Geochemical associations of Sellafield-derived radionuclides in saltmarsh deposits of the Solway Firth

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This paper describes a study of the geochemical associations of Sellafield waste radionuclides in saltmarsh sediments from south-west Scotland. The contaminant radionuclides are transported to this environment in association with particulate material and 137Cs was found to be predominantly (80–90%) non-extractable. In the case of 239+240Pu there was a redistribution from the oxalate extractable oxide fraction to the pyrophosphate extractable organic fraction as a consequence of on-shore transfer of contaminated sediment. The relatively aggressive nature of the chemical extractants required to remove the radionuclides from the sediments suggests that they were in a form which was unlikely to result in their being released into the aquatic environment or taken up by plants. Plutonium had a greater potential mobility or bioavailability than Cs. Values of Kd for the desorption of 137Cs from the sediment by freshwater, groundwater and seawater were all approximately 10^5 L kg^-1, confirming its immobility in this environment. The desorption Kd values for stable 133Cs were all approximately 10^5 L kg^-1, so the stable Cs did not have a significant influence on the radioactivity in this sediment.

Keywords: Saltmarsh deposits; radiocaesium; plutonium; selective extraction; desorption

Introduction

Radionuclides discharged as low-level radioactive waste from the Sellafield nuclear fuel reprocessing plant become associated with off-shore sediments to varying extents depending on their geochemical properties. Subsequently, some of this contaminated sediment is transported on-shore and deposited in surrounding intertidal and floodplain areas such as those of the Solway Firth (MacKenzie et al., 1994). During this on-shore transfer, the geochemical conditions affecting the radionuclides change from the well-oxygenated, alkaline marine environment of the Irish Sea to a terrestrial location with slightly acidic conditions, variable redox potential and an increasing influence of freshwater. Despite the fact that only a small percentage of the total Sellafield discharge is involved in on-shore transfer, significant radionuclide inventories (up to 1.3 × 10^6 Bq m^-2 of 137Cs) are found in the saltmarsh sediment (Allan, 1993). In the light of the magnitude of these inventories, speciation studies are necessary to determine the geochemical behaviour of the radionuclides, which is of importance in evaluating their potential mobility, availability and, ultimately, their contribution to human radiation exposure.

Materials and Methods

Sediment was collected from three locations within an area of saltmarsh forming the floodplain of a small river, the Southwick Water, on the Solway coast of south-west Scotland (UK Ordnance Survey ref. NX914562). Surface (0–2 cm) intertidal sediment was collected using a trowel. Samples of saltmarsh sediment at the mean high water mark (MHWM) and at 10 m inland were collected by excavating sections with a spade. A clean vertical face was prepared and samples removed from increasing depths using a trowel. Previous studies had indicated that this is an area of accreting sediment, with an accumulation rate at the MHWM of about 3–4 cm y^-1 (MacKenzie et al., 1994), and a decreasing rate of accumulation on moving inland (Allan et al., 1996). The sediment was predominantly a fine sand (57% to 76%), with smaller amounts of silt-sized (12% to 26%) and clay-sized (2% to 9%) particles. Coarse sand-size particles constituted less than 0.5%. Loss on ignition at 650°C for 8 hours was used to assess organic matter content, which ranged between 2.7% and 7.3% (Allan, 1993).

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Sequential extraction

The geochemical associations of $^{137}$Cs and $^{239+240}$Pu were measured by sequential extraction using the procedure of McLaren and Crawford (1973), including the modifications of Lu et al. (1981) and Cook et al. (1984a). This technique uses a series of increasingly aggressive chemical reagents to remove radionuclides associated with a group of operationally defined, notionally discrete components of the sediment. These associations and their extractants were readily available (0.05 M CaCl₂), exchangeable and bound to specific sorption sites (0.5 M acetic acid), chelated to organic matter (0.1 M tetrasodium pyrophosphate), occluded or co-precipitated with secondary iron and manganese minerals (0.1 M oxalic acid/0.175 M ammonium oxalate, pH 3.25), acid soluble (0.1 M HNO₃), and residual (HF digestion). While this technique is widely used for sediment and soil studies, the degree of selectivity of the extractants is still the subject of some debate. Most researchers accept that the components extracted do not correspond exactly to the assigned fractions, and so it is preferable to refer to calcium chloride extractable, acetic acid extractable etc.

Measurement of $^{137}$Cs

The extraction of radiocaesium from aqueous media followed the method of MacKenzie et al. (1979), which was based on those of Prout et al. (1965) and Boni (1966). This involved passing the filtered solution through a cartridge of potassium hexacyanocobaltate II ferrate II (KCFC) ion-exchange resin and measuring the activity in the dried cartridge using a NaI (TI) scintillation detector. This procedure was adopted for all of the selective extracts except the acid-soluble and residual components. The acid-soluble fraction was boiled to dryness, transferred to a 50 ml beaker with a calibrated detection efficiency and the gamma spectrum recorded using a high resolution HPGe detector. The residual phase was dried at 110°C, weighed and transferred to a container with a calibrated detection efficiency and the gamma spectrum recorded as described by McDonald et al. (1990, 1992).

Measurement of $^{239+240}$Pu

Analysis of $^{239+240}$Pu was by the method of Lally and Eakin (1978), modified by Cook et al. (1984a). Following addition of $^{244}$Pu yield tracer to the leaching solutions, separation of plutonium was effected using anion-exchange techniques and electrodeposition of the final sample on to a stainless-steel planchette for subsequent alpha spectrometry using a silicon surface barrier (SSB) detector.

Flow desorption extraction of radiocaesium

In order to characterise the desorption behaviour of $^{137}$Cs from the sediment, samples from the surface (0–5 cm) and depth (40–45 cm) were leached with a range of aqueous media which reflected the varying environmental conditions in the saltmarsh, i.e. freshwater (tap water), groundwater (field drainage pipe at Southwick Water) and seawater (from Kinghorn, Fife, in order to avoid significant contamination by Sellafield-derived radionuclides). A 20 g aliquot of wet sediment was placed in a glass column (15 cm by 2 cm) which was wrapped in aluminium foil to exclude light and so prevent algal growth. The leaching solution was passed through it from a 10 L PVC aspirator at a rate of approximately 0.1 ml min⁻¹. In total, approximately 300 L were passed through the columns. In the case of the surface sediment leached with freshwater, this was extended to 1250 L to check the constancy of the $K_d$ value. The leachate was collected in a 15 L plastic container, filtered through a 0.22 μm Millipore membrane filter, with a Whatman No. 1 pre-filter, and then passed through a cartridge of KCFC. Upon completion, the KCFC cartridge was dried and analysed using a NaI (TI) scintillation detector as before.

Neutron activation analysis

Instrumental NAA was used to establish the concentration of stable $^{133}$Cs in the samples taken at the MHWM in order to characterise any influence of $^{133}$Cs on the partitioning of $^{137}$Cs. Sediment samples and corresponding standards were exposed to a flux of thermal neutrons using the Scottish Universities Research and Reactor Centre's TRIGA MARK II research reactor. After irradiation, the samples were left for varying times to allow the decay of short-lived radionuclides and gamma spectroscopy was performed using an HPGe gamma photon detector.

To measure desorption of $^{133}$Cs, 100 g of sediment from the 0–5 cm interval of the section taken at the MHWM was suspended in 1 L of freshwater and left to equilibrate for up to 64 days. The aqueous phase was filtered, reduced in volume and the residue scraped into polythene vials for irradiation and gamma spectroscopy as described above.

Results and Discussion

$^{137}$Cs speciation

Sequential extraction of $^{137}$Cs from the intertidal sediment showed that 98% was associated with the residual phase and only 2% with the slightly more mobile acid-soluble component (Table 1). In contrast, for sediment at the MHWM only 80–85% of the $^{137}$Cs was in the residual phase, with 13–19% in the slightly more mobile phases extracted by 1 M HNO₃ acid oxalate (Table 2). Consistent values were observed to a depth of 70 cm, corresponding to a depositional age of approximately 28 years. However, extraction of $^{137}$Cs from a sediment profile 10 m inland from the MHWM showed a pattern to a depth of 30 cm which