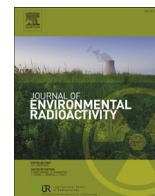


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## Bioaccessibility of U, Th and Pb in solid wastes and soils from an abandoned uranium mine

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### ABSTRACT

Bioaccessible U, Th, Pb and the <sup>238</sup>U decay products <sup>214</sup>Pb and <sup>210</sup>Pb have been determined, using a modified Unified BARGE Method (UBM), in waste solids and soils from an abandoned uranium mine in South West England, UK. Maximum extractable concentrations for U, Th and Pb were 16,200, 3.8 and 4750  $\mu\text{g g}^{-1}$ , respectively. <sup>238</sup>U had highest activity concentrations near the mine shaft, where the decay products <sup>214</sup>Pb and <sup>210</sup>Pb had values of 235 and 180  $\text{Bq g}^{-1}$ , respectively. UBM extractions gave mean gastro-intestinal bioaccessibility factors (BAFs) for U and Pb in the waste solids of 0.05 and 0.03, respectively, whereas those for the soils were significantly higher at 0.24 and 0.17. The mean BAFs for the transient radionuclides, <sup>214</sup>Pb and <sup>210</sup>Pb, were similar to those for stable Pb implying that the stable and radioactive Pb isotopes were attached to similar sites on the particles. The doses arising from the ingestion of particulate <sup>210</sup>Pb due to soil pica behaviour were in the range 0.2–65 and < 0.1–6.2  $\mu\text{Sv day}^{-1}$  for a 1-year old child or an adult (>17 years), respectively. The results suggest that the health risk posed by abandoned uranium mines, with waste rock and tailings, throughout the world should take account of the dose due to both bioaccessible radionuclides, as well as their stable counterparts.

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### 1. Introduction

Uranium mining within Europe reached its height between 1960 and 1990, after which the deposits became depleted and mines closed (Dittmar, 2013). Consequently, there are ca.150 redundant uranium mines in the EU, likely augmented by others as it expands eastwards (Falck, 2008; Raeva et al., 2014). These mines have legacies of millions of tonnes of waste rock and mill tailings (wise-uranium.com; World Nuclear Association, 2015). The human health impact of solid waste comprising naturally-occurring radioactive material (NORM) is not fully understood (Brugge and Buchner, 2011) and is of concern in abandoned mines for example in France (Cuvier et al., 2015), Poland (Kozak et al., 2013), Portugal (Neiva et al., 2014), Serbia (Momčilović et al., 2013) and Spain (Villa et al., 2011), where workers and members of the general public may be exposed to health risks.

Risk assessments for land contaminated with NORM are particularly important for children, who are the most likely sector

of the general public to ingest soils whether purposefully or inadvertently (Abrahams, 2002). Soil pica behavior, that is hand (or object)-to-mouth transfer of particulate matter, together with inhalation, can result in soil intakes of about 100  $\text{mg day}^{-1}$  in children and 50  $\text{mg day}^{-1}$  in adults (US EPA, 2011). Ingestion of soils containing radionuclides results in the dual effects from the chemo-toxicity of heavy elements and the radio-toxicity of ionizing radiation (Kathren and Burklin, 2008). <sup>238</sup>Uranium, comprising 99% of total uranium, has a tendency to accumulate in human bones (66%), kidneys (8%), and liver (16%) where it can cause significant damage to the surrounding tissues as a result of gamma rays and high linear energy transfer associated with the emissions of charged  $\alpha$ - and  $\beta$ -particles from <sup>238</sup>U and its decay products. The chemical toxicity associated with exposure resulting from ingestion of <sup>238</sup>U may lead to pathological alterations of the kidneys (Brugge and Buchner, 2011).

Bioaccessibility is considered to be that fraction of a constituent that is desorbed from particulate material by human digestive liquids (Wragg et al., 2011a). Thus, it represents the maximum amount of the constituent potentially available for absorption into the blood via the epithelium. A key research challenge concerns the development of reproducible *in-vitro* methods suitable for the

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determination of the fraction of bioaccessible radioactive contaminants in particulate matter. The Physiologically Based Extraction Test (PBET) (Ruby et al., 1993), or subsequent modifications thereof, has been applied to various solids containing uranium (e.g. Frelon et al., 2007; Höllriegel et al., 2010; Jovanovic et al., 2012), however, these methods may not accurately reproduce human gastrointestinal digestive processes which has led to the design of improved *in-vitro* methodologies (summarized by Tokahoğlu et al., 2014). In particular, the Bioaccessibility Research Group of Europe (BARGE) developed the Unified BARGE Method (UBM) which has been successfully compared with *in vivo* studies (Wragg et al., 2011a; Denys et al., 2012) and has been widely applied to metal-contaminated soils (Barsby et al., 2012; Broadway et al., 2010; Farmer et al., 2011; Juhasz et al., 2011b; Pelfrène et al., 2013). However, the UBM has not been applied to situations where the land is contaminated with solids arising from uranium mining.

The aim of the investigation was to examine (i) the bioaccessibility of NORM found in waste materials and soils and (ii) to assess any differences in the bioaccessibility of the stable and radioactive isotopes of Pb. To achieve this aim the bioaccessible gastric (termed STOM) and gastro-intestinal (termed STOM + INT) concentrations of U, Pb and Th were determined in waste solids (defined as samples from the mine shaft, spoil heap and the adit) and soils from an abandoned uranium mine in south west England. The results of the analyses were used to estimate effective doses to children and adults associated with the ingestion of NORM-contaminated solids.

## 2. Methods

### 2.1. Site description

The South Terras mine in Cornwall, South West England is situated on the banks of the upper River Fal (Fig. 1). The underlying geology consists of metamorphic zones with micro-granitic dykes containing deposits of U, Fe and other metals, including Pb (Gillmore et al., 2001). The primary uranium ores were uraninite (UO<sub>2</sub>) and pitchblende (U<sub>3</sub>O<sub>8</sub>), together with secondary deposits of torbernite and autunite and early assays indicated a maximum content of 30% uranium (Dines, 1956). The mine was active from 1870 to 1930 during which Fe, U and Ra, and to a lesser extent Pb and As, were extracted. For most of its working life a stamp engine was used for the crushing and grinding of the ore and in 1922 an extraction plant was installed, processing about 200 tonnes of ore before closure. Subsequently, no major remediation has taken place because in 1996 it was designated as a Special Site of Scientific Interest (SSSI) by the UK government ([www.sssi.naturalengland.org.uk](http://www.sssi.naturalengland.org.uk)). Analyses of elemental concentrations at spoil heap 1, located on the banks of the river, gave values for U and Th in the range 66–10,800 and 8–10 µg g<sup>-1</sup>, respectively (Read et al., 1991). Elevated activity concentrations of atmospheric <sup>222</sup>Rn are common in the vicinity of the mine (Gillmore et al., 2002). Contamination of the nearby waters and sediments of the River Fal by U isotopes appears to be variable downstream of the spoil heaps (Moliner-Martinez et al., 2004; Siddeeg et al., 2015). Recent measurements of the radioactive dose over the whole site, by an aerial surveillance system, identified the dressing floor as a radiation hot-spot (Martin et al., 2015). The land nearby hosts residential properties, including a farm, and the area is accessible to the general public (Gillmore et al., 2002).

### 2.2. Experimental strategy

Solid waste is scattered around the abandoned mine, for example at the mine shaft, the dressing floor, adit and spoil heaps

(Fig. 1). Spoil heap 2 was located in a field, where waste materials had, over time, been incorporated into the soil matrix. The sampling strategy involved collection of samples of waste solids and field soils with a range of radioactivities, sampling being informed, to some extent, by readings from a hand-held Geiger counter. In the laboratory the particulate samples were dried and sieved to obtain the <250 µm fraction, which is assumed to be size most likely to adhere to the fingers and hands and is consequently available for accidental oral intake (Juhasz et al., 2011a). The analytical objective was to determine the aqua regia extractable, the bioaccessible gastric (STOM), and gastro-intestinal (STOM + INT) concentrations of U, Th and Pb on four replicates of each sample. Importantly, the same soil samples were used to determine the activity concentrations of radio-isotopes in the <sup>238</sup>U decay series, specifically <sup>214</sup>Pb and <sup>210</sup>Pb, by gamma spectrometry, before and after UBM extraction.

### 2.3. Sample collection, preservation and pre-treatment

Samples of waste solids were collected from the surface of the dressing floor, near the mine shaft, spoil heap 1 and from the entrance to the main adit. The dressing floor was an area where the uranium ores were crushed, separated from gangue minerals, containing Pb, and then sorted. Soil samples were obtained from the field, at depths of 5–20 cm and 35–50 cm, using a soil auger on a transect starting at the edge of spoil heap 2 (Fig. 1). The field sampling methodology and objectives broadly cohered, where possible, with a national monitoring programme for <sup>238</sup>U, <sup>232</sup>Th and <sup>40</sup>K (Environment Agency, 2007).

All samples were freeze dried for 48 h and dried samples were stored in desiccators to minimise uptake of moisture. To facilitate gentle disaggregation and self-attrition, the dried samples were sealed into acid-washed high density polyethylene bottles, which contained alumina balls, and which were rotated on a trundle mill for about 24 h. Sample homogeneity after trundling was achieved by sieving the particulate matter across a 250 µm mesh nylon sieve, under a fume hood. The size-fractionated soil samples were stored in sealed plastic bottles which were wrapped in separate plastic bags to minimise exposure to air.

### 2.4. Aqua regia extractions

Aqua regia extractions of the pre-treated solids and soils were carried out in quadruplicate using accurately weighed samples, approximately 0.5 g, placed into acid-washed, dry, long-necked (reflux type) Tecator™ digestion tubes. Exactly 4 mL of concentrated HCl (Fisher Scientific, UK) and 1 mL of concentrated HNO<sub>3</sub> (Trace Analysis Grade; Trace Analysis Grade; Fisher Scientific, UK) were added to each of the tubes, giving a solid:solution ratio of 0.1. The digestion tubes were placed in a cold Foss Tecator™ digestion block to undertake a low temperature pre-digestion of easily oxidised material to avoid a vigorous reaction during heating. After 1 h of pre-digestion, a further 0.5 mL of concentrated HNO<sub>3</sub> (Trace Analysis Grade; Fisher Scientific, UK) was added to each of the digestion tubes and the contents were heated to 95 °C on the digestion block and refluxed for 2 h. After cooling, the digests were diluted with 2% HNO<sub>3</sub>, and filtered into 50 mL volumetric flasks and made to the mark with 2% HNO<sub>3</sub>.

The efficiency of the aqua regia extract was assessed using the certified reference materials (CRMs) LKSD-4 (CANMET Mining and Mineral Science Laboratories, Canada), EnviroMAT SS-1 (SCP Science, Canada) and Montana Soil 2711a (National Institute of Standards, USA) (Table 1). LKSD-4 and EnviroMAT SS-1 were specifically chosen because their certified values were obtained using aqua regia digestion methods and they had a reasonable matrix-match

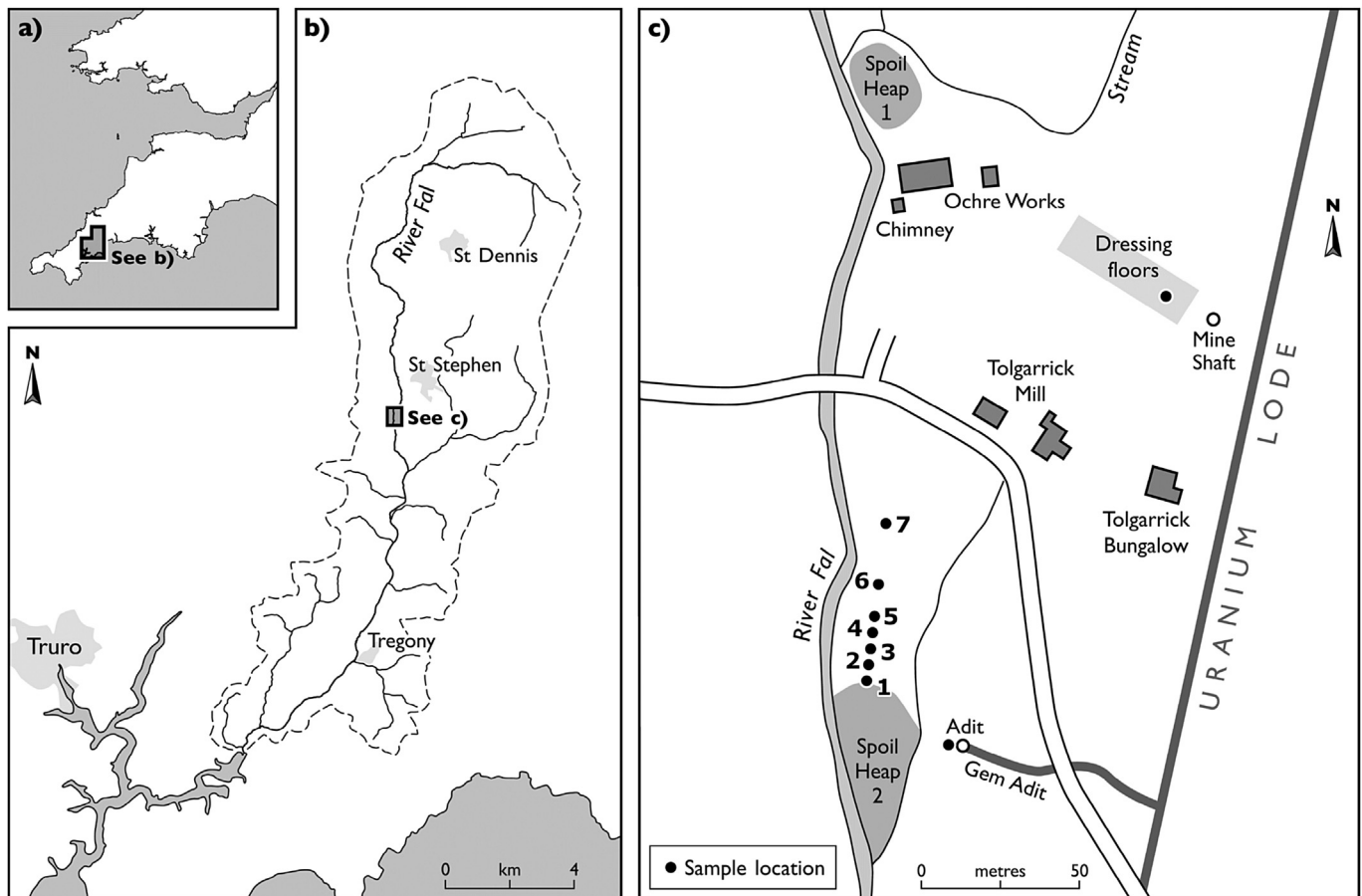


Fig. 1. The South Terras Mine, Cornwall, UK and sample sites.

**Table 1**  
Results of aqua regia extractions and UBM digests of certified reference materials ( $n = 3$ ).

CRM	Uranium		Thorium		Lead	
	Certified	Measured	Certified	Measured	Certified	Measured
<b>Totals</b>						
LKSD-4	31.0 <sup>a</sup>	29.8 ± 0.1	5.1 <sup>a</sup>	4.79 ± 0.72	93 <sup>a</sup>	90.1 ± 4.1
Lake Sediment						
EnviroMAT SS1	0.76 <sup>a</sup>	0.74 ± 0.05			764 ± 15	804 ± 42
Contaminated Soil						
NIST 2711a	3.01 ± 0.12	2.55 ± 0.18	15 ± 1 <sup>a</sup>	12.1 ± 0.6	1405 ± 10	1366 ± 60
Montana Soil						
<b>Bioaccessible Fraction</b>						
BGS-102						
Ironstone Soil						
STOM	0.27 ± 0.05 <sup>b</sup>	BD	0.12 ± 0.05 <sup>b</sup>	0.14 ± 0.01	13 ± 6	10.7 ± 1.0
STOM + INT	0.20 ± 0.06 <sup>b</sup>	BD	0.23 ± 0.08 <sup>b</sup>	0.30 ± 0.02	1.9 ± 0.4	2.3 ± 0.1

<sup>a</sup> Reference values.

<sup>b</sup> Hamilton et al., 2015; BD=Below Detection.

to the samples from the South Terras mine. The accuracy of the analyses of the bioaccessible fractions of the elements was assessed against BGS-102, ironstone soil, using the UBM procedure (Hamilton et al., 2015). Procedural blanks of the method were made alongside each run of 18 digestions as a quality control.

### 2.5. Bioaccessible STOM and STOM + INT digests

Bioaccessible extractions of the dried, size-fractionated soil samples were carried out, in quadruplicate, using the UBM procedure (Wragg et al., 2011b). The composition of the simulated

digestive fluids, comprising the UBM, were saliva, gastric, duodenal and bile fluids were made up using an established protocol (see the Supplementary Material in Broadway et al., 2010), which has been previously applied in our lab (Tokahoglu et al., 2014). These were prepared 24 h prior to undertaking the extractions to ensure that all of the reagents were thoroughly dissolved. The pHs of the simulated fluids were checked, with a calibrated pH meter, before use to ensure they were within the prescribed limits and pH adjustments were performed with either 37% HCl or 1 M NaOH. Each test soil sub-sample was about 1.2 g (with the simulated fluid additions scaled proportionally to maintain the solid to liquid ratio) and four

replicates per test sample. Increasing the masses of the samples also provided a better representation of the repeatability of the extractions. A set of procedural blanks were also prepared alongside the STOM and STOM + INT extractions for the purposes of quality control.

### 2.5.1. STOM extraction procedure

The extractions were carried out in quadruplicate on each sample. Exactly 18 mL of simulated saliva fluids were pipetted into 1.2 g of an accurately weighed sample of dried soil contained in centrifuge tubes, which were then capped and thoroughly shaken for 30 s. Then 27 mL of simulated gastric fluid was added and the centrifuge tubes re-capped and placed into a shaking water bath and incubated at  $37 \pm 2$  °C for 1 h. After incubation the centrifuge tubes were removed from the water bath and the pH of the suspension measured with the calibrated pH meter. If the pH was in the range 1.2–1.7, the extraction was considered complete. If the pH of a particular sample was not within range, the gastric extraction was repeated and the pH adjusted to 1.2–1.7 using up to 1 mL HCl (37%). During our extractions three sample suspensions did not meet this criterion and were repeated. STOM phase extracts were then centrifuged at 3000 rpm for 15 min. The supernatants were carefully decanted into a second centrifuge tube and 1 mL of HNO<sub>3</sub> (70%) accurately pipetted to preserve the extraction. The extractions were stored at 4 °C prior to analysis. The four dried residues from the STOM extractions from each site were combined and packed into pre-weighed, screw-top, plastic vials of 4 mL volume, which were sealed with adhesive tape and incubated for 30 days prior gamma counting, see Section 2.7.

### 2.5.2. STOM + INT extraction procedure

The first stage was to repeat the STOM extraction above (neglecting the gamma counting stage), using acid-washed, clean Nalgene 125 mL HDPE screw top bottles (in place of 50 mL centrifuge tubes to accommodate the additional fluids required) for 1 h of incubation. All samples met the pH criterion. The second stage was to accurately pipette 54 mL of simulated duodenal fluid and 18 mL of simulated bile fluid into the bottles which were re-capped. They were shaken for 30 s and the pH checked, with a calibrated pH meter, to ensure that it was in the range 5.8–6.8. If the pH tolerance was not met, the pH was adjusted by the dropwise addition of 37% HCl or 1.0 M NaOH as required. The bottles were placed in a shaking water bath at 37 °C and incubated for a further 4 h. After incubation the pH was measured and the suspensions were decanted into centrifuge tubes and centrifuged for ten minutes at 3000 rpm. During the centrifugation the extraction bottles were rinsed with 2% HNO<sub>3</sub>. After centrifugation the supernatants were then carefully decanted back into their corresponding extraction bottles and 2 mL of HNO<sub>3</sub> (70%) was accurately pipetted into the bottles as a preservative. The extractions were then stored at 4 °C prior to analysis by ICP-MS. The four dried residues from each of the STOM + INT extractions were combined into pre-weighed, screw-top plastic 4 mL vials, which were sealed with adhesive tape and incubated for 30 days prior to gamma counting, see Section 2.7.

### 2.6. Analysis of aqua regia extractable and UBM digests by ICP-MS

Calibration standards of U, Th, Pb, Fe and Mn together with internal standards of Cs, Ir and were carried out using standard solutions diluted with 2% HNO<sub>3</sub> ('Aristar' grade, VWR, Poole, Dorset). Procedural blanks and extractions of CRMs for all digests were also run alongside all analyses for purposes of quality control and validation. After the digests had been quantitatively transferred to 50 mL volumetric flasks and made up to the mark, using 2% HNO<sub>3</sub>,

they were measured for the selected elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Six multi-element calibration standards were made up in the concentration range 0–10,000 µg L<sup>-1</sup> using 2% HNO<sub>3</sub> as the diluent. Each digest was then spiked with 0.5 mL of a 10 mg L<sup>-1</sup> Ir and In solution, to act as internal standards. Three measurements were conducted on each replicate to obtain a mean concentration and standard deviation for each replicate.

To matrix match the calibration standards to the STOM and STOM + INT digests, they were made up using the respective fluids used in the digests. Therefore, two sets of calibration standards were made up in the concentration range 0–400 µg L<sup>-1</sup> using the respective fluid. Each gastric digest was then spiked with 0.46 mL of a 10 mg L<sup>-1</sup> Cs solution as an internal standard and each gastro-intestinal digest was also spiked with 1.19 mL of the Cs standard to correct for matrix interferences. A Cs standard was used as opposed to the previously used Ir and In standards as there was the potential for In to precipitate given the enzymes present in the fluids and the varying of the pH. Three measurements were conducted on each replicate. The concentrations of the procedural blanks and limits of detection for the aqua regia, gastric and gastro-intestinal digests for each element are shown in [Supplementary Table S1](#). The measured and certified concentrations of Fe and Mn are shown in [Supplementary Table S2](#).

### 2.7. Analysis of activity concentrations by gamma spectrometry

The geometry of the STOM and STOM + INT extracted soil samples in 4 mL vials from each site were closely matched to that of the calibration standard. The activity concentrations of the gamma-emitting radionuclides in the vials were determined, after 30 days incubation to allow secular equilibrium between <sup>226</sup>Ra and gaseous <sup>222</sup>Rn to be established. The gamma spectrometer consisted of a high purity germanium well-type detector (GWL-170-15-S; N-type; ORTEC, Wokingham, UK), which had a full width-half maximum (FWHM) for the 1330 keV line of Co-60 of 1.76 keV and a relative efficiency of 25%. The efficiency calibration of the gamma spectrometer was performed using a natural, homogenised soil, with low background activity, spiked with a radioactive traceable standard solution (SRS-80717-669; Eckert & Ziegler Analytics, Atlanta, Georgia). The spiked standard soil, and the samples, were each counted for at least 80,000 s and the results quoted with a 2-sigma counting error. The gamma energies of the target radionuclides were 46.5 keV for <sup>210</sup>Pb, 63.3 keV for <sup>234</sup>Th and 295 and 352 keV for <sup>214</sup>Pb. Determinations of the activity concentrations of the radionuclides were quality controlled by participation in IAEA worldwide proficiency tests using soils IAEA-CU-2009-03 and IAEA-TEL-2012-03, which were packed and sealed in the same geometry as the samples.

## 3. Results

### 3.1. Analytical quality assurance

Our measured values for U, Th and Pb in LKSD-4 and EnviroMAT SS1 using an aqua regia extraction had good agreement with the certified values ([Table 1](#)). However, the mean measured concentrations for NIST 2711a were approximately 15% lower than the certified values which were obtained using a total digest ([Table 1](#)). Analyses of U, Th and Pb for the STOM and STOM + INT stages of the UBM digests in BGS-102 ironstone showed that the accuracy and precision were in good agreement for Th and Pb but U was below detection ([Table 1](#)).

Determinations of the radionuclides were verified by participation in IAEA worldwide proficiency tests. In particular, analyses

of  $^{238}\text{U}$ ,  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  in soils (IAEA-CU-2009-03; IAEA-TEL-2012-03) indicated agreement between the IAEA activity concentrations and those from our laboratory (Table 2). Radioactive analyses of three separate samples, from two sites at South Terras had relative standard deviations for  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  of 1.3% and 5.9%, respectively, indicating particle homogeneity within the samples.

### 3.2. Aqua regia extractable concentrations of U, Th and Pb

Aqua regia extractable concentrations of U in solids from spoil heap 1 and the mine shaft were elevated; viz  $16,200 \pm 2800$  and  $13,330 \pm 200 \mu\text{g g}^{-1}$ , respectively (Fig. 2a). The dressing floor solids, and those near the adit, had total U concentrations which were typically  $<100 \mu\text{g g}^{-1}$ . The surface field soils (Fig. 2b) had the highest concentration near spoil heap 2,  $1900 \pm 20 \mu\text{g g}^{-1}$ , and the U concentrations declined away from the heap to about  $80 \pm 2 \mu\text{g g}^{-1}$  at 50 m. The field soils at depth had U concentrations of similar magnitude and trend to the surface values (Fig. 2c).

The aqua regia extractable Th concentrations in the waste solids (Fig. 2d) had maximum concentrations of  $3.8 \pm 0.1$  and  $3.1 \pm 0.1 \mu\text{g g}^{-1}$  for spoil heap 1 and the mine shaft, respectively. The dressing floor samples were all  $<1 \mu\text{g g}^{-1}$  whereas the adit samples had similar values of  $1.8 \pm 0.2 \mu\text{g g}^{-1}$ . The highest Th concentration in the surface field samples was close to spoil heap 2 (Fig. 2e),  $1.7 \pm 0.1 \mu\text{g g}^{-1}$ . The remainder were within a narrow range of  $0.6\text{--}0.9 \mu\text{g g}^{-1}$  until at 50 m, where Th concentrations increased slightly to  $1.2 \pm 0.8 \mu\text{g g}^{-1}$ . The samples on the transect, at depth (Fig. 2f), had Th concentrations that were of similar magnitude, and trend, to those at the surface.

The highest aqua regia extractable concentrations of Pb were  $4750 \pm 80$  and  $5000 \pm 50 \mu\text{g g}^{-1}$  were obtained at spoil heap 1 and the mine shaft, respectively (Fig. 2g). The Pb concentrations on the dressing floor were relatively constant, in the range  $500\text{--}700 \mu\text{g g}^{-1}$ , while the adit samples had slightly lower concentrations. Surface soil at the edge of spoil heap 2 had an aqua regia extractable Pb concentration of  $1720 \pm 26 \mu\text{g g}^{-1}$ , which declined to  $70 \pm 1 \mu\text{g g}^{-1}$  at 50 m (Fig. 2h). For the soils at depth, the trend and concentrations of Pb (Fig. 2i) were similar to those at the surface.

### 3.3. Concentrations of U, Th and Pb in the STOM and STOM + INT phases

For the waste solids (Fig. 2a) the STOM digest had significantly lower U concentrations than the aqua regia extract. Generally, the concentration of U in the STOM + INT extract was slightly lower than the STOM, with the exception of the sample from the mine shaft. The surface field soils had STOM concentrations of U that were lower than the aqua regia extracts, whereas the STOM + INT concentrations were slightly lower or similar to the STOM concentration (Fig. 2b). The STOM + INT concentration showed a significant decrease in the field samples at depth compared to the

aqua regia concentration (Fig. 2c).

The concentration of Th mobilised by the STOM solution, compared to that of the aqua regia extractable, was lower by approximately two orders of magnitude for the waste solids (Fig. 2d) and was about one order of magnitude lower for the field samples from the surface (Fig. 2e) and at depth (Fig. 2f). However, there was a significant, and persistent, increase in the amount of Th released from both the waste solids and the field soils, from the surface and at depth, by the STOM + INT solution, compared to the STOM solution alone.

For Pb, extracting the waste solids with the STOM solution resulted in the release of concentrations of Pb that were one to two orders of magnitude lower than the aqua regia extractable (Fig. 2g). The STOM + INT solution resulted in the release of lower amounts of Pb from the particles. A similar pattern of behaviour was observed in the field samples, at the surface and at depth. Generally, higher Pb mobilisation from the particles was observed in the acidic STOM solution (Fig. 2h; 2i).

### 3.4. Activity concentrations of $^{214}\text{Pb}$ , $^{210}\text{Pb}$ and $^{238}\text{U}$

Concentrations of  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  radio-isotopes, following extraction by the STOM and STOM + INT solutions, were estimated from the solid phase gamma spectroscopic analyses via:

$$A_R = A_T - A_M \quad (1)$$

where  $A_R$  is the activity concentration removed by either the STOM or the STOM + INT solution,  $A_T$  is the total activity concentration and  $A_M$  is the measured activity concentration on the post STOM or STOM + INT residues, with all activity concentrations in  $\text{Bq g}^{-1}$ . The activity concentrations of  $^{214}\text{Pb}$  (Fig. 3a) in the untreated waste samples are all elevated, typically about  $100 \text{Bq g}^{-1}$ , with the exception of samples outside the adit, which are approximately two orders of magnitude lower. Total activity concentrations of  $^{214}\text{Pb}$  in the soil samples from the field were lower and they declined away from spoil heap 2 and the STOM fraction was highest at the foot of the spoil heap and then remained relatively constant (Fig. 3b). The STOM + INT fraction was lower than the STOM fraction again indicating less mobilisation of  $^{214}\text{Pb}$  by the gastro-intestinal solution. The activity concentrations of  $^{214}\text{Pb}$  in the samples at 35–50 cm depth, following extraction by aqua regia, and by STOM and STOM + INT solutions (Fig. 3c) are similar to the surface values.

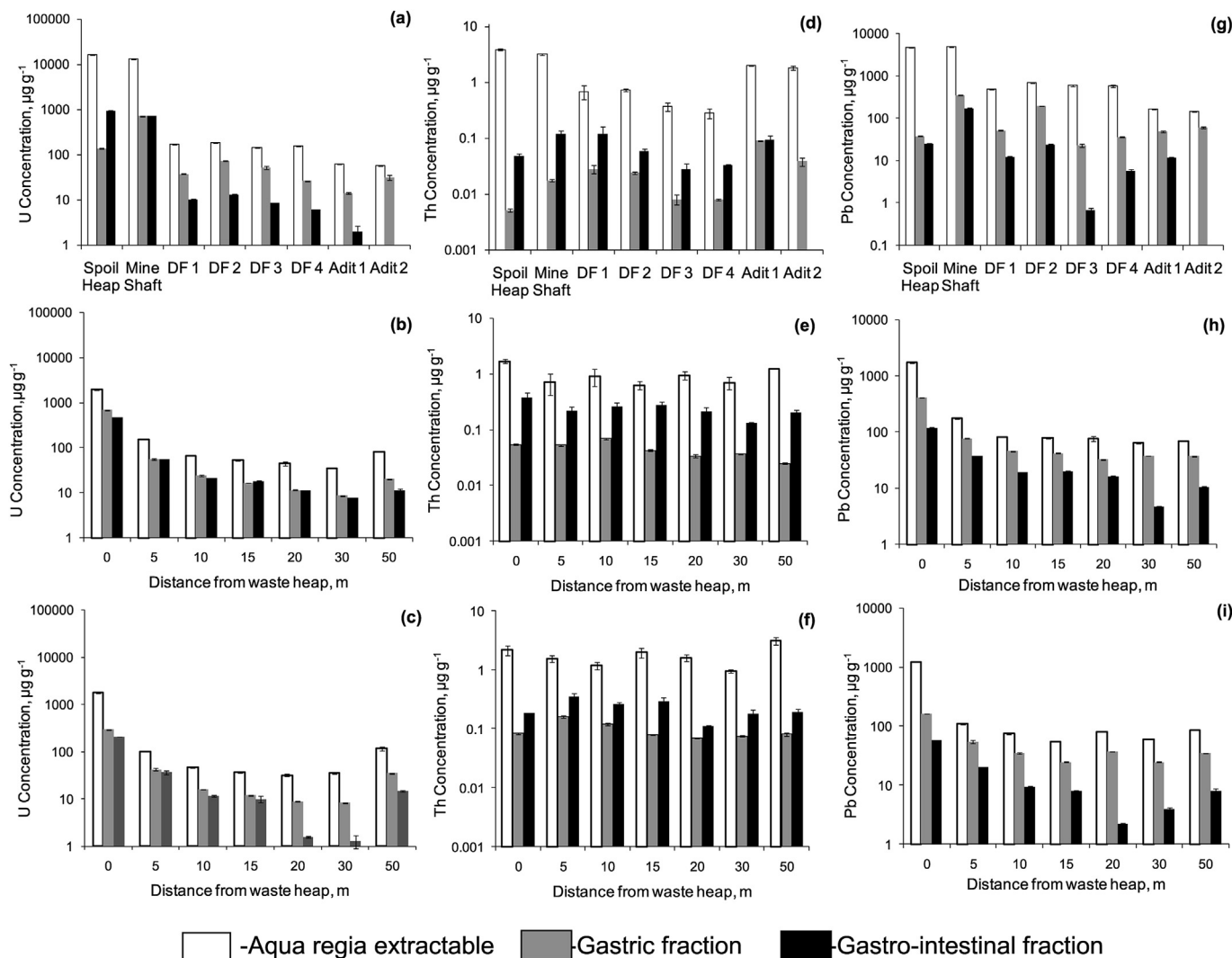
The total activity concentrations of  $^{210}\text{Pb}$  in the waste solids were relatively constant at about  $100 \text{Bq g}^{-1}$  with the exception of the adit samples, which were about two orders of magnitude lower (Fig. 3d) with a similar profile to that of  $^{214}\text{Pb}$ . The trend in the STOM and STOM + INT fractions was also similar to that observed for  $^{214}\text{Pb}$ . The activity concentrations of  $^{210}\text{Pb}$  in the surface field soils were one to two orders of magnitude lower than the waste solids, including the edge of spoil heap 2 (Fig. 3e). At depth the activity concentrations in the three fractions had a similar magnitude and followed the same trend as the surface values (Fig. 3f).

Activity concentrations for  $^{238}\text{U}$  were estimated from the activity concentrations of  $^{234}\text{Th}$  following the establishment of secular equilibrium in the sealed samples after 30 days incubation. The activity concentrations of  $^{234}\text{Th}$  in the aqua regia, the STOM and STOM + INT extractions were plotted against the activity concentrations estimated from the product of the U concentration determined by ICP-MS analysis of the sample digests and the specific activity of  $^{238}\text{U}$  (Fig. 4). Linear regression of this data gives an almost 1:1 relationship:  $y = 1.037x + 0.679$ ;  $n = 44$ ;  $R^2 = 0.996$ ;  $p < 0.001$ , indicating that the ICP-MS analyses of U are significantly related with the gamma spectrometric analyses.

**Table 2**

Comparison of certified activity concentrations of radionuclides,  $\text{mBq g}^{-1}$ , in IAEA soils with measured values.

Radionuclide	Certified activity Concentration, $\text{mBq g}^{-1}$	Measured activity Concentration, $\text{mBq g}^{-1}$
<b>IAEA Moss soil (IAEA-CU-2009-03)</b>		
$^{214}\text{Pb}$	$26.0 \pm 2.0$	$22.8 \pm 1.2$
$^{210}\text{Pb}$	$424 \pm 20$	$457 \pm 12$
<b>IAEA Soil (IAEA-TEL-2012-03)</b>		
$^{238}\text{U}$	$23.6 \pm 0.7$	$28.8 \pm 3.3$
$^{210}\text{Pb}$	$595 \pm 19$	$642 \pm 14$



**Fig. 2.** Aqua regia extractable and bioaccessible concentrations of U, Th and Pb ( $\mu\text{g g}^{-1}$ ) in waste solids and field soils: Open, grey and filled bars represent total concentrations, concentrations available to the STOM extract and concentrations available to the STOM + INT extract (a) U in waste solids, (b) U in surface field soils, (c) U in field soils at depth, (d) Th in waste solids, (e) Th in surface field soils, (f) Th in field soils at depth, (g) Pb in waste solids, (h) Pb in surface field soils and (i) Pb in field soils at depth. DF = Dressing Floor.

### 3.5. Bioaccessibility factors (BAFs)

Bioaccessibility factors were estimated by dividing the concentration in the STOM + INT fraction,  $\mu\text{g g}^{-1}$ , (or activity concentration,  $\text{Bq g}^{-1}$ ) by the aqua regia extractable concentration  $\mu\text{g g}^{-1}$ , (or activity concentration,  $\text{Bq g}^{-1}$ ) (Tables 3–5). The mean STOM + INT for the waste solids all had BAFs  $<0.10$  (Table 6). In contrast, the field soils had mean BAFs for the STOM + INT fraction that were significantly higher than the equivalent fraction from the waste solids, with the exception of Th.

### 3.6. Dose calculations

#### 3.6.1. Doses of heavy elements

The daily doses of bioaccessible U, Th and Pb due to ingestion of waste solids and/or soils at South Terras,  $D_E$ , were estimated from:

$$D_E = I_{\text{Soil}} \times C_E \times \text{BAF} \quad (2)$$

where  $I_{\text{Soil}}$  is the daily ingestion rate of soil,  $\text{g day}^{-1}$ ,  $C_E$  is the total concentration of U, Th or Pb in the samples and BAF is the fraction of the total element available to the STOM + INT extract of the UBM.

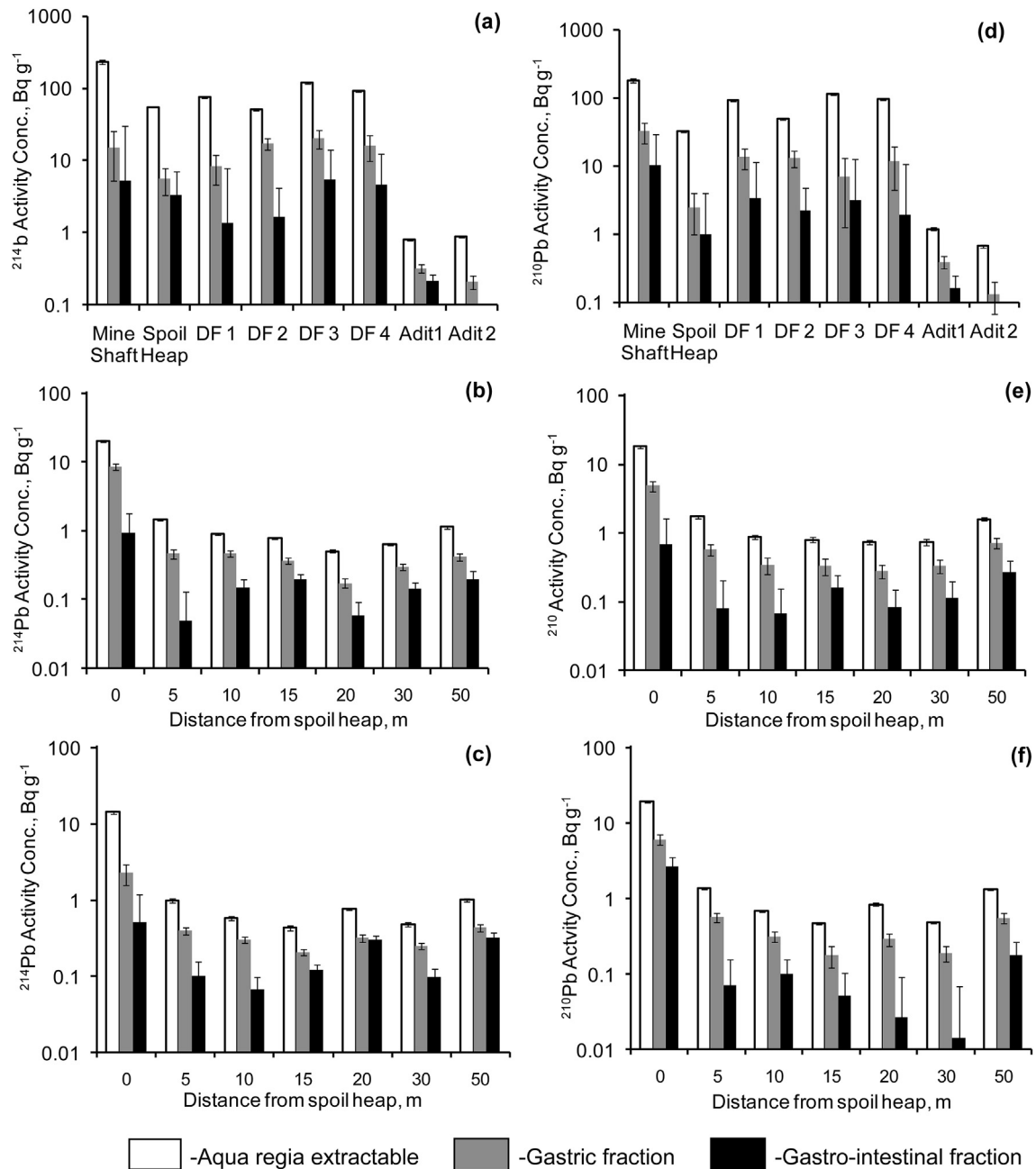
The solution to Eq. (2) requires selection of appropriate values for  $I_{\text{Soil}}$ , defined as the daily direct soil ingestion, hand-to-mouth soil ingestion and object-to-mouth soil ingestion. The ingestion rate is highly age-dependent amongst individuals but recommended values have been evaluated using data in the literature (US EPA, 2011). The general population central tendency for soil, plus dust, ingestion rates for children 1 to  $<6$  years is  $0.10 \text{ g day}^{-1}$ , whereas adults ( $>17$  years) typically ingest about  $0.05 \text{ g day}^{-1}$ . Using Eq. (2) the potential daily doses of bioaccessible U to children and adults are in the range  $0.2\text{--}94 \mu\text{g day}^{-1}$  and  $<0.1\text{--}47 \mu\text{g day}^{-1}$  (Table 3) respectively, whereas Th doses were significantly lower,  $4\text{--}51 \text{ ng day}^{-1}$  for children and  $1\text{--}19 \text{ ng day}^{-1}$  for adults (Table 4). Bio-accessible Pb gave values of  $0.5\text{--}24 \mu\text{g day}^{-1}$  for children and  $<0.1\text{--}12 \mu\text{g day}^{-1}$  for adults (Table 5).

#### 3.6.2. Committed effective dose of radionuclides

The total committed effective daily dose of radionuclides via the ingestion pathway,  $D_R$  in  $\text{Sv day}^{-1}$ , is given by:

$$D_R = I_{\text{Soil}} \times A_T \times DC_{\text{Ing}} \quad (3)$$

where  $DC_{\text{Ing}}$ ,  $\text{Sv Bq}^{-1}$ , is the committed dose coefficients for



**Fig. 3.** Activity concentrations, Bq g<sup>-1</sup>, of Pb isotopes in various solids (a) <sup>214</sup>Pb in waste solids, (b) <sup>214</sup>Pb in surface field soils, (c) <sup>214</sup>Pb in field soils from depth, (d) <sup>210</sup>Pb in waste solids, (e) <sup>210</sup>Pb in surface field soils, (f) <sup>210</sup>Pb in field soils from depth. Open, grey and filled bars represent aqua regia extractable concentrations (or total activity concentrations), STOM concentrations (or activity concentrations) and STOM + INT concentrations (or activity concentrations), respectively. DF = Dressing Floor.

ingestion of various radionuclides for a one-year old child and adults aged >17 years (ICRP, 2012). The age-specific values of  $DC_{Ing}$  vary by several orders of magnitude such that the total committed effective doses of <sup>238</sup>U (Table 3), <sup>232</sup>Th (Table 4) and <sup>214</sup>Pb (Table 5) are in the nSv day<sup>-1</sup> range whereas the committed effective doses for <sup>210</sup>Pb (Table 5) are three orders of magnitude higher.

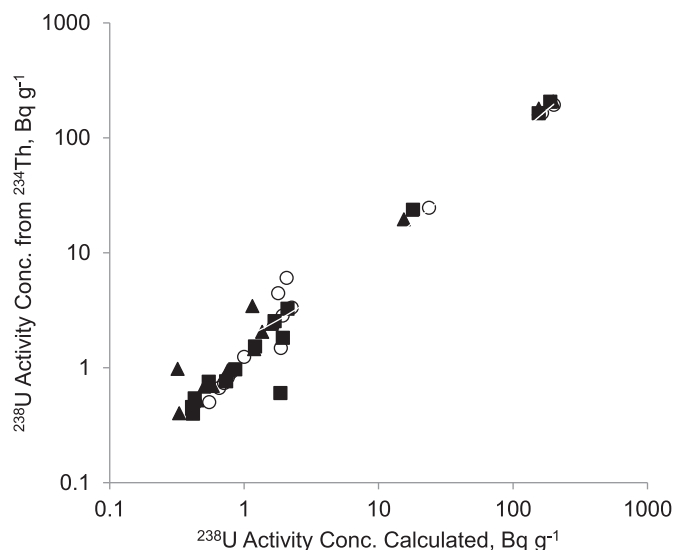
## 4. Discussion

### 4.1. Concentrations of U, Th and Pb

#### 4.1.1. Aqua regia extractable U, Th and Pb

Uranium concentrations in waste solids from the spoil heaps

and the dressing floor, were similar with previous values (Read et al., 1991), wherein they are elevated over the mean U concentration of  $2.06 \pm 0.98 \mu\text{g g}^{-1}$  in soils from the South West, UK (Environment Agency, 2007) and  $2.36 \pm 2.35 \mu\text{g g}^{-1}$  in European top soils (Salminen et al., 2005). Thus, the concentrations of U found in waste solids at South Terras are significantly above natural levels and the greatest values approached concentrations normally found in high grade U ore, which has concentrations of approximately  $20,000 \mu\text{g g}^{-1}$  (World Nuclear Association, 2015). Our values for aqua regia extractable U generally cohere with samples from former U mines in Serbia (Momčilović et al., 2013), Portugal (Neiva et al., 2014) and Germany (Träber et al., 2015). Also, soils from an area of natural U-mineralisation in northern Australia (Frostick



**Fig. 4.** Plot of  $^{238}\text{U}$  activity concentration,  $\text{Bq g}^{-1}$ , assuming secular equilibrium with  $^{234}\text{Th}$  versus the product of  $^{238}\text{U}$  concentration,  $\mu\text{g g}^{-1}$ , from the ICP-MS concentration and its specific activity ( $1.24 \times 10^4 \text{ Bq g}^{-1}$ ). ○-aqua regia extractable; ▲-gastric; ■-gastro-intestinal.

et al., 2011), and from an area of radium and uranium refining in Canada (Jovanovic et al., 2012), had U concentrations that encompassed the values reported here. Uranium concentrations found at South Terras, and at the sites mentioned above, are significantly higher than the Canadian guideline for soil ingestion of  $33 \mu\text{g g}^{-1}$  (Canadian Council of Ministers of the Environment, 2007), implying a potential human health impact via ingestion.

Our range of Th concentrations in South Terras mine waste,  $0.28\text{--}3.85 \mu\text{g g}^{-1}$ , and soils,  $0.63\text{--}1.69 \mu\text{g g}^{-1}$ , are generally lower than the mean values,  $8\text{--}10 \mu\text{g g}^{-1}$ , obtained by Read et al. (1991) in white-grey clays found beneath spoil heap 1. Soils from the SW UK had concentrations  $8.38 \pm 2.72 \mu\text{g g}^{-1}$  (Environment Agency, 2007), similar to European top soils of  $8.21 \pm 6.15 \mu\text{g g}^{-1}$  (Salminen et al., 2005). The lower values reported here may be due, in part, to the

efficiency of the aqua regia extractability on South Terras particulate matter. Total concentrations of Th in soils from a Serbian mine were in the range  $1.6\text{--}27 \mu\text{g g}^{-1}$  (Momčilović et al., 2013) and a median value of  $26.2 \mu\text{g g}^{-1}$  in the soils from the Pinhal do Souto area of Portugal (Neiva et al., 2014). Thorium in the mineralised area of the Ranger Anomaly #2, northern Australia, had relatively high concentrations in the range  $9.6\text{--}16.2 \mu\text{g g}^{-1}$  (Frostick et al., 2011), which are a factor of five higher than values obtained at South Terras.

Concentrations of aqua regia extractable Pb in waste solids were elevated and were of similar magnitude to the mean Pb concentration of  $2020 \mu\text{g g}^{-1}$  obtained previously (Read et al., 1991). These concentrations greatly exceed  $40 \mu\text{g g}^{-1}$  the value normally found in UK soils (Markus and McBratney, 2001) and they are also greater than the mean value for European top soils of  $32.6 \pm 56.9 \mu\text{g g}^{-1}$  (Salminen et al., 2005). The concentrations of Pb in the Ranger Anomaly #2 were relatively high, in the range  $986\text{--}4230 \mu\text{g g}^{-1}$  (Frostick et al., 2011), and similar to those at South Terras.

#### 4.1.2. Activity concentrations

Our analyses show waste solids and field soils, at South Terras, had  $^{238}\text{U}$  activity concentrations in the range  $0.74\text{--}193$  and  $0.5\text{--}25 \text{ Bq g}^{-1}$ , respectively. Sediments in the River Fal, downstream of spoil heaps 1 and 2, had  $^{238}\text{U}$  and  $^{226}\text{Ra}$  activity concentrations in the range  $0.01\text{--}4.35$  and  $0.04\text{--}1.77 \text{ Bq g}^{-1}$ , respectively (Siddeeg et al., 2015). These values are orders of magnitude higher than the mean activity concentration of  $^{238}\text{U}$  in soils from SW England of  $0.025 \pm 0.012 \text{ Bq g}^{-1}$  (Environment Agency, 2007). The Ranger Anomaly #2, in northern Australia, had  $^{238}\text{U}$  and  $^{226}\text{Ra}$  activity concentrations in the ranges  $17.5\text{--}47.2$  and  $13.6\text{--}29.2 \text{ Bq g}^{-1}$ , respectively (Frostick et al., 2011), which are significantly higher than those recorded at South Terras. In contrast, samples from a former French mining site showed that there was disequilibrium in the  $^{238}\text{U}$  decay chain but the activity concentrations of  $^{210}\text{Pb}$  were in the range  $0.05\text{--}1.7 \text{ Bq g}^{-1}$  (Cuvier et al., 2015).  $^{238}\text{U}$  activity concentrations in the metal contaminated Huelva Estuary, Spain were  $<0.01\text{--}0.34 \text{ Bq g}^{-1}$  (Villa et al., 2011). Thus, both sites have  $^{238}\text{U}$  activity concentrations at least one-order of magnitude lower than the values recorded at South Terras.

**Table 3**  
Aqua regia extractable concentrations of U and estimated activity concentration of  $^{238}\text{U}$  (specific activity:  $1.24 \times 10^4 \text{ Bq g}^{-1}$ ). Doses of U ( $\mu\text{g day}^{-1}$ ) estimated using Eq. (2) and committed effective doses of  $^{238}\text{U}$  ( $\text{nSv day}^{-1}$ ) for children (1 year old) and adults via ingestion of soil particles estimated via Eq. 3. The dose coefficient for children (1 year old) is  $1.2 \times 10^{-7} \text{ Sv Bq}^{-1}$  and for adults is  $4.5 \times 10^{-8} \text{ Sv Bq}^{-1}$  (ICRP, 2012).

Samples	Aqua Regia Extractable U			Activity $^{238}\text{U}$			
	Concentration, $\mu\text{g g}^{-1}$	BAF	Dose, $\mu\text{g day}^{-1}$		Concentration, $\text{Bq g}^{-1}$	<sup>a</sup> Dose, $\text{nSv day}^{-1}$	
			Child	Adult		Child	Adult
<b>Waste Solids</b>							
Mine Shaft	16,242	0.06	94	47	201	2410	450
Spoil Heap 1	13,290	0.05	70	35	165	1980	370
DF 1	167	0.06	1.0	0.5	2.07	25	5
DF 2	182	0.07	1.3	0.6	2.26	27	5
DF 3	144	0.06	0.8	0.4	1.79	21	4
DF4	156	0.04	0.6	0.3	1.94	23	4
Adit 1	61	0.03	0.2	<0.1	0.76	9	2
Adit 2	57	—	—	—	0.71	9	2
<b>Field Soils</b>							
0 m	1920	0.24	46	23	23.8	290	54
5 m	152	0.36	5.5	2.7	1.88	23	4
10 m	65	0.32	2.1	1.0	0.80	10	2
15 m	53	0.34	1.8	0.9	0.65	8	1
20 m	44	0.26	1.1	0.6	0.55	8	<1
30 m	35	0.05	0.2	<0.1	0.44	5	<1
50 m	81	0.14	1.1	0.6	1.00	12	2

<sup>a</sup> Committed effective dose.



**Table 4**

Aqua regia extractable concentrations of Th and estimated activity concentration of  $^{232}\text{Th}$  (specific activity:  $4.057 \times 10^3 \text{ Bq g}^{-1}$ ). Doses of Th ( $\text{ng day}^{-1}$ ) estimated using Eq. (2) and committed effective doses of  $^{232}\text{Th}$  ( $\text{nSv day}^{-1}$ ) for children (1 year old) and adults via ingestion of soil particles estimated via Eq. (3). The ICRP dose coefficient for the ingestion of soil particles by children (1 year old) is  $4.5 \times 10^{-7} \text{ Sv Bq}^{-1}$  and by adults is  $2.3 \times 10^{-7} \text{ Sv Bq}^{-1}$  (ICRP, 2012).

Sample	Aqua Regia Extractable Th				Activity $^{232}\text{Th}$			
	Conc., $\mu\text{g g}^{-1}$	BAF	Dose, $\text{ng day}^{-1}$		Concentration, $\text{mBq g}^{-1}$	$^a$ Dose, $\text{nSv day}^{-1}$		
			Child	Adult		Child	Adult	
<b>Waste Solids</b>								
Mine Shaft	3.85	0.01	6	2	16	0.7	0.2	
Spoil Heap 1	3.18	0.04	16	6	13	0.6	0.1	
DF 1	0.68	0.17	16	6	2.8	0.1	<0.1	
DF 2	0.74	0.08	8	3	3.0	0.1	<0.1	
DF 3	0.37	0.08	4	1	1.5	<0.1	<0.1	
DF 4	0.28	0.11	4	2	1.1	<0.1	<0.1	
Adit 1	2.01	0.05	13	5	8.2	<0.1	<0.1	
Adit 2	1.80	–	–	–	7.3	–	–	
<b>Field Soils</b>								
0 m	1.69	0.22	51	19	6.9	<0.1	<0.1	
5 m	0.71	0.31	30	11	2.9	<0.1	<0.1	
10 m	0.91	0.20	35	13	3.7	<0.1	<0.1	
15 m	0.63	0.44	37	14	2.6	<0.1	<0.1	
20 m	0.94	0.23	29	11	3.8	<0.1	<0.1	
30 m	0.70	0.19	18	7	2.8	<0.1	<0.1	
50 m	1.22	0.17	28	10	4.9	<0.1	<0.1	

<sup>a</sup> Committed effective dose.

**Table 5**

Aqua regia extractable concentrations of Pb and measured activity concentrations of  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$ . Doses of Pb ( $\mu\text{g day}^{-1}$ ) and committed effective doses of  $^{214}\text{Pb}$  ( $\text{nSv day}^{-1}$ ) and  $^{210}\text{Pb}$  ( $\mu\text{Sv day}^{-1}$ ) were estimated using Eqs. (2) and (3), respectively. The ICRP dose coefficient for the ingestion of  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  on soil particles by children (1 year old) are  $1.0 \times 10^{-9}$  and  $3.6 \times 10^{-6} \text{ Sv Bq}^{-1}$ , respectively and by adults are  $1.4 \times 10^{-10}$  and  $6.9 \times 10^{-7} \text{ Sv Bq}^{-1}$ , respectively (ICRP, 2012).

Sample	Aqua Regia Extractable Pb				Activity $^{214}\text{Pb}$				Activity $^{210}\text{Pb}$			
	Conc., $\text{mg kg}^{-1}$	BAF	Dose, $\mu\text{g day}^{-1}$		Conc., $\text{Bq g}^{-1}$	BAF	$^a$ Dose, $\text{nSv day}^{-1}$		Conc., $\text{Bq g}^{-1}$	BAF	$^a$ Dose, $\mu\text{Sv day}^{-1}$	
			Child	Adult			Child	Adult			Child	Adult
<b>Waste Solids</b>												
Mine Shaft	4750	0.01	24	12	235	0.02	24	1.6	180	0.06	65	6.2
Spoil Heap 1	5000	0.04	18	8.8	55.3	0.06	5.5	0.4	32.2	0.03	12	1.1
DF 1	487	0.03	1.3	0.6	25.4	0.02	2.5	0.2	92.4	0.04	33	3.2
DF 2	675	0.04	2.4	1.2	50.7	0.03	5.1	0.4	50.2	0.04	18	1.7
DF 3	604	0.00	0.6	<0.1	120	0.05	12	0.8	114	0.03	41	3.9
DF 4	583	0.01	0.6	0.3	92.7	0.05	9.3	0.7	95.9	0.02	35	3.3
Adit 1	163	0.07	1.2	0.6	0.798	0.27	<0.1	<0.1	1.19	0.13	0.4	<0.1
Adit 2	144	–	–	–	0.890	–	<0.1	<0.1	0.673	–	0.2	<0.1
<b>Field Soils</b>												
0 m	1720	0.07	12	5.8	20.4	0.38	2.0	0.1	17.9	0.04	6.4	0.6
5 m	177	0.21	3.7	1.9	1.46	0.03	0.1	<0.1	1.73	0.05	0.6	0.1
10 m	82	0.23	1.9	0.9	0.916	0.16	<0.1	<0.1	0.878	0.08	0.3	<0.1
15 m	79	0.25	2.0	1.0	0.791	0.25	<0.1	<0.1	0.795	0.20	0.3	<0.1
20 m	76	0.21	2.0	0.8	0.510	0.11	<0.1	<0.1	0.726	0.11	0.3	<0.1
30 m	64	0.07	0.5	0.2	0.642	0.23	<0.1	<0.1	0.736	0.16	0.3	<0.1
50 m	69	0.15	1.0	0.5	1.13	0.18	0.1	<0.1	1.59	0.17	0.6	0.1

<sup>a</sup> Committed effective dose.

**Table 6**

Mean ( $\pm 1\sigma$ ) gastro-intestinal bioaccessibility factors (BAFs) for the waste solids (mine shaft, dressing floor and adit) and the field soils determined in this study.  $f_i$  is the fractional absorption of radionuclides from the gut to the body fluids (ICRP, 2012).

Element/ Isotope	Bioaccessibility factors		$f_i$
	Waste Solids	Field Soils	
$^{238}\text{U}$	$0.05 \pm 0.01$	$0.24 \pm 0.12$	0.02
$^{232}\text{Th}$	$0.08 \pm 0.05$	$0.26 \pm 0.09$	0.005
Pb	$0.03 \pm 0.03$	$0.17 \pm 0.07$	0.4
$^{210}\text{Pb}$	$0.07 \pm 0.09$	$0.19 \pm 0.11$	0.4
$^{214}\text{Pb}$	$0.05 \pm 0.04$	$0.11 \pm 0.06$	0.4

## 4.2. Chemical factors affecting the bioaccessibility of U, Th and Pb

Our mean results indicate variable fractions of the analytes are released by the STOM and STOM + INT solutions, such that U and Pb are preferentially released by the STOM solution, whereas solubilisation of Th occurs predominantly in the STOM + INT phase (Fig. 3). This behaviour is largely dependent on the chemistry of the lixiviants. In the carbonate-rich juices of the small intestine, at near neutral pH, U is readily solubilised in a polyatomic form, such as  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Read et al., 1991). However, speciation experiments have shown that even in the presence of strong carbonate-complexes the formation of a uranyl orthophosphate precipitate,  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}_{(s)}$ , is favoured, having a minimum solubility

about pH 6 (Sandino and Bruno, 1992). The influence of precipitate formation is evident when comparing the results of the UBM extraction of U from soils with other *in vitro* methods. For example, Jovanovic et al. (2012) extracted soils from Port Hope, Canada, using the PBET and found that U in the STOM + INT solution was greater (48.4%) than that in the STOM solution (20.8%). Höllriegel et al. (2010) extracted  $^{238}\text{U}$  from a U-containing therapeutic soil using the DIN 19738 and US Pharmacopoeia methods. In both studies the percentage of  $^{238}\text{U}$  extracted by the STOM + INT solution was greater than the STOM solution. Träber et al. (2014, 2015) also extracted U-containing soils using the DIN 19738 method, although the STOM values were not given. A common feature of these results, where the STOM extraction of U is lower than the STOM + INT, is that they were obtained using digests with relatively low concentrations of phosphate. In contrast, the UBM involves significant concentrations of  $\text{NaH}_2\text{PO}_4$  in the saliva ( $0.888\text{ g L}^{-1}$ ) and gastric ( $0.266\text{ g L}^{-1}$ ) solutions and  $\text{KH}_2\text{PO}_4$  ( $0.080\text{ g L}^{-1}$ ) is present in the duodenal solution. Thus, *in vitro* methods where phosphate concentrations are lower than the UBM may inhibit the precipitation of  $(\text{UO}_2)_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}_{(s)}$  following the increase in pH between the stomach and small intestine. Extractions of U from soils from Northern Ireland using the UBM (Barsby et al., 2012) showed the STOM + INT fraction of U persistently lower than the STOM, as we have shown for the sample analyses presented here.

Thorium has a tendency to hydrolyse such that in an acidic gastric solution the species  $\text{Th}(\text{OH})_2^{2+}$  is predominant and causes retention by the particulate phase, whereas in the small intestine it may form mixed hydroxy-carbonate complexes, such as the anionic species  $\text{Th}(\text{OH})_3(\text{CO}_3)^-$  (LaFlamme and Murray, 1987). Therefore, it is sensitive to increases in carbonate concentrations encountered in the small intestine causing mobilisation from particulate matter and increases in Th in the STOM + INT fraction.

Solubilisation of Pb in the STOM + INT phase is less than the STOM. The likelihood is that Pb undergoes a reduction in solubility between the stomach and the intestine due to the higher pH causing re-adsorption to the solid phase or, assuming phosphate is present, precipitation as  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$ . The results from UBM extractions of soils from various locations in the UK (Farmer et al., 2011; Barsby et al., 2012), Europe (Denys et al., 2012) and Australia (Juhász et al., 2011b) showed persistently lower values for the STOM + INT phase, in common with the results presented here.

#### 4.3. Bioaccessibility factors (BAFs)

The relatively low BAFs for U in the waste solids (Table 6) were in agreement with those for studies of U bioaccessibility in “healing earth” (Träber et al., 2014) using the DIN 19738 method. Similarly, the mean BAF for U obtained for UBM-extracted soils from Northern Ireland was 0.065 (Barsby et al., 2012). However, significantly higher BAFs were found for the elements and radionuclides in our field soils compared with the waste solids. Certain elements with a strong particle-binding capacity, such as U, Th and Pb may be “immobilised” in rocks but can be released during weathering, particularly if siderophore complexes are present in the soils. Desferrioxamine B is probably the most common siderophore in aerobic soils and laboratory experiments have shown its ability to enhance the mobility of strongly bound particle metals (Kraemer et al., 2015).

Our BAFs for stable Pb in the field soils (Table 6) are like those in Scottish soils,  $0.22 \pm 0.09$  (range 0.02–0.42) (Farmer et al., 2011), and in soils from Northern Ireland where the mean was 0.11, (Barsby et al., 2012). The stable forms  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  have originated over geological time from the radioactive decay of  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and  $^{235}\text{U}$ , respectively. Particles containing NORM contain transient decay products such as  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$ , which are

daughters of  $^{226}\text{Ra}$ . These decay products originate from gaseous  $^{222}\text{Rn}$  which is likely trapped, rather than adsorbed, in particle interstices. The migration of  $^{222}\text{Rn}$  produced on, or within, particles may be promoted by  $^{226}\text{Ra}$   $\alpha$ -recoil forces (Sasaki et al., 2004) and raises the question as to which sites  $^{214}\text{Pb}$ , and subsequently  $^{210}\text{Pb}$ , finally become attached, over time. They may remain internalised within the particle matrix which could aid their retention, or migration to surface sites may render them more labile. Thus, the sorption of transient Pb radio-isotopes contrasts with their stable counterparts, which, arguably, over millennia have become strongly adsorbed consequent on ageing. However, our data (Table 6) show that Pb isotopes have very similar bioaccessibilities but further experiments are required to confirm this result.

The epithelium is a barrier that facilitates the transfer of dietary nutrients, electrolytes and other substances from the gastro-intestinal tract into the blood. The ICRP term,  $f_1$ , is defined as the fraction of an ingested element absorbed directly into body fluids (ICRP, 2012). The  $f_1$  values are regarded as upper limits because radionuclides and/or elements are not always solubilised in a chemical form suitable for passage across the selective filter that is the epithelium. For the waste solids, the BAFs (Table 6) indicate only minor quantities of all the analytes are released into solution within the small intestine ( $<0.10$ ) and are available to pass across the epithelium. Coupling this with the relatively low values for  $f_1$ , especially for  $^{238}\text{U}$  and  $^{232}\text{Th}$ , suggests that the quantity of the radio- and stable isotopes, in South Terras mine waste, passing from the fluids of the small intestine into the blood is relatively low. On the other hand, the BAFs for the field soils are about a factor of five higher than those of the waste solids meaning similar intakes of contaminated soils would have higher concentrations in the small intestine. The  $f_1$  for the Pb isotopes are one to two orders of magnitude higher than those from  $^{238}\text{U}$  and  $^{232}\text{Th}$ , which suggests that particles from the field are potentially a source of stable Pb,  $^{214}\text{Pb}$  and  $^{210}\text{Pb}$  to the blood.

#### 4.4. Doses of heavy elements and radionuclides

##### 4.4.1. Doses of heavy elements

The health impact from the ingestion of NORM-contaminated particulate matter originates from the dual effects of the heavy element and the effects of radioactive decay (Kathren and Burklin, 2008). For U, the tolerable daily intake (TDI) is  $0.6\text{ }\mu\text{g kg body weight}^{-1}\text{ day}^{-1}$  (WHO, 2011). A 2-year old child is assumed to have a mean body weight of 13.6 kg, whereas the mean body weight of an adult is 68 kg (Juhász et al., 2011a). The product of the TDI and the body weights for children and adults gives U doses of  $8\text{ }\mu\text{g day}^{-1}$  and  $41\text{ }\mu\text{g day}^{-1}$ , respectively. For children, the ratio of the dose from the ingestion of South Terras particulate matter to the tolerable dose was 12:1 for solids from the mine shaft and 9:1 for spoil heap 1, whereas all other samples had ratios less than unity. The field soils had a ratio  $\ll 1$ , except for the sample close to spoil heap 2 where it was about 6:1. Thus, the doses to children, compared to adults, are most pronounced where the U concentrations are highest. Commenting on the TDI for Pb,  $3.5\text{ }\mu\text{g kg body weight}^{-1}\text{ day}^{-1}$ , is complicated due to the TDI having been withdrawn because a TDI may not be health protective (WHO, 2011). However, using the original ingestion rate gives a TDI for Pb in children and adults of  $47.6\text{ }\mu\text{g day}^{-1}$  and  $240\text{ }\mu\text{g day}^{-1}$ , respectively. Thus, at South Terras, despite the high aqua regia extractable Pb concentrations and low BAFs, the ratio of the measured Pb daily intake to the TDI for children and adults is  $< 1$  for all samples.

The heavy element doses of U and Pb from the ingestion of soils are relatively low largely because only ~3% of particulate Pb is available to the gastro-intestinal solution. Thus, the likely concentrations of Pb to be found in the bloodstream are small, given the

non-linear relationship between Pb ingested and Pb in blood. However, as a consequence of elevated concentrations, the doses of absorbable U from soils on the field and dressing floor are most pronounced for children. Whether there are any adverse health effects from doses of the magnitude found in this study is not known because, to our knowledge relationships predicting the blood U concentration from the amount of U ingested are not known.

#### 4.4.2. Committed effective dose of radionuclides

In addition to the heavy element dose ingested these particles also contain bioaccessible radionuclides. Assuming, to a first approximation, that the whole of the soluble fraction of radionuclides is absorbable in the bloodstream, for the waste solids the committed effective doses for  $^{238}\text{U}$  are in the  $\text{nSv day}^{-1}$  range. However, the committed effective doses are most evident for  $^{210}\text{Pb}$ , where the maximum value is  $65 \mu\text{Svday}^{-1}$  at the mine shaft. A 2-year old child ingesting  $100 \text{ mg day}^{-1}$  at this site would be taking in approximately 6.5% per day of the recommended annual dose limit for the general public, in addition to the dose from natural background ionizing radiation. The dressing floor soils had a maximum absorbable dose of  $^{210}\text{Pb}$  in a narrow range of 18–41  $\mu\text{Sv day}^{-1}$  (i.e. 1.8–4.1% of the annual dose), whereas the doses from adit solids and field soils were negligible. The estimated doses of the bio-accessible radionuclides should be regarded as upper limits because they are not all solubilised in a chemical form suitable for absorption in the epithelium. Thus, the potential daily absorption of radionuclides, based on assumed pica behaviour, is considered to be relatively small in the case of the South Terras mine. However, the possibility of long-term chronic effects on human beings from radionuclides, such as somatic or hereditary damage, cannot be entirely discounted.

## 5. Conclusions

The UBM technique, while not a precise chemical and physiological mimic of the human gastro-intestine tract, improves our general understanding of the likely human uptake of digestible particles contaminated with radionuclides and metals. Within the area of the abandoned South Terras uranium mine there is considerable contamination of land by NORM radionuclides, significant fractions of which are bioaccessible. Their ingestion may result in small quantities of uranium, and its decay products, being taken into the human cardio-vascular system, with consequent damage to sensitive cells. This study demonstrates that the estimation of dose, and hence risk, from ingestion of particulate matter at abandoned uranium mines would benefit from a quantitative measure of bioaccessible radionuclides as opposed to total elemental values alone. The impact of particulate matter from such mine sites on the genetic integrity of humans from the heavy elements themselves and their radioactive components when acting in combination needs further investigation. The South Terras abandoned uranium mine, where wastes have their own unique radiochemical characteristics, serves as an analogue for similar sites prevalent across Europe where workers, and the citizenry, may be exposed to NORM contamination. The results presented in this study suggest that consideration could be given to making such sites inaccessible to the general public and any plans for remediation or future development treated with caution.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvrad.2016.11.030>.

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