

The behaviour of technetium during microbial reduction in amended soils from Dounreay, UK

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Abstract

Radioactive technetium-99 forms during nuclear fission and has been found as a contaminant at sites where nuclear wastes have been processed or stored. Here we describe results from microcosm experiments containing soil samples representative of the UKAEA site at Dounreay to examine the effect of varying solution chemistry on the fate of technetium during microbial reduction. Analysis of a suite of stable element redox indicators demonstrated that microbial activity occurred in a range of microcosm experiments including unamended Dounreay sediments, carbonate buffered sediments, and microcosms amended with ethylenediaminetetraacetic acid (EDTA) a complexing ligand used in nuclear fuel cycle operations. During the development of anoxia mediated by indigenous microbial populations, TcO_4^- was removed from solution in experiments. In all cases, the removal of TcO_4^- from solution occurred during active microbial Fe(III)-reduction when Fe(II) was growing into the microcosms. Tc removal was most likely via reduction of TcO_4^- to poorly soluble Tc(IV) which is retained on the sediments. The potential stability of Tc associated with the soil to remobilisation via complexation with EDTA was examined as reduced Tc-labelled sediments were contacted with a de-oxygenated EDTA solution. No remobilisation of Tc(IV) in the presence of EDTA was observed.

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1. Introduction

Technetium-99 is a high yield product of nuclear fission and has been found as a contaminant in the vicinity of sites where nuclear wastes have been processed or stored (Morris et al., 2000; Standring et al., 2002; Lloyd and Renshaw, 2005). Additionally, the long half life of technetium (2.1×10^5 years) makes it one of the key radionuclides of interest when considering long-term disposal options for nuclear waste. As Tc is

present only at ultra-trace concentrations in the natural environment, environmental data for the radionuclide are relatively scarce. In the UK, studies on Tc behaviour have focused on marine and coastal environments impacted by the authorised discharges of effluent from the Sellafield reprocessing facility (Morris et al., 2000; Keith-Roach et al., 2003; Burke et al., 2005, 2006; McCubbin et al., 2006). In contrast, to our knowledge there are few site specific studies of radionuclide behaviour at UK nuclear sites even though Tc is a reported groundwater contaminant at the Sellafield facility (Nuclear Decommissioning Authority, 2006). This is in contrast to the increasing body of literature available for sites in the USA where Tc is considered a priority radionuclide (Fredrickson et al., 2004; Istok

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et al., 2004; Lloyd and Renshaw, 2005; McBeth et al., in press).

The redox chemistry of technetium is the major control on its environmental solubility. Under oxic conditions, technetium exists as the Tc(VII) pertechnetate ion, TcO_4^- , which is poorly sorbed by minerals in aerobic environments across a wide range of environmentally relevant pH values (Bondietti and Francis, 1979). By contrast, under reducing conditions pertechnetate is converted to lower valency species, of which Tc(IV) tends to predominate. Typically, the Tc(IV) oxidation state readily precipitates as an insoluble hydrous oxide ($\text{TcO}_2 \cdot x\text{H}_2\text{O}$ solubility at pH 7–9 is $10^{-9} \text{ mol l}^{-1}$; Meyer et al., 1991); or at lower concentrations is otherwise removed from solution by association with mineral surfaces.

During sediment burial, sediments are isolated from the atmosphere and bacteria have evolved to couple the oxidation of sediment organic matter to terminal electron acceptors other than oxygen. According to this classic model of sediment anoxia, the expected order of terminal electron accepting processes is oxic respiration followed by nitrate-, manganese(IV)-, iron(III)- and sulfate-reduction (Lovley, 1991). During anaerobic microbial metabolism, Tc(VII) is potentially affected by either direct, enzymatic reduction to form hydrous TcO_2 (Lloyd and Macaskie, 1997; Lloyd et al., 2000; De Luca et al., 2001); or under different conditions (see below) it may be indirectly reduced to Tc(IV) by abiotic transfer of electrons from reduced species such as Fe(II) (Lloyd et al., 2000). Direct enzymatic reduction of technetium is associated with hydrogenase enzymes, is thought to be adventitious (Lloyd and Macaskie, 1997; De Luca et al., 2001) and is only efficient at relatively high molar concentrations of Tc (Lloyd et al., 1999). In most contaminated environments, Tc is found at ultra-trace concentrations (2×10^{-8} – $2 \times 10^{-11} \text{ mol l}^{-1}$; Beasley et al., 1998; Morris et al., 2000) and at these concentrations, Tc(VII) reduction is most likely mediated via abiotic reaction with microbial reduction products such as Fe(II) (Lloyd et al., 2000; Fredrickson et al., 2004; Burke et al., 2005) although one study suggests that enzymatic reduction may be important under certain environmentally relevant conditions (Wildung et al., 2004). Clearly, at these ultra-trace concentrations Tc(IV) sorption processes are likely to dominate rather than discreet formation of hydrous TcO_2 .

The potential for indigenous bacteria to mediate reduction and immobilization of TcO_4^- has led to suggestions that “biostimulation” can be promoted thus encouraging in-situ microbial reduction at contaminated sites (Fredrickson et al., 2004; Istok et al., 2004; Lloyd and Renshaw, 2005). The presence of co-

contaminants such as carbonate and organic ligands such as ethylenediaminetetraacetic acid (EDTA) used in nuclear fuel cycle processing has the potential to significantly alter the behaviour of technetium in these environments. For example, Tc(IV) produced by dissimilatory metal reducing bacteria reportedly forms a soluble Tc(IV)-carbonate complex in the presence of high HCO_3^- (Wildung et al., 2000). Additionally, in the presence of diethylenetriaminepentaacetic acid (DTPA; a complexing ligand similar to EDTA), *Clostridium* sp. reduced Tc(VII) to Tc(IV) which then formed a soluble Tc(IV)-DTPA complex (Francis et al., 2002). Here, we describe soil microcosm experiments that examine the solubility of TcO_4^- in the context of development of reducing conditions in a saturated soil environment representative of the UKAEA nuclear site at Dounreay, UK to provide baseline information on the biotransformation behaviour of Tc within this environment. The microcosms were spiked with relatively low levels ($0.3 \mu\text{mol l}^{-1}$) of TcO_4^- . Additionally, Tc(VII) behaviour was observed as reducing conditions developed in the presence of: (i) an elevated bicarbonate concentration (10 mmol l^{-1}); and (ii) the chelating agent EDTA, at a concentration representative of environments where nuclear wastes are processed or stored (0.2 mmol l^{-1} ; Hansen et al., 2001) to assess the effect of different solution compositions on the mobility of Tc during the development of microbial anoxia.

2. Materials and methods

2.1. Sampling

Soil was collected from close to the UKAEA Dounreay site (LAT: $58^\circ 34' 40'' \text{ N}$, LONG: $3^\circ 44' 50'' \text{ W}$) in January 2005. The soil was sampled from a depth of ca 5 cm below the surface into sterile plastic buckets and stored at 4° C prior to use in soil microcosms.

2.2. Microcosm experiments

Microcosms containing 12 g Dounreay soil and 120 ml of an artificial ground water representative of groundwater found at the UKAEA site (Table 1; D. McAllister personal comm.) were made up in sterile glass serum bottles and sealed with butyl rubber stoppers and aluminium crimps. One triplicate set of soil microcosms contained unamended artificial groundwater (unamended), a second set were amended to a final concentration of $10 \text{ mmol l}^{-1} \text{ HCO}_3^-$ (carbonate amended), a final set were amended with sodium-EDTA to a final concentration of 0.2 mmol l^{-1} (EDTA

Table 1
Composition of artificial groundwater (pH 5.1)

Component	Concentration (mg l ⁻¹)	Concentration (mmol l ⁻¹)
Ca ²⁺	99	2.5
Mg ²⁺	24	1
K ⁺	5	0.13
Cl ⁻	227	6.4
SO ₄ ²⁻	40	0.42

Based upon composition of selected Dounreay groundwater samples (D. McAllister personal comm.).

amended). Sterile controls were prepared by autoclaving soil samples at 120 °C for 20 min, and all solutions were filter sterilised (<0.2 µm). Microcosms were spiked with a ⁹⁹Tc spike (as ammonium pertechnetate) to a final concentration of 3.2 × 10⁻⁷ mol l⁻¹ (20 Bq ml⁻¹) and were incubated at 21 °C in the dark. Microcosm bottles were then sampled periodically over a 67 day period. In a separate experiment to examine the potential for a chelating agent to remobilise reduced Tc, microcosms containing unamended artificial groundwater and soil were spiked with technetium to a concentration of 3.2 × 10⁻⁷ mol l⁻¹ and incubated for >90 days. After this time the concentration of Tc in solution in the pre-reduced bottles was determined. The bottles were then spiked under anaerobic conditions with a deoxygenated solution of Na-EDTA to a final concentration of 2 × 10⁻⁴ mmol l⁻¹ and sampled periodically over 15 days. Sampling was done in an anaerobic cabinet (Coy Laboratory Products Inc, MI) using aseptic technique. Microcosms were shaken and soil slurry samples were withdrawn. Samples were centrifuged (10 min, 16,000 g) and then analysed for a relevant range of redox indicators and Tc (see below).

2.3. Soil characterisation methods

The bulk mineral and chemical composition of the Dounreay soil was determined by X-ray diffraction on a Phillips PW1050 and X-ray fluorescence on a Thermo ARL 9400. Soil colour was described using the Munsell Soil Colour Chart System (Munsell Color Company, USA). Soil texture was described by following the procedures in a Soil Texturing Guide. Soil pH was determined using the method of Thomas (1996). Soil cation exchange capacity (CEC) was determined using the Na⁺ saturation method (Bunker et al., 2000).

2.4. Geochemical methods

Total Tc activity in pore waters was determined by liquid scintillation counting (LSC) typically by counting 1

ml of solution on a Packard Tri-Carb 2100TR (detection limit ca 0.4 Bq or <2% of the total spike added). In addition to total Tc analysis in solution, a speciation technique on liquid samples involving extraction of TcO₄⁻ into an organic phase consisting of tetraphenylarsoniumchloride (TPAC) in chloroform was performed at selected sample points (Tribalat and Beydon, 1953 cited in Wildung et al., 2000). The activity of TcO₄⁻ extracted into the organic phase was compared with total Tc activity in the aqueous solution assessed on a parallel sample to determine the amount of TcO₄⁻ in solution. Total Fe and Mn(II) in pore waters were determined by standard UV-vis spectroscopy methods on a Cecil CE 3021 (Goto et al., 1977; Viollier et al., 2000). Ingrowth of Fe(II) to sediments was determined by extraction in 0.5 N HCl for 60 min (Lovley and Phillips, 1986). This solid-phase chemical extraction has been shown to extract Fe(II) representative of microbially produced Fe(II) in sediments, although small amounts of mineral-derived Fe(II) may also be measured (Tuccillo et al., 1999). Sulfate, nitrate and chloride were determined by ion chromatography. Standards were used regularly to check the method quality and calibration, and normally produced *r*-squared values of >0.99. Eh and pH readings were taken using an Orion 420 A meter and calibrated electrodes.

2.5. Geochemical modelling

The technetium speciation in solution in all three systems (*unamended*, *carbonate amended* and *EDTA amended*) was modelled using the PHREEQE (version phrq96) equilibrium modelling software (U.S. Geological Survey) and the CHEMVAL (version 6) thermodynamic database using the solution compositions given in Table 1. Modelling was performed for each solution at 0, 32 (or in the case of *unamended* experiments 45) and 67 days and experimentally derived values for Eh, pH and total Fe_(aq) were used as model inputs as progressive anoxia developed (Table 2). Concentrations of EDTA and CO₃⁻ in relevant systems were set to values of 2 × 10⁻⁴ mol l⁻¹ and 0.01 mol l⁻¹ respectively, the concentrations at which carbonate and the EDTA salt were added to the simulated groundwater in the sealed microcosms.

3. Results and discussion

3.1. Soil characteristics

The main minerals in the soil as determined by X-ray diffraction were quartz, feldspars, chlorite and mica. Analysis by X-ray fluorescence indicated the Dounreay

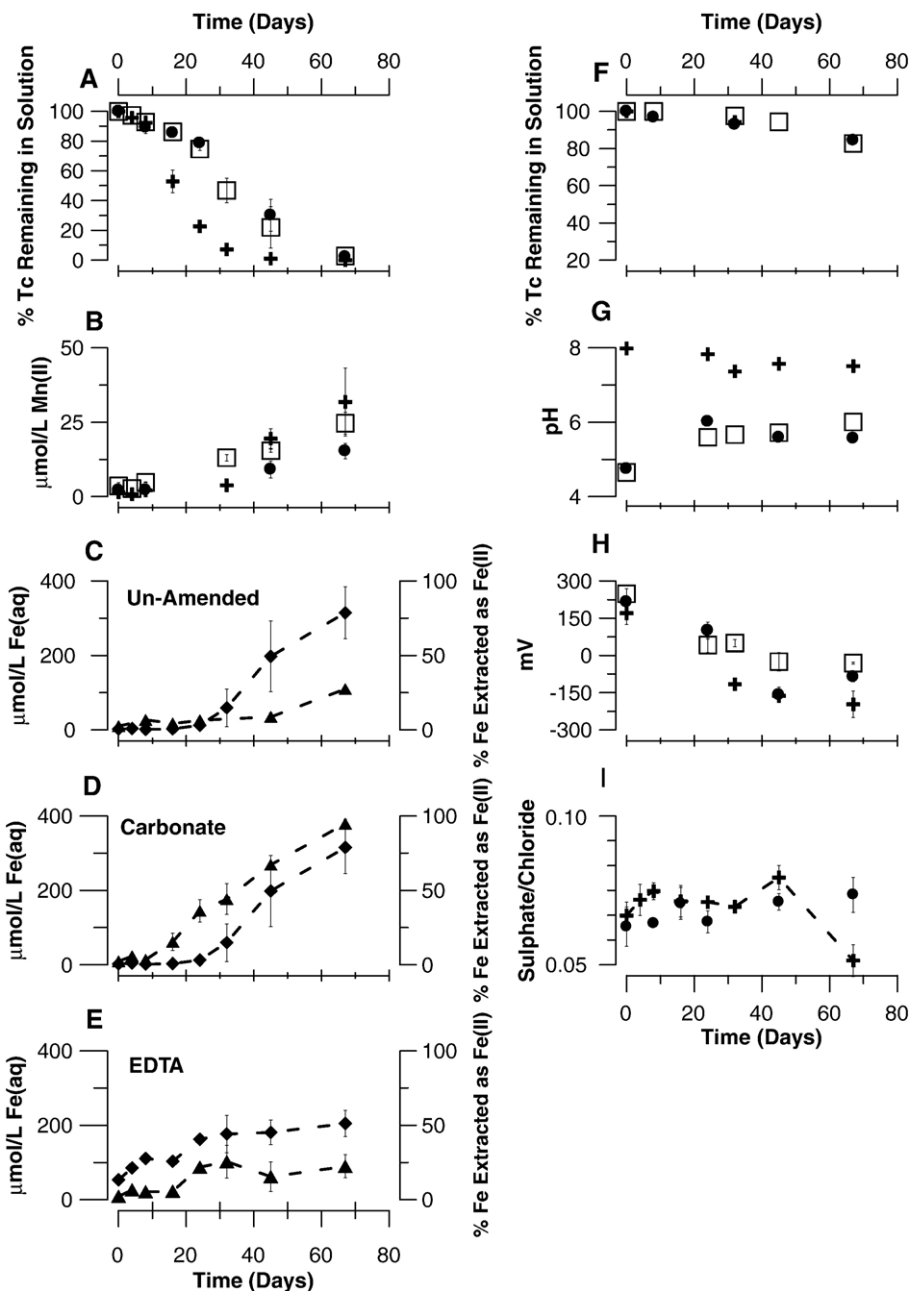


Fig. 1. Microcosm time-series data showing: (A) Tc removal from solution in microbially active unamended (●), carbonate amended (+) and EDTA amended (□) experiments; (B) changes in Mn(II) concentrations in microbially active unamended (●), carbonate amended (+) and EDTA amended (□) experiments; (C) changes in total dissolved Fe concentrations in solution (◆), and Fe(II) ingrowth to solid phases (▲) in microbially active unamended experiments; (D) changes in total Fe concentrations in solution (◆), and Fe(II) ingrowth to solid phases (▲) in microbially active carbonate amended experiments; (E) changes in total Fe concentrations in solution (◆), and Fe(II) ingrowth to solid phases (▲) in microbially active EDTA amended experiments; (F) Tc concentrations in solution in heat killed unamended (●), carbonate amended (+), and EDTA amended (□) experiments; (G) changes in microcosm pH in microbially active unamended (●), carbonate amended (+), and EDTA amended (□) experiments; (H) changes in Eh in microbially active unamended (●), carbonate amended (+), and EDTA amended (□) experiments; and (I) changes in $\text{SO}_4^{2-}/\text{Cl}^-$ ratio in microbially active unamended (●) and carbonate amended (+) experiments. Error bars are normally 1σ of triplicate results in carbonate and unamended incubations. Error bars in EDTA microcosms are the range of duplicate results.

soil was rich in Si (69%), consistent with sediments with high quartz content, and also contained Al (12%), K (4%), Fe (2.9%) Na (2.8%), Mg (0.9%) and Ca (0.2%). Air dried Dounreay soil was ascribed a notation of 10 YR 6/3 and was designated a pale brown colour. The soil was best described as a sandy loam with an approximate particle composition of 70% sand, 20% silt and 10% clay. Soil solution pH was 5.3 and cation exchange capacity was determined to be $1.06 \pm 0.07 \text{ mol}_c \text{ kg}^{-1}$.

3.2. Biogeochemical redox indicators

The results from the progressively anoxic soil microcosm experiments are shown in Fig. 1. In all microbially active amendments, the initially oxic microcosms developed anoxia via progression of the key terminal electron accepting processes as expected. In terms of redox indicators, there was no nitrate in the simulated groundwater and significant concentrations of Mn(II) in solution were not seen until 32 days (Fig. 1B). In solids, Fe(II) (the 0.5 N HCl extractable fraction) was present at measurable concentrations at day 0 in all systems (<2.5%), showed small but measurable ingrowth over the first few time points and significant ingrowth after 45 days in *unamended*-, 16 days in *carbonate amended*- and 24 days in *EDTA amended*-incubations (Fig. 1C, 1D, 1E). This suggested that Fe(III)-reduction was active throughout the incubation period in all experiments, and that the microbial population in the *carbonate amended* incubations was optimised for Fe(III)-reduction, presumably due to its circumneutral pH compared to the other experiments. Indeed, the final percentage of 0.5 N HCl extractable Fe(II) in solids was much greater in *carbonate amended* incubations (>94%) than in both *EDTA* and *unamended* systems (22% and 27% respectively) as expected from the higher microbial activity predicted in the carbonate system. In the *carbonate amended* incubations, measurable extractable Fe(II) ingrowth to solids preceded the appearance of aqueous Fe in pore waters by ca 16 days which is similar to the timing seen for soluble Fe(II) ingrowth by other workers for both aquifer (Islam et al., 2004) and estuarine sediments (Burke et al., 2005). In *EDTA amended* systems, relatively high levels of Fe in pore waters were seen from day 0, indicating that the EDTA had complexed and solubilised soil Fe(III). This is consistent with observations that at pH less than 6, fast and extensive formation of soluble Fe(III)-EDTA_(aq) occurs (Nowack and Sigg, 1997; Nowack et al., 2001). Parallel experiments with the *EDTA amended* system performed under oxic conditions, which measured both

total dissolved iron and Fe(II) in solution, confirmed that the increase in dissolved Fe in solution in the *EDTA amended* experiments under initial oxic conditions was attributable to Fe(III)-EDTA_(aq) complexation (Fig. 2).

In both *unamended* and *EDTA amended* incubations, the pH values rose over the duration of the experiment (Fig. 1G). This rise in pH is consistent with the production of OH⁻ and HCO₃⁻ during microbial respiration of Mn(IV) and Fe(III). This confirms that even under relatively acidic starting conditions (pH ~5–6) the indigenous microbial population can facilitate a range of terminal electron accepting processes leading to bioreduction. By contrast, in *carbonate amended* systems, pH values dropped over the duration of incubation. In all incubations Eh values fell over the course of the experiment from approximately +200 mV at day 0 to <-30 mV at day 67 (Fig. 1H).

3.3. Technetium removal from solution during progressive anoxia

In all microbially active systems, the original Tc(VII) spike was removed from pore waters to below the detection limit of the liquid scintillation counting technique (i.e. <98% of the original spike) during incubation with Dounreay soil over 67 days (Fig. 1A) presumably by reductive sorption to sediments as Tc(IV). In sterile controls from the *unamended* and *EDTA amended* incubations, >80% of the Tc remained in solution for the duration of the experiment indicating that the majority of TcO₄⁻ removal from porewaters was biologically mediated (Fig. 1F). Additionally, in *carbonate amended* sterile controls, sterility was maintained until 32 days when >94% of the Tc-spike was present in solution, again indicating that Tc removal in microbially active *carbonate amended* systems was biologically mediated (Fig. 1F).

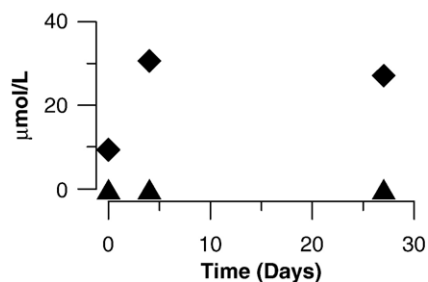


Fig. 2. Dissolved iron speciation in oxic sediment incubations amended with 0.02 mM EDTA. Total dissolved Fe (◆) and Fe(II)_(aq) (▲). Error bars are 1σ of triplicate results and are within range of the symbols used.

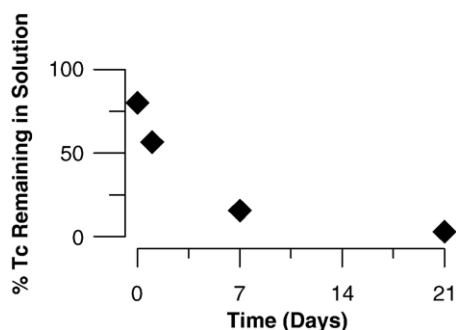


Fig. 3. Abiotic removal of Tc from solution in sterile, pre-reduced Fe(III)-reducing (ca 50% Fe(II) in solids) microcosms which were heat killed prior to spiking with TcO_4^- . Error bars are 1σ of triplicate results and are within range of the symbols used.

In the microbially active systems, Tc removal was broadly concurrent with ingrowth of 0.5 N HCl extractable Fe(II) in solids and Tc removal from solution was complete (>98%) before the onset of sulfate reduction, which occurred only in the *carbonate amended* incubations at the final time point at 67 days (Fig. 11). In *carbonate amended* incubations, measurable Tc was removed from porewaters prior to the accumulation of significant concentrations of either aqueous Fe(II) or Mn(II) in porewaters in agreement with the fact that these species are reportedly ineffectual as TcO_4^- reductants at circumneutral pH (Cui and Eriksen, 1996; Fredrickson et al., 2004; Burke et al., 2005). The concentration of 0.5 N HCl extractable, sediment associated Fe(II) in the microcosms at the final time point was ca $0.1\text{--}0.5 \times 10^{-3}$ moles which corresponds to three to four orders of magnitude molar excess of solid phase Fe(II) in the microcosms compared to the starting TcO_4^- concentration in the experiments (ca 4×10^{-8} moles). Indeed, stoichiometrically even a small percentage ingrowth of microbially produced, reactive solid Fe(II) in Dounreay soils (as observed during the early phases of the experiments) would be sufficient to reduce all of the TcO_4^- present in solution in these experiments. Overall, this evidence suggests that the Tc-removal seen throughout the experiments is associated with Fe(III)-reduction consistent with observations in other sediment-based microcosm experiments (Lloyd et al., 2000; Fredrickson et al., 2004; Wildung et al., 2004; Abdelouas et al., 2005; Burke et al., 2005).

Finally, to provide insight into the dominant mechanism of reduction in the microcosms, TcO_4^- was added to *unamended* microcosms which had been pre-reduced to the point that Fe(III)-reduction dominated (0.5 N HCl extractable Fe(II) ca 50%), and then sterilized by autoclaving. Preliminary experiments con-

firmed that autoclaving pre-reduced sediments did not significantly alter their 0.5 N HCl extractable Fe(II) concentrations. In these sterile Fe(III)-reducing sediments, the Tc-spike was removed from solution to below the liquid scintillation counting detection limit (>98%) over 21 days (Fig. 3). This confirmed that removal was possible by abiotic transfer of electrons from ingrown, reduced species such as Fe(II). This relatively slow removal rate in abiotic systems in combination with the gradual Tc removal observed in the microbially active incubations suggests that the dominant removal mechanism for Tc in these systems is most likely mediated by abiotic reduction with microbially produced Fe(II) and that this reaction is kinetically hindered in these sediments.

Interestingly, the *EDTA amended* experiments showed broadly similar trends to the *unamended*- and *carbonate-amended* systems with Tc-removal occurring as anoxia developed over the approximately two month incubation period. This suggested that EDTA complexation of reduced Tc(IV) was not solubilising the radionuclide under the experimental conditions. Indeed, parallel soil incubations in the presence of 100 fold elevated concentrations of EDTA (0.02 mol l^{-1} ; data not shown) showed similar ($28 \pm 2\%$) removal of Tc from solution after 30 days compared with the 0.2 m mol l^{-1} system. This confirmed that even in the presence of very high molar excess concentrations of EDTA, Tc removal from solution occurred as anoxia developed. Furthermore, when de-oxygenated EDTA (0.2 mmol l^{-1}) was added to

Table 2
Predicted speciation of technetium in soil incubations at selected time points

Day	Species	% of original Tc	pH	Eh (V)	$\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ Saturation Index
<i>Unamended</i>					
0	TcO_4^-	55.3	4.75	0.20	0.95
	$\text{TcO}(\text{OH})_2$	44.4			
45	$\text{TcO}(\text{OH})_2$	99.9	5.59	-0.16	1.3
67	$\text{TcO}(\text{OH})_2$	99.9	5.57	-0.08	1.3
<i>Carbonate amended</i>					
0	TcO_4^-	100	7.98	0.16	-9.4
32	$\text{TcO}(\text{OH})_2$	100	7.37	-0.11	1.3
67	$\text{TcO}(\text{OH})_2$	100	7.51	-0.19	1.3
<i>EDTA amended</i>					
0	TcOOHEDTA^{3-}	99.9	4.65	0.24	-3.3
32	TcOOHEDTA^{3-}	99.9	5.67	0.05	-2.3
67	TcOOHEDTA^{3-}	99.9	6.01	-0.03	-2.0

Species concentrations are shown as the percentage of original Tc spike. For all time points, the experimentally derived pH and Eh values used in modelling are also given.

pre-reduced Fe(III)-reducing, Tc-labelled sediments there was no remobilization of Tc after 15 days incubation again suggesting Tc(IV)-EDTA complexation did not lead to solubilisation of the radionuclide.

3.4. Geochemical modelling results

Thermodynamic modelling of the *unamended* experiments suggested that at the start of the experiment (pH 4.8, Eh +200 mV), both TcO_4^- and $\text{TcO}(\text{OH})_2$ were predicted to be present in solution and hydrous TcO_2 was just under saturated (Table 2). By contrast, speciation extractions with TPAC showed that Tc was present as TcO_4^- at the start of the experiment. By day 45, geochemical modelling suggested that reduced Tc (IV) would be the dominant aqueous species and that hydrous TcO_2 was over saturated whilst experimentally at this time point 30% of Tc remained in solution and the TPAC extraction technique indicated it was present as TcO_4^- . Thus, for the *unamended* system, the geochemical modelling at best reflected general trends in the experiments rather than a detailed biogeochemical progression with time. For the *carbonate amended* experiments, geochemical modelling was more successful with the speciation calculations predicting progression from soluble TcO_4^- at the start of the experiment to oversaturated with respect to TcO_2 by day 67 as the Eh dropped. Nonetheless, at day 32, experimentally 10% of the total Tc spike was present in solution largely as TcO_4^- , whilst modelling suggested that all Tc would be reduced to hydrous TcO_2 by this time point (Table 2).

In the *EDTA amended* system modelling suggested that a soluble Tc(IV)-EDTA complex (TcOOHEDTA^{3-}) dominated the system throughout. This anionic Tc(IV)-EDTA complex is predicted from past work (Russell et al., 1980) and would be predicted to have little interaction with negatively charged soil surfaces (Maset et al., 2006). However, the experimentally observed Tc behaviour in the *EDTA amended* system was similar to both the *unamended* and *carbonate amended* experiments, particularly with respect to the removal of Tc as anoxia developed. Overall, this suggested that, contrary to geochemical modelling predictions, in our experimental systems the predicted anionic Tc-EDTA complex does not seem to be the dominating control on Tc behaviour. Indeed, TPAC extractions on experimental solutions indicated that in the *EDTA amended* system, Tc was present as 100% TcO_4^- at $t=0$ and that the remaining soluble Tc at days 32 and 67 was dominated (>90%) by TcO_4^- . Overall, the thermodynamic modelling suggested that in the *unamended* and *carbonate amended* systems the development of anoxia would

result in oversaturation of $\text{TcO}(\text{OH})_2$. This was in broad agreement with the experimental results, but did not reflect the rates of removal observed in experiments suggesting a kinetic dependence for the Tc(VII)→Tc(IV) reduction reaction. In the *EDTA amended* system, modelling predicted the dominance of anionic Tc(IV)-EDTA complexes throughout the experiments which we predict would have poor interaction with negatively charged sediment surfaces. In contrast, experimental results in *EDTA amended* microcosms showed strong similarity in Tc removal behaviour with *unamended* and *carbonate amended* systems. This suggests that, contrary to thermodynamic modelling predictions, anionic Tc(IV)-EDTA complexes do not have a significant impact on Tc-solubility as bioreduction develops in these complex sediment microcosms. Indeed, workers have recently reported similar observations to ours on Tc behaviour in EDTA amended soil microcosms (Maset et al., 2006).

4. Conclusions

Here we show that soil microcosms representative of the UKAEA Dounreay site are capable of removing TcO_4^- from solution during the development of microbially-mediated anoxia and under a range of different solution chemistries. Immobilization of Tc was observed in the presence of three different initial solution compositions: *unamended*; *carbonate amended*; and *EDTA amended* microcosms. Pure culture experiments have suggested that in the presence of either a complexing agent (DTPA) or elevated carbonate concentrations, microbial reduction of Tc(VII) may result in the formation of a soluble Tc(IV) species (Wildung et al., 2000; Francis et al., 2002). The present work, suggests that at contaminated environment relevant concentrations of a complexing agent (EDTA) or with elevated carbonate concentrations (10 mmol l^{-1}), microbially mediated reduction in these soils reductively removes Tc (VII) from solution, presumably to form poorly soluble Tc(IV). Attempts to remobilise the sediment associated Tc with de-oxygenated EDTA were unsuccessful indicating that, contrary to modelling predictions in environmental settings, reduced Tc associated with sediments will be recalcitrant to remobilization if contacted with groundwaters containing EDTA, a common co-contaminant at nuclear facilities.

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