



Geochemical association of Pu and Am in selected host-phases of contaminated soils from the UK and their susceptibility to chemical and microbiological leaching



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ARTICLE INFO

Article history:

Received 8 August 2014

Received in revised form

6 January 2015

Accepted 7 January 2015

Available online 4 February 2015

Keywords:

Plutonium
Actinides
Remediation
Biogeochemistry
Contaminated soil
Bioleaching

ABSTRACT

Understanding the biogeochemical behaviour and potential mobility of actinides in soils and ground-water is vital for developing remediation and management strategies for radionuclide-contaminated land. Pu is known to have a high K_d in soils and sediments, however remobilization of low concentrations of Pu remains a concern. Here, some of the physicochemical properties of Pu and the co-contaminant, Am, are investigated in contaminated soils from Aldermaston, Berkshire, UK, and the Esk Estuary, Cumbria, UK, to determine their potential mobility. Sequential extraction techniques were used to examine the host-phases of the actinides in these soils and their susceptibility to microbiological leaching was investigated using acidophilic sulphur-oxidising bacteria. Sequential extractions found the majority of $^{239,240}\text{Pu}$ associated with the highly refractory residual phase in both the Aldermaston (63.8–85.5%) and Esk Estuary (91.9–94.5%) soils. The ^{241}Am was distributed across multiple phases including the reducible oxide (26.1–40.0%), organic (45.6–63.6%) and residual fractions (1.9–11.1%). Plutonium proved largely resistant to leaching from microbially-produced sulphuric acid, with a maximum 0.18% leached into solution, although up to 12.5% of the ^{241}Am was leached under the same conditions. If Pu was present as distinct oxide particles in the soil, then ^{241}Am , a decay product of Pu, would be expected to be physically retained in the particle. The differences in geochemical association and bioleachability of the two actinides suggest that this is not the case and hence, that significant Pu is not present as distinct particles. These data suggest the majority of Pu in the contaminated soils studied is highly recalcitrant to geochemical changes and is likely to remain immobile over significant time periods, even when challenged with aggressive “bioleaching” bacteria.

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1. Introduction

Plutonium contamination in the environment has arisen from global fallout from nuclear weapons testing, as well as from

controlled and accidental discharges of nuclear material (Harley, 1980; Kimber et al., 2011). Americium is often a co-contaminant with Pu due to the formation of ^{241}Am from the beta decay of ^{241}Pu , which is itself formed via successive neutron captures in ^{239}Pu and ^{240}Pu . Even in significantly contaminated environments, Pu and Am isotopes often only exist in low mass concentrations and thus, synchrotron radiation techniques, which provide useful insight into chemical speciation, often cannot be used. However, sequential extraction techniques, in which the sediment or soil is separated into defined, sequentially-dissolved phases via a series of increasingly aggressive chemical extractions, can be used to determine their geochemical associations indirectly. This can

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provide useful information on the potential migration of the Pu in soils and under which geochemical conditions, if any, it may be remobilized. The geochemical fractions defined in this study followed the Tessier scheme (Tessier et al., 1979), and were: exchangeable or adsorbed; carbonate-bound; oxide-bound; organically-bound; and residual. In sequential leaching experiments, the actinides associated with the exchangeable phase are taken as being susceptible to mobilization by changes in the compositions of the groundwater. Actinides bound to the carbonate fraction may be susceptible to changes in pH with those bound to the reducible oxide fraction susceptible to changes in Eh. Oxidising conditions may promote the release of organic-bound actinides into solution, whilst actinides associated with the residual fraction are unlikely to be released into solution over a significant time span under most (bio)geochemical conditions.

Associations with several of these components may be affected by microbial respiration, which can alter mineralogy directly through enzymatic redox reactions or indirectly through changes to, for example, pH and Eh (Ehrlich, 1996; Lovley and Phillips, 1988). If the actinides are associated with phases susceptible to dissolution or degradation then microbial activity may result in their mobilization. The potential for Pu and Am mobilization has implications for the management of contaminated land since it can be either a possible benefit in remediation, or increase the risk through migration.

Despite the low Kd values of Pu in soils and sediments (McCubbin et al., 2004; Serne, 2007), the potential remobilization of small quantities of the actinide is still a concern (Kersting et al., 1999; Santschi and Roberts, 2002; Xu et al., 2014). Previous work by the current authors has demonstrated that negligible Pu present in environmental contaminated soils (from the AWE Aldermaston site) is released into solution (<0.01%) under induced-reducing conditions, suggesting that little Pu is mobilized despite the inferred dissolution of oxide minerals and presence of microorganisms linked to Pu reduction (Kimber et al., 2012). Therefore, it seemed unlikely any change in Pu oxidation state occurred as both Pu(III) and Pu(V) are more mobile relative to Pu(IV) which is the dominant Pu species in soils (Begg et al., 2013; Choppin et al., 1997; Kaplan et al., 2004; Powell et al., 2014; Silva and Nitsche, 1995). However, sulphur-oxidising bacteria are effective at leaching metal contaminants and are commonly used in biomining and soil washing (White et al., 1998). Reduced sulphur or iron compounds in the biosphere can be used by sulphur-oxidising bacteria for chemolithotrophic growth under aerobic conditions, leading to production of soluble metal sulphates and sulphuric acid (Norris, 1990). Therefore, bioleaching of Pu and Am through sulphuric acid production could offer a possible mechanism for Pu and Am remobilization or bioremediation.

Particle size and form can also influence the mobility of Pu in the environment; low molecular mass species and colloidal Pu are more mobile than particulate Pu (Kersting et al., 1999; Salbu et al., 2004). Therefore, characterisation of Pu-containing particles can also help to predict its environmental behaviour. Particles can be characterised using autoradiography techniques, in which alpha and gamma radiation can be detected in a soil sample using a storage phosphor imager (Lloyd and Macaskie, 1996). These particles can then be isolated and further characterised using, for example, scanning electron microscopy.

Here, we investigate the biogeochemical behaviour of Pu and Am in contaminated sediments from two sites in the UK with different Pu source terms; weapons manufacturing at Aldermaston and nuclear fuel reprocessing in the Esk Estuary. Our principal aim is to understand better which geochemical conditions could lead to remobilization of the two actinides. To achieve this, we detail the results of sequential leaching of $^{239,240}\text{Pu}$, ^{238}Pu and ^{241}Am to identify and compare the geochemical associations of Pu and Am at

the two sites studied. Furthermore, by comparing our data with similar but more historic work on Pu in Esk Estuary soils, our study provides further information on more long term Pu behaviour. In addition, the bioleachable fraction of both actinides was investigated and compared in the Aldermaston soils, using sulphuric acid-producing, sulphur-oxidising bacteria to determine the potential of bioleaching in remobilizing Pu or Am. Finally, further characterization of the Pu in the Aldermaston soils was conducted using autoradiography, with the alpha-emitting particles identified then examined under ESEM.

2. Materials and methods

2.1. Soil and groundwater collection

Soil and groundwater were provided by AWE from their Aldermaston site, Berkshire. Due to the varied industrial history of AWE's sites, areas of soil and groundwater have become contaminated with both radioactive and chemical substances, including plutonium and americium. Contaminated Land at AWE is regulated by the Office for Nuclear Regulation (ONR) under The Nuclear Installations Act and by the Environment Agency through; Environmental Permits and Environmental Protection Act, Part 2A. Soils and groundwater were collected and stored as described previously (Kimber et al., 2012). The Aldermaston site lies on Quaternary plateau gravels underlain by Tertiary sands and gravels of the Lower Bagshot Beds. In turn, these rest on a layer of London Clay, which acts as a barrier to groundwater flow from the site into the underlying Chalk aquifer. The soils had a pH between 6 and 6.5 with an Eh range between 200 and 250 mV.

Archived sediment samples from the Esk estuary (UK National Grid Reference O88,947), located near the Sellafield nuclear waste reprocessing site, were used. These were collected on 19 March 2008 at low tide. The core sample taken (30 cm depth, approximate age range 1950 to present) was divided into 6 sections. The 10–15 cm horizon was used in this study as the maximum discharges from Sellafield (during the 1970s) are reflected in this horizon (Mccarthy and Nicholls, 1990; Sajih and Livens, 2010). While most Pu released from the Sellafield pipeline into the North Sea is readily adsorbed by silt and hence is deposited on the seabed, resuspension of fine particles can lead to deposition of the radioactive material in intertidal regions of local estuaries (Cambray and Eakins, 1982; Morris et al., 2000). Previous work has identified the bulk soils from the same sample site as being composed of 74.5% silt, 18.6% clay (mostly consisting of illite), and 6.5% sand (Morris et al., 2000). For the 10–15 cm soil horizon, the reducible manganese and iron oxide fractions were between 1.30–1.40 g kg⁻¹ and 5.13–6.11 g kg⁻¹, respectively, and weight loss on ignition was between 8.6 and 10.5% (Morris et al., 2000).

2.2. Sequential extraction

Sediment samples (10 g) from both Aldermaston and the Esk estuary were subjected to sequential extraction (Tessier et al., 1979). This involved isolating the following fractions: (a) exchangeable, extracted with 100 ml 1 M MgCl₂ (pH 7) for 1 h; (b) carbonate-bound, extracted with 100 ml 1 M CH₃COONa, adjusted to pH 5 with CH₃COOH for 5 h; (c) reducible oxide-bound, extracted with 100 ml of 0.04 M NH₂OH·HCl in 25% v/v CH₃COOH, adjusted to pH 2 with NaOH and stirred at 96 °C for 6 h; (d) organic matter bound, extracted with 30 ml 0.02 M HNO₃ and 50 ml of 30% H₂O₂, adjusted to pH 2 with HNO₃ and stirred for 2 h at 85 °C. A further 30 ml 30% H₂O₂ (pH 2 with HNO₃) was then added and stirred as before. Next, 50 ml 3.2 M CH₃COONH₄ in 20% v/v HNO₃ was added, the solution was diluted to 200 ml with distilled deionised water

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