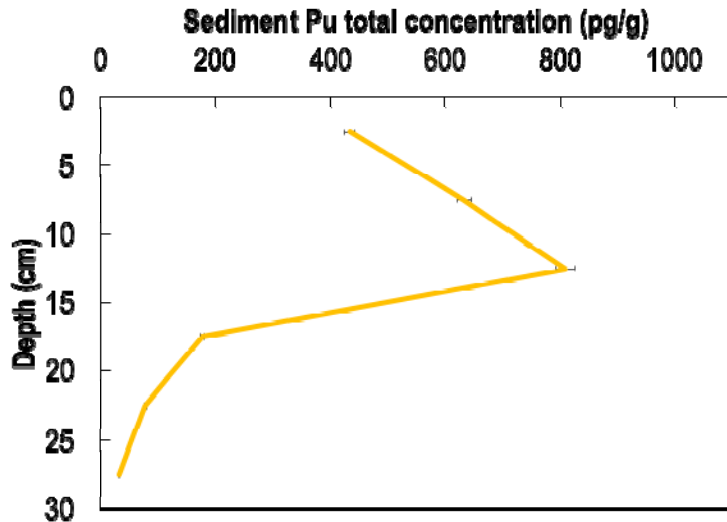


Figure 4: Sediment Pu total concentration in respect to depth. Note: highest concentration of Pu was found in between 0 to 20 cm.

Batch desorption experiments

The goal is to examine the factors affecting the mobility of Pu in redox stratified sediments by conducting desorption experiments of contaminated Ravenglass sediments under both oxic and anoxic conditions (**Figure 5**). Desorption experiments were conducted over an eight-month period. The anoxic desorption experiments have been completed and were conducted in a Coy anerobic chamber and sampling occurred after 1, 27, 80 and 240 days. Atmospheric (oxic) desorption experiments are currently underway and sampling was completed after 1 and 80 days. The oxic experiments were started in an anaerobic chamber and subsequently moved to atmospheric conditions -bottles capped with porous bungs, shaken daily. In all the desorption experiments, Ravenglass sediments from each layer were mixed with degassed artificial seawater (ASW) to yield 10 g/L suspensions. The experiments were periodically sampled to determine the amount of desorbed Pu via MC-ICP-MS - (Multi Collector Inductively Couple Mass Spectrometry) and redox indicators (Eh, pH and extractable Fe(II)). Genera- level composition of the microbial community in the anoxic and oxic desorption experiments is underway.



Figure 5: Anoxic batch desorption experiments in glovebox (*left*) and oxic batch desorption experiments (*right*) on the benchtop.

Sample processing and analysis

Separation chemistry techniques were used to purify plutonium from matrix elements and other actinides prior to MC-ICP-MS measurements. Two different exchange resins were used: an anion exchange resin (BioRad AG1X8) and a cation exchange resin (Eichrom TEVA). **Figure 6** demonstrates the column purification processes.

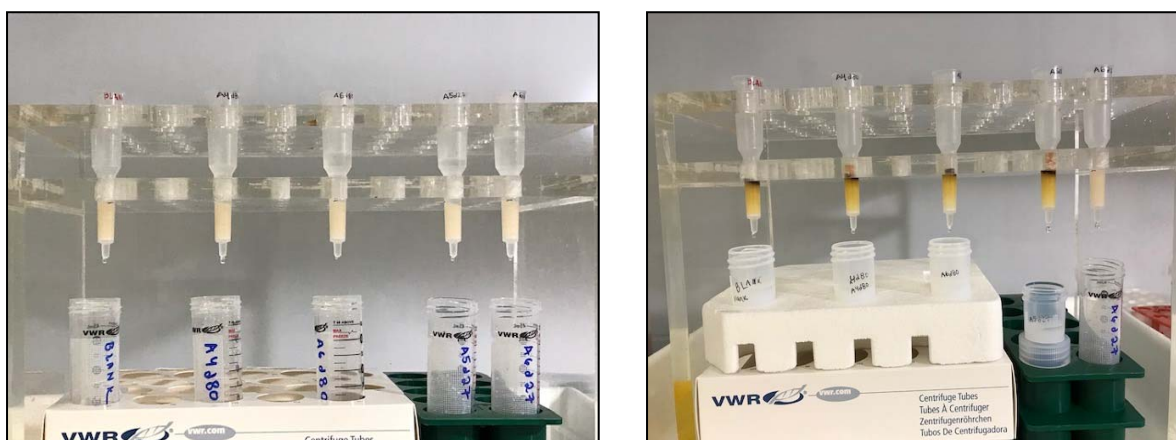


Figure 6: Poly-Prep BioRad columns with resin prior to experiment (*left*) during Pu purification (*right*).

Samples were spiked with a well calibrated ^{244}Pu tracer to determine plutonium isotope concentration by isotope dilution mass spectrometry (IDMS). The samples were analyzed on the Nu Plasma II Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). The plutonium isotopic ratios were measured on ion counters. The MC-ICP-MS instrument was utilized because the Pu concentrations in the soils were considerably small (pg/g) as observed in **Figure 4**. Therefore, the MC-ICP-MS can analyze very small concentrations of Pu with precision as opposed to a regular ICP-MS. An example of the Pu isotopic ratio analyzed on the MC-ICP-MS can be found in **Figure 7**.

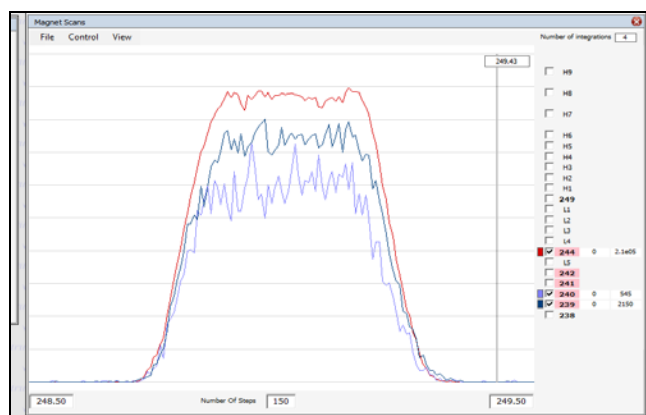


Figure 7: Pu isotopic ratio analyzed on MC-ICP-MS

SIDE PROJECT: Accelerator Mass Spectrometry Sample Protocol Development

Parallel to the preparation of samples for Pu analysis via MC-ICP-MS, we worked on developing a sample preparation method to conduct multi-actinide measurements via Accelerator Mass Spectrometry (AMS). Analysis of desorption solutions via AMS should allow for a more comprehensive understanding of actinide desorption behavior from Ravensglass sediments, complementing the information obtained via MC-ICP-MS (Pu only measurements).

Standard AMS target preparation for actinides measurements usually involves separation chemistry (cation/anion exchange resins). Purified aliquots of actinides are then co-precipitated in Fe hydroxide solid and prepared as targets for AMS measurement.

For this part of the project we worked on developing an AMS sample preparation technique to allow for simultaneous quantification of multiple actinides at ultra-trace concentrations in various matrix. Our goal was to directly precipitate various Pu-spiked Fe hydroxide carriers (amorphous Fe oxides, or goethite FeOOH) without performing a Pu pre-purification. We investigated: 1) if transformation of amorphous iron oxide to goethite 2) effect on number of rinses of the target material could potentially improve AMS analysis.

AGED AMS SAMPLE PREPARATION

For the AMS sample preparation, three matrixes were considered: Seasalt, Artificial Seawater and MilliQ water. These solutions were placed in their respective Teflon containers, acidified with concentrated HNO₃, and spiked with a pure Fe standard and an aliquot of pure ²⁴²Pu spike was added to all matrixes. A total of 12 samples was prepared. In 6 of the total experiments, ferrihydrite was aged to goethite.

The procedure was modified from Quinto et. al (Quinto et al., 2015). Briefly, the solutions were placed on a hot plate for two hours to evaporate and were removed when a third of the total volume had evaporated. After the samples were thoroughly cooled, the samples were pH adjusted with concentrated NH₄OH to create an iron precipitate. During the pH adjustment process, the NH₄OH was added drop-wise and the samples were swirled after each addition. Once a pale-yellow color was achieved, the samples were closed and left to sit for a few hours for the iron precipitate to form.

Once the iron precipitate formed, the samples were rinsed twice (or five times) with milliQ H₂O adjusted to pH 8. For the aging process, after the rinsing procedure, a concentrated base (such as KOH) was added to the samples to convert amorphous Fe hydroxide to goethite (Schwertmann and Cornell, 2000). The samples were then placed on the hot plate to age overnight. The next day, the aged samples were rinsed and centrifuged. After the final rinse, a few drops of ethanol were added to the aged iron drop so that it could be transferred and placed on X-Ray Diffraction (XRD) plates to dry. A summary of these matrixes and their respective contents can be found in **Table 1**.

The Fe precipitates were dried at 400°C in a furnace for 8 hours. Once dried Fe-oxide powders were mixed with Nb metal and pressed into AMS target holders.

Table 1: AMS aged sample preparation for Seasalt, Artificial Seawater (ASW) and MilliQ Water matrixes.
Note: Seasalt matrix is highlighted (blue) since the data was read on PXRD

Matrix Type	Contents
Seasalt	Fe drop + ²⁴²Pu + 2 rinses
Seasalt	Fe drop + ²⁴²Pu + 5 rinses
Seasalt	Aged Fe drop + ²⁴²Pu + 2 rinses
Seasalt	Aged Fe drop + ²⁴²Pu + 5 rinses
Artificial Seawater	Fe drop + ²⁴² Pu + 2 rinses
Artificial Seawater	Fe drop + ²⁴² Pu + 5 rinses
Artificial Seawater	Aged Fe drop + ²⁴² Pu + 2 rinses
Artificial Seawater	Aged Fe drop + ²⁴² Pu + 5 rinses
MilliQ Water	Fe drop + ²⁴² Pu + 2 rinses
MilliQ Water	Fe drop + ²⁴² Pu + 5 rinses
MilliQ Water	Aged Fe drop + ²⁴² Pu + 2 rinses
MilliQ Water	Aged Fe drop + ²⁴² Pu + 5 rinses

4. RESULTS AND ANALYSIS

4.1 Desorption experiments

The results and analysis are still ongoing for all results presented in this work. Therefore, all discussion below is considered preliminary.

In **Figure 8**, the data set represents the sampling periods on day 27 (diamond) and day 80 (triangle, unfilled) under anoxic conditions. The data suggests that in the 0-5 cm samples desorption decreases with time.

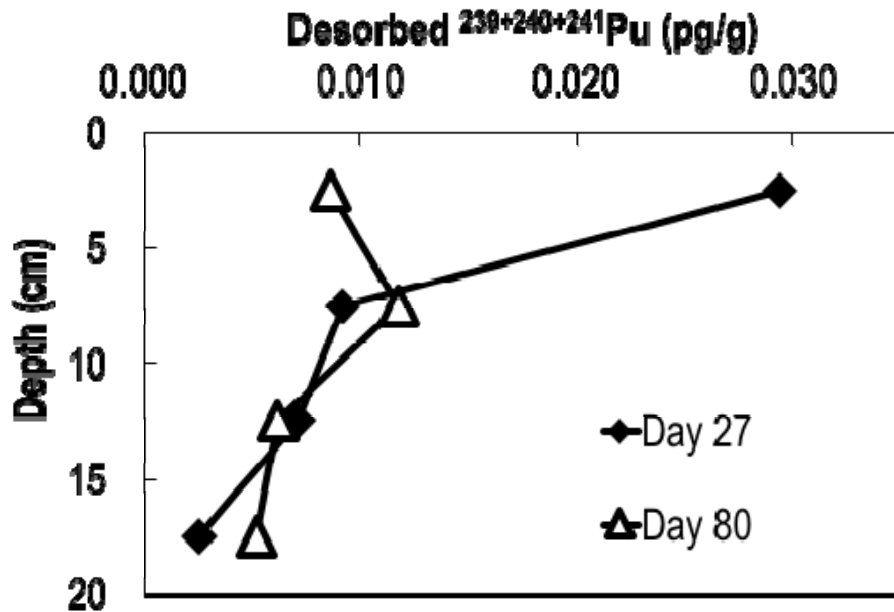


Figure 8: Comparison of anoxic Pu desorption data at 27 and 80 days. Desorption changes with time in shallow sediments.

In **Figure 9**, the data set depicts the desorption of Pu between oxic and anoxic conditions on day 27. The data suggests that under oxic conditions, less plutonium is desorbed from the sediments. In comparison to the anoxic data, more Pu was desorbed in solution which suggests that anoxic conditions increase Pu mobility. Further, there was a higher concentration of Pu in solution in shallow sediments in both oxic and anoxic data, indicating that Pu mobilization is enhanced in the shallow sediments and is independent of the Pu concentration in the soil (**Figure 4**). These results were not expected because it was understood that under oxic conditions, Pu is more likely to mobilize due to its redox chemistry.

Figure 10 depicts the $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratios from the anoxic (black), oxic (blue) and total sediment Pu data (yellow) found in these experiments. The shifts in the Pu isotopic ratio from 10 cm to 20 cm layers likely represent changes in Pu discharge from Sellafield. Historical archive search is ongoing to compare the isotopic ratios from these experiments to the initial discharge at Sellafield.

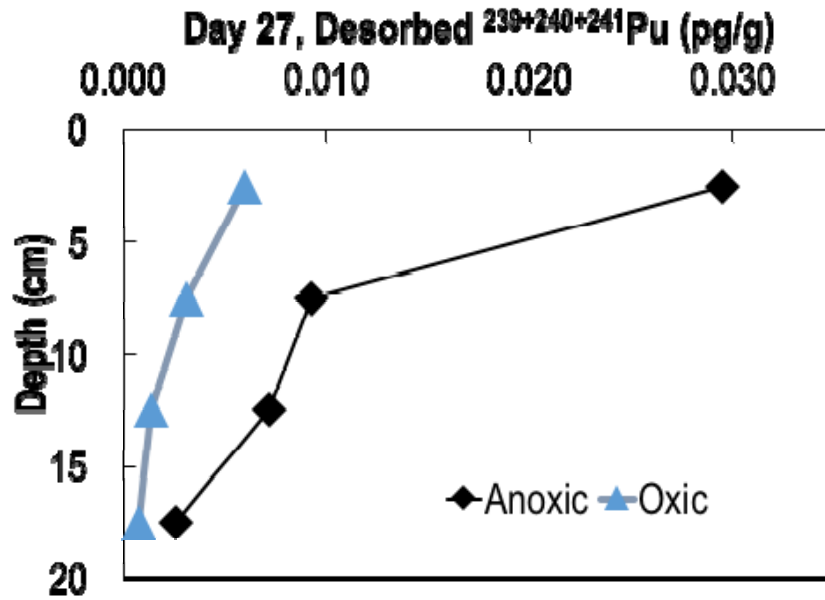


Figure 9: Comparison of **oxic** and anoxic Pu desorption data at day 27. Anoxic conditions INCREASE Pu mobility.

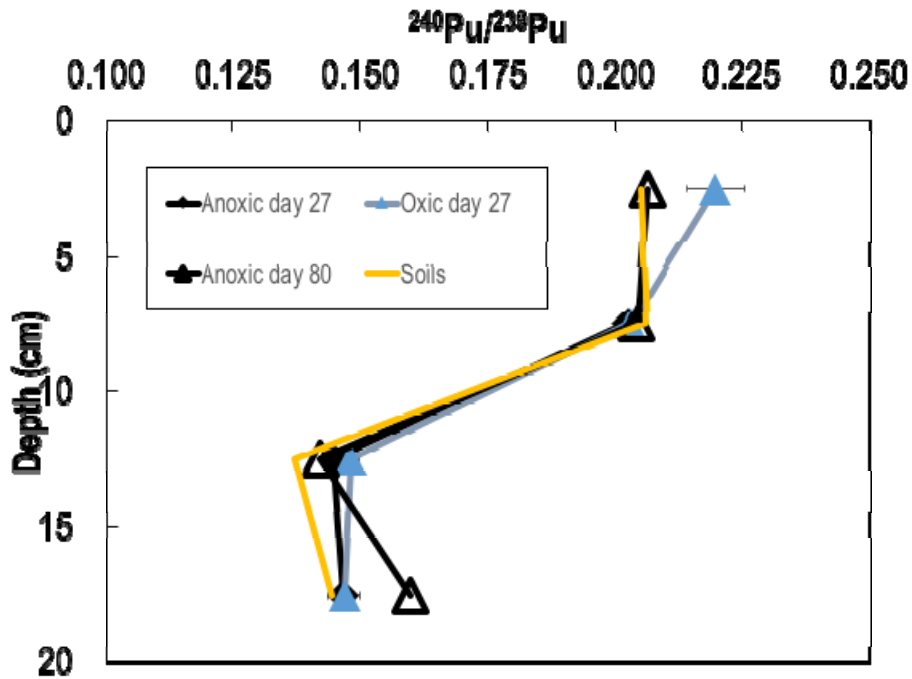


Figure 10: $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio of the desorbed Pu. Shifts may represent changes in Pu discharge at Sellafield in respect to depth.

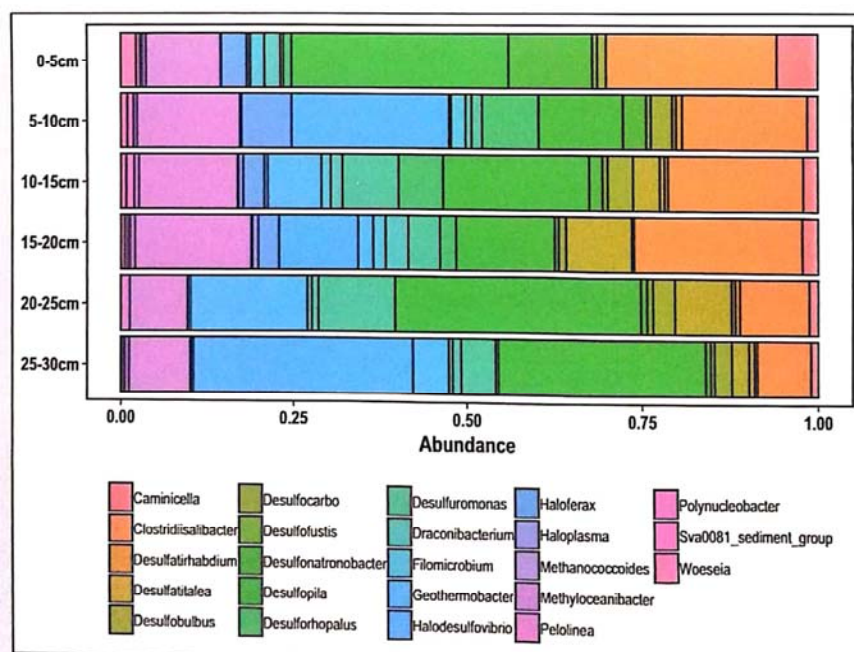


Figure 11: Genera-level composition of microbial community in anoxic sediment slurries after 8 months. Note: Most abundant microbes were halophilic (blue) and sulfate-reducing (green).

The microbial community composition at the beginning and end of the desorption experiments is also being characterized. For example, Figure 12 shows the microbial communities for each soil layer collected at the end of the anoxic desorption experiments (239 days, all layers). The microbial community in the samples mainly consists of halophiles and sulfate-reducing (green) and halophile (blue) microorganisms, which is consistent with what is expected for Ravenglass sediments (Newsome et al., 2014). Other potential metabolisms include anaerobic heterotrophy (e.g., Caminicella), methanogenesis (e.g., Methanococcoides, Pelolinea), and methylotrophy (e.g., Methyloceanibacter). The profiles were obtained by 16S rRNA sequencing of the V4 region and processed through Dada2 and Phyloseq. Therefore, preliminary conclusions can be drawn where Pu mobilization is greater in shallower sediments.

Microbial staining indicated that bacterial cells were still alive after the 9-month desorption experiments in the anaerobic glovebox (data not shown). This observation suggest that these microbes could potentially influence the fate and transport of Pu under anoxic conditions. This hypothesis may contribute to the interesting results found in these experiments where Pu mobility increased in anoxic conditions.

4.2 Preparation of samples for AMS

In **Figure 12**, the aging process from amorphous iron oxide to goethite is shown. In brief, after the sample precipitates were prepared, the samples were spiked with KOH and allowed to age overnight on the hotplate. The next day, the amorphous Fe hydroxide samples were covered

to goethite. The aged samples were rinsed and centrifuged the next day, in preparation for XRD analysis. The finalized sample drop can be observed on the right-side of **Figure 12**.

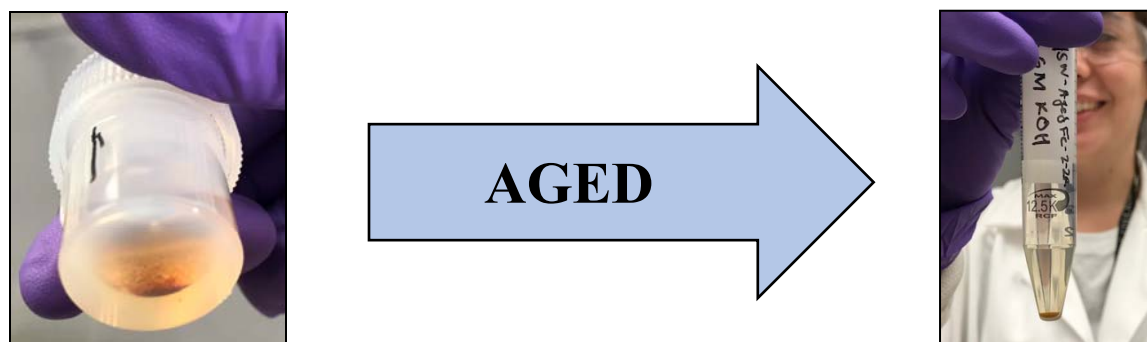


Figure 12: Aging process from amorphous iron oxide to Goethite

In **Figure 13**, the x-ray diffraction (XRD) pattern of Aged Crystalline Iron Oxide (**blue**) and Amorphous Iron Oxide (**red**) can be observed. The dashed line is representative of the diffraction peaks characteristic of goethite (FeOOH), a crystalline iron oxi-hydroxide (**black**). The y-axis represents diffraction intensities (arbitrary unit) while the diffraction angle (2θ). These results show that amorphous Fe hydroxide was successfully transformed into goethite with our designed experimental protocol. The AMS run is scheduled for October 3rd 2019. Results of this AMS run will provide insights into effects of sample rinses (2 or 5) and nature of the Fe precipitate prepared for the target (amorphous or crystalline) affect the quality of AMS data.

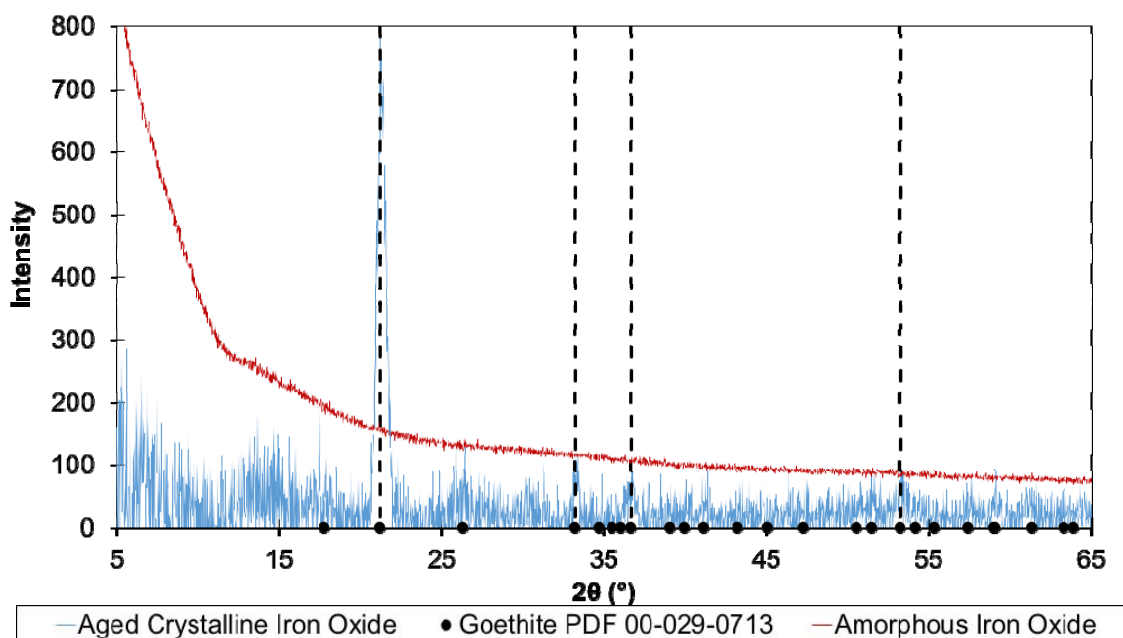


Figure 13: XRD characterization amorphous iron oxide and goethite targets

5. CONCLUSION

The Ravenglass saltmarsh presents a unique natural laboratory to study the long-term biogeochemistry of anthropogenic radionuclides under natural environmental conditions. The desorption of Pu (and other radionuclides) may be influenced by redox conditions, organic content and microbial community composition. Data analysis is still ongoing, but preliminary conclusions suggests that Pu desorption (and mobilization) increases under anoxic conditions. This would require a paradigm shift in our understanding of plutonium redox and its impact on radionuclide migration.

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