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Technetium Retention and Remobilization Potential after Prolonged Reaction in Fe(III)- and Sulfate-Reducing Model Aquifer Systems

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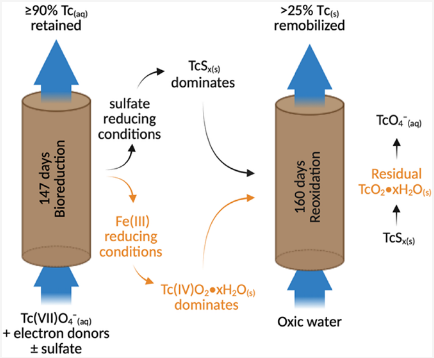
ABSTRACT: ^{99}Tc is a long-lived radioactive fission product whose subsurface mobility is governed by redox conditions. Under oxic conditions, soluble Tc(VII)O_4^- is mobile, whereas under reducing conditions, poorly soluble Tc(IV) phases limit transport. Microcosm studies have frequently reported TcO_2-like solids and, less consistently, Tc(IV)-sulfides. The stability of Tc(IV)-sulfides under environmentally relevant conditions remains unclear. Here, we used flowing sediment columns representative of the Sellafield subsurface to examine Tc speciation and stability over ∼1 year. Under reducing conditions, >90% of added TcO_4^- (400 μg) was retained under both Fe(III)- and sulfate-reducing conditions. X-ray absorption spectroscopy showed TcO_2-like phases dominated in Fe(III)-reducing columns, while Tc(IV)-sulfides dominated after sustained sulfate reduction. Sequential extractions indicated that Tc in sulfidic sediments was more recalcitrant (≤23% released by weak acids) than in Fe(III)-reducing systems (∼60% released). With oxic groundwater pumping, effluent Tc sourced from the sediments rose rapidly. Over 160 days, the sulfidic columns remobilized ∼25% of their Tc inventory compared to ∼50% in Fe(III)-reducing columns. The Tc(IV)-sulfides also gradually oxidized to form TcO_2 phases. While Tc(IV)-sulfides may enhance Tc retention under reducing conditions, TcO_2 phases more likely govern ^{99}Tc mobility during long-term redox cycling. Our findings provide new constraints for modeling Tc fate at contaminated sites and in radioactive waste disposal.



KEYWORDS: *technetium-99, redox cycling, sulfate-reduction, flowing column experiments, X-ray absorption spectroscopy, contaminated aquifers*

1. INTRODUCTION

Technetium-99 (^{99}Tc) is a β-emitting, high-yield radioactive fission product present in radioactive wastes, and an extant subsurface contaminant at several globally significant nuclear licensed sites (e.g., Sellafield, UK, and Hanford, USA).[1,2] Due to its long half-life (2.14 × 10^5 years), high mobility, and radiotoxicity, understanding the factors that could limit Tc transport in the geosphere is critical.[3−5] The oxidation state and coordination environment of ^{99}Tc are key controls on its environmental mobility. Under oxidizing conditions, the highly soluble [Tc(VII)O_4^-] oxyanion dominates speciation, and sorbs poorly onto geomedia.[6,7] Under reducing conditions, poorly soluble Tc(IV) phases form.[8] Tc(VII) can be reduced via multiple pathways in the environment. Although enzymatic reduction is possible,[9−12] in the geosphere, Tc(VII) reduction is most likely governed by reactions with the byproducts of microbial metabolism (principally Fe(II) and sulfide phases).[13−17] Tc(IV)$_{(s)}$ products, such as TcO_2 octahedra, octahedral chains, or discrete hydrous TcO_2-phases, which sorb to mineral surfaces, are commonly reported in Fe(III)-reducing systems.[15,18−22] The long-term stability of these Tc(IV)-phases is uncertain: if redox conditions become oxic through, for example, lack of electron donor supply and/or oxic groundwater intrusion, Tc(IV)-phases may undergo oxidative remobilization. Typically, reoxidation of Tc(IV)- and Fe(II)-containing microcosm systems shows significant (>50%) Tc(VII)$_{(aq)}$ production and remobilization.[18−20,23−25] Studies with pure mineral phases have also reported incorporation of Tc(IV) into the lattice of neo-forming Fe(II)-bearing minerals, such as magnetite and green rust.[26−31] Although incorporation has been suggested to better protect Tc(IV) from oxidative remobilization via "armoring" in model systems,[25,28,30,32] longer-term studies in complex dynamic systems (e.g., aquifer materials with groundwater flow), completed at more environmentally representative Tc concentrations, are needed to bridge between laboratory- and field-scale conditions.

In addition to TcO_2-like phases, early studies of Tc environmental chemistry also highlighted that sulfide would

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reduce $Tc(VII)_{(aq)}$ to $Tc(IV)_{(s)}$, with Tc(IV) likely incorporating into sulfide-bearing minerals.[33−35] Further, when Tc was added to mackinawite (FeS), four Tc(IV)-sulfide species were documented: (i) TcS_2-like species, (ii) Tc_2S_7-like species, (iii) TcS_x-like species, and (iv) Tc(IV)-FeS coprecipitates.[36−40] Tc(IV)-sulfides have also been reported in more complex environmental systems, but here, observations have been inconsistent. For example, in selected microcosm studies where sulfate-reducing conditions developed, only TcO_2-like phases were reported[22,24,41−44] and Tc(IV) sulfides were suggested to have low environmental relevance.[45,46] By contrast, in other pure culture, sediment, and contaminated site studies, mixed TcO_2 and Tc(IV)-sulfide phases have been observed or inferred.[33,36,47−51] Interestingly, in systems where Tc(IV)-sulfides have been directly observed, specific conditions (e.g., a low solid-phase Fe/S ratio, high concentrations of HS^- and FeS) seem to encourage their formation.[51,52] Further, Tc(IV)-sulfide formation seems prevalent in systems that have not undergone prior extended periods of Fe(III)-reduction.[53]

Interestingly, Tc(IV)-sulfides may offer increased resistance toward Tc oxidative remobilization. In previous studies, the oxidation of Tc(IV)-sulfides seems to proceed via a phase transition to TcO_2-like phases, often with limited $Tc(VII)_{(aq)}$ generation, and possible Tc(IV) incorporation into the lattice of neo-forming goethite.[36,38,43,49,54] As such, formation of Tc-sulfides may offer an extra buffer to Tc(IV) oxidative remobilization, further limiting ^{99}Tc migration through the subsurface.[51,53] Overall, Tc(IV)-sulfide formation and stability are observed across a range of microcosm systems, but the balance between TcO_2 and Tc(IV)-sulfide formation pathways requires further study in more environmentally representative systems.

Accordingly, the aim of this submission was to investigate the end-point stability of reduced Tc(IV) phases formed under well-defined Fe(III)- or sulfate-reducing conditions, using more environmentally relevant column systems representative of the Tc-contaminated aquifer underlying the UK Sellafield nuclear site (flowing systems; site-representative sediments with an indigenous microbial community; longer time scales; fluctuating redox conditions; and lower $^{99}Tc_{(aq)}$ concentrations). XAS and sequential extractions identified the reduced Tc phases that were formed after bioreduction, and following reoxidation. Overall, we show that Tc(IV)-sulfides have enhanced stability if reducing conditions are maintained, but that TcO_2 phases will likely be more important during longer-term reoxidation regardless of Tc(IV)-sulfide formation.

2. MATERIALS AND METHODS

2.1. Sediment and Synthetic Groundwater. Sediment was collected from a well-characterized site next to the Calder River, Cumbria, UK (Lat. 54°26′30 N, Long 03°28′09 W). Material from the site is representative of the UK Sellafield nuclear licensed site subsurface, and has been used for past studies.[23,44,55−58] Large stones were handpicked from the sediment upon collection, and the remaining material was stored in sterile HDPE bags at 10 °C in the dark until use.[57] Synthetic groundwater representative of the Sellafield site (autoclaved, pH set to 7) was used in experiments (see Supporting Information (SI) Section S1 for further details).[23] All chemicals used were of analytical grade. Sediment characteristics, including mineralogy and elemental composition are summarized in SI Section S2. The sediment contains 6.5 wt % Fe of which ∼10% is present as bioavailable Fe(III).

2.2. Column Design and Experimental Systems. A sediment column system with flowing groundwater, as developed by Ho et al.,[57] was used to explore ^{99}Tc behavior under conditions more representative of the subsurface. A schematic of the column setup is provided in SI Section S3 (SI Figure S1). Briefly, a 10 cm polypropylene column with 1 cm internal diameter was packed tightly with sediment (∼8 g) and terminated on each end with glass wool and quartz sand. After assembly, groundwater was pumped through the columns at a rate of 0.5 ± 0.1 mL/h using a peristaltic pump. The flow rate is representative of the Sellafield subsurface[1] and has been used in past Sellafield studies.[55,57] Effluent was periodically sampled under anoxic conditions from the top of the columns by attaching a syringe to a 3-way valve (SI Figure S1).

^{99}Tc was added to synthetic groundwater as $Tc(VII)O_4^{-}{}_{(aq)}$ at a concentration of 2.2 μM (140 Bq/mL). Three synthetic groundwater compositions were used in the study (SI Table S1). An “oxic system” was established to examine ^{99}Tc behavior under oxic groundwater conditions, and here, an air bubbler was used to maintain dissolved-O_2 in the influent. Two separate bioreducing groundwater treatments were used to examine long-term Tc behavior under sustained Fe(III)- or sulfate-reducing conditions i.e., systems where the dominant microbially mediated terminal electron accepting process was either Fe(III) or SO_4^{2-} reduction for a prolonged period (>1 month). To achieve sustained microbially mediated Fe(III)-reduction, the influent groundwater was amended with 2 mM acetate and 2 mM lactate, while sulfate was omitted.[57] This is called the “electron-donor−amended” system. To examine the impact of sustained sulfate-reduction on Tc behavior, 0.4 mM sulfate was added to the influent groundwater alongside 2 mM acetate and 2 mM lactate.[57] This is called the “electron-donor + sulfate−amended” system. The bioreducing experiment groundwaters were thoroughly sparged with Ar before use and pumped from a capped bottle with Ar in the headspace. Groundwaters were replaced every 7−14 days. O_2 ingress into the groundwater may have occurred. All the column systems ran under constant flowing conditions for 147 days, in the dark, at 21 ± 2 °C.

Additionally, parallel Tc-doped electron-donor−amended, and electron-donor + sulfate−amended columns, were run in tandem for 147 days. These parallel columns were then used in reoxidation experiments where, at the end of bioreduction, the influent groundwater was changed to oxic groundwater with no added Tc, sulfate, or electron donor amendments. An air bubbler was used to maintain O_2 in the influent groundwaters, which were pumped at the same flow rate (0.5 ± 0.1 mL/h) for 160 days.

2.3. Sampling, Column Sacrifice, and Geochemical Characterization. The electron-donor and electron-donor + sulfate−amended systems were run in triplicate, and one column was set up as an oxic control system. Effluent samples were collected at regular intervals under flowing Ar; all subsequent sample manipulations were made under O_2-free conditions. The samples were centrifuged (1.4×10^4 g, 10 min) to separate solids and solution. Thereafter, solution pH and Eh were measured using calibrated electrodes (Mettler-Toledo InLab Micro sensors for pH and redox, respectively). NO_2^- and total Fe were measured spectrophotometrically (NO_2^- λ = 536.5 nm, ε = 0.027; Fe λ = 562 nm, ε = 0.003).[59,60] NO_3^-, SO_4^{2-}, and Br^- (inert tracer) were measured by ion chromatography (Dionex ICS 6000). Mn was measured by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7800) from acidified (0.5% HNO_3) samples. ^{99}Tc in the supernatant was also measured using liquid scintillation counting (LSC) with a PerkinElmer Tri-Carb 2910TR and Optiphase HiSafe-3 liquid scintillation cocktail.

At experiment end points (147 days of bioreduction, 160 days of reoxidation), columns were transferred into an Ar-filled glovebag for sacrificial sampling. The columns were then sliced along their length and sectioned at 0.5 cm intervals. Sectioned samples were stored in sealed Eppendorf tubes under an Ar atmosphere at −80 °C prior to solid-phase analysis, which included X-ray absorption spectroscopy (XAS) measurements and 16S rRNA gene sequencing. Additionally, ∼0.1 g of select sectioned sediment samples were also sequentially digested in increasing concentrations of HCl (0.001, 0.01, 0.1, 1, 2, 3, 4, and 6 M) to explore variations in sediment-associated ^{99}Tc retention within the column.[23,30] Sediment samples were digested for 30 min in 10 mL of acid, which had been Ar sparged before use. This was then centrifuged (1.4×10^4 g, 10 min) and the supernatant was decanted prior to ^{99}Tc analysis. The next, higher concentration of acid was then added, and the process was repeated. After the 30 min 6 M HCl digestion, there were additional 24-h and 4-day 6 M HCl digestions. Finally, a 4 h boiling aqua regia digest targeted any residual ^{99}Tc.

2.4. X-ray Absorption Spectroscopy (XAS). ^{99}Tc speciation and local coordination were investigated using X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) analysis. ^{99}Tc K-edge XAS data were collected at the INE-Beamline at the KIT Light Source,[61,62] Germany, in fluorescence mode, at 298 K, with two Vortex SDD detectors (ME4 and 60EX, Hitachi) and an inline Mo foil. Data were also collected at beamline B18 at Diamond Light Source, UK, from the ^{99}Tc K-edge in fluorescence mode, at 77 K, with a 36-element Ge detector and an in-line Mo foil. Background subtraction, normalization of data, and linear combination fitting (LCF) of XANES between Tc standards (Tc(VII) as TcO_4^-, from,[63] and Tc(IV) as TcO_2 and/or TcS_x, both from[51]) were completed in Athena.[64] EXAFS spectra were fitted shell by shell in Artemis,[64] informed by the relevant literature. Here, F-testing was applied to determine the statistical viability of additional backscattering shells.[65] The fitting procedure was constrained to fixed values for the passive electron reduction factor (S_0^2) and Debye−Waller factor (σ^2) to determine trends in Tc coordination number (CN).[23]

2.5. DNA Extraction and Microbial Community Characterization. Changes in the microbial community structure during experiments were examined with DNA extracted from select sediment samples taken from each system. 16S rRNA genes from the extant microbial communities were amplified and sequenced. Further details on the methodology are provided in SI Section S4.

3. RESULTS AND DISCUSSION

3.1. Bioreducing Experiments. *3.1.1. Column Effluent Geochemistry and Microbial Ecology.* Three different ^{99}Tc-(VII)-labeled groundwater systems: (i) oxic, (ii) electron-donor−amended, and (iii) electron-donor + sulfate−amended, were pumped through sediment columns for 147 days. The effluent pH from all the column systems varied between pH 7−9.5 throughout the experiments (SI Figure S3). This was likely due to bicarbonate alkalinity in the influent groundwaters (SI Table S1) and/or alkalinity generation in the microbially active sediment columns, which is consistent with past work.[56,57] In the oxic system, the effluent Eh (SI Figure S4) ranged between +30 and −30 mV and trended downward over time. NO_3^- was added to the oxic influent at a concentration of 300 μM (SI Table S1) but was not detected in the effluent (SI Figure S5). Transient NO_2^- was present in the oxic effluent at elevated concentrations during day 1 of the experiment (SI Figure S6), indicating NO_3^- reduction was active. After day 1, NO_2^- concentrations remained at the limit of detection suggesting full denitrification was occurring. The sediment contains limited amounts of indigenous C_{org} which may support such metabolic reactions. Effluent Mn (SI Figure S7) and Fe (SI Figure S8) were generally present at low levels (<1.3 μM), confirming that the oxic control maintained aerobic/denitrifying conditions and did not support significant metal reduction, which is similar to past oxic column treatments with these materials.[56,57] However, occasional spikes in effluent Fe (SI Figure S8) were noted and may indicate isolated periods of limited Fe(III) reduction.

^{99}Tc (VII) was added to the oxic influent at 2.2 μM and was typically present in the effluent at 100 ± 10% of the influent concentration (Figure 1) throughout the experiment, confirming that ^{99}Tc did not react significantly with the sediment under the oxic/denitrifying conditions (SI Table S2). This is consistent with thermodynamic data and past observed ^{99}Tc behavior under oxic and denitrifying conditions, where Tc(VII) dominates and shows limited sorption at circum-neutral pH.[4,5,44,44,55,66,67] Tc(VII) is also expected to be an inefficient terminal electron acceptor at low concentrations and is not used as a terminal electron acceptor by denitrifying bacteria.[44,68]

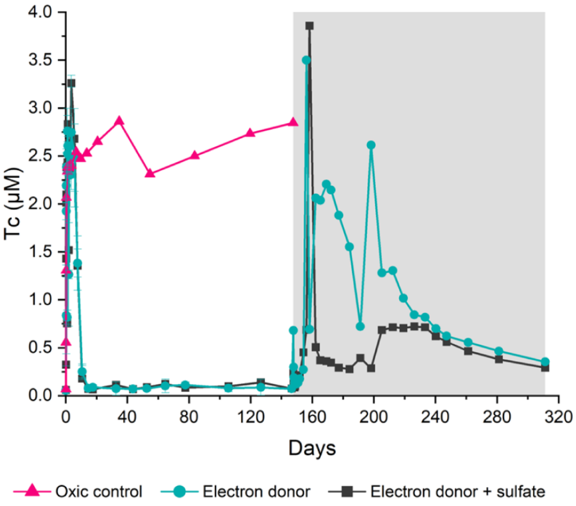

Figure 1. ^{99}Tc concentrations in column effluents during 147 days of bioreduction (unshaded) and then, during 160 days of oxidation (shaded): oxic system with no added electron donor (pink triangles), electron-donor−amended system (green circles), and electron-donor + sulfate−amended system (black squares). Error bars for the electron-donor−amended, and electron-donor + sulfate−amended systems are 1-σ from triplicate column experiments. When error bars cannot be seen, they are within the symbol size. The oxic system and reoxidized systems were single columns and do not include error bars.

To study the behavior of ^{99}Tc under well-defined bioreducing conditions, acetate (2 mM) and lactate (2 mM) were continually supplied to the electron-donor−amended and

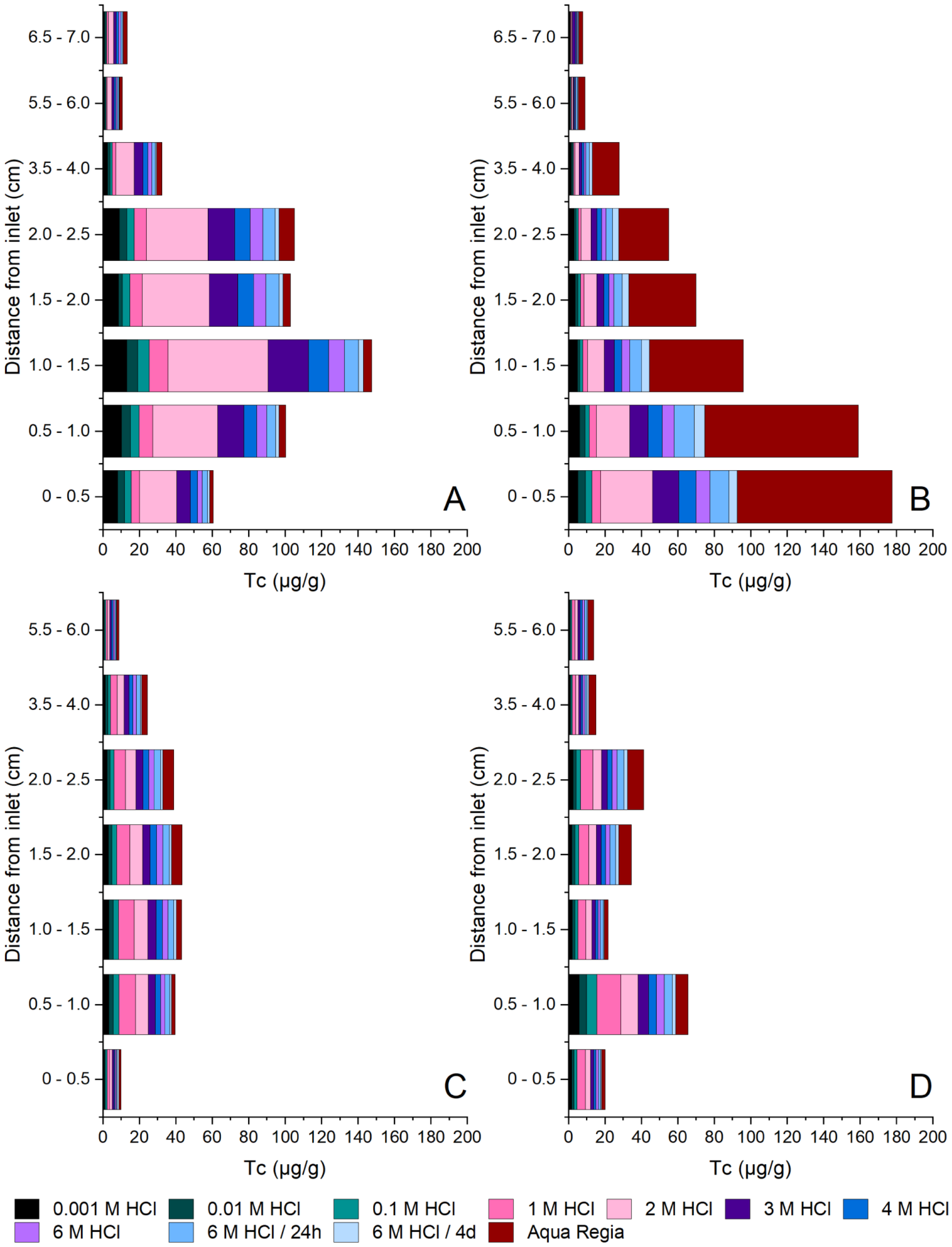

Figure 2. Total ^{99}Tc extracted from select sediment samples (0.5 cm depth increments) for: (A) electron-donor−amended system, (B) electron-donor + sulfate−amended system, (C) electron-donor−amended system after oxidation, and (D) the electron-donor + sulfate−amended system after oxidation. Sediment samples were sequentially digested in increasing HCl concentrations (0.001, 0.01, 0.1, 1, 2, 3, 4, and 6 M for 30 min), followed by extractions in 6 M HCl for 24 h, 6 M HCl for 4 days, and finally, boiling aqua regia for 4 h (see key).

electron-donor + sulfate−amended column systems. Past work with this sediment has demonstrated that it contains bioavailable Fe(III) but does not contain significant sulfate.[56,57] However, it does contain an indigenous microbial community capable of maintaining Fe(III)- and sulfate-reducing conditions (SI Section S4).[58] As such, the exclusion of sulfate from the column influent was targeted at creating an experiment that progressed to, and then sustained, microbially mediated Fe(III)-reduction for a period >1 month. In contrast, addition of sulfate to the groundwater in the electron-donor + sulfate−amended column systems targeted an experiment that transitioned from Fe(III)-reduction to then facilitate sustained (>1 month) sulfate-reduction. Trends in effluent groundwater chemistry (SI Section S5) indicated that a cascade of microbially mediated terminal electron accepting processes occurred in both bioreducing systems as expected, and these were consistent with past column work under similar scenarios.[57] Briefly, the Eh (SI Figure S4) of both bioreducing systems decreased from ∼0 mV to −10 mV at the start of experiments, to −50 to −80 mV at experiment end points. Both systems consumed influent NO_3^- (SI Figure S5; added at 300 μM) and produced NO_2^- (SI Figure S6) from the start of the experiments, suggesting that robust dissimilatory NO_3^- reduction was occurring. Past experiments indicate that a stable denitrifying community may develop in such columns.[44,56] Metal-reducing conditions then developed in the dynamic column environment while active NO_3^- reduction was occurring, with Mn (SI Figure S7) and Fe (SI Figure S8) present in the effluent after 5 days. Relative to the oxic control, there was also an increase in dissimilatory metal-reducing bacteria in both bioreducing systems (SI Figure S2).

Effluent Fe concentrations in the electron-donor–amended system increased for the first ∼40 days and then decreased, presumably as bioavailable Fe(III) was gradually depleted (SI Figure S8). $Fe(II)_{(s)}$ would have also increased in the columns, as per our past work with the same aquifer material (e.g., ref 57). Indeed, the vast majority of Fe(II) created in aquifer materials is known to remain associated with the solids.[69,70] As expected,[57] there was no indication of a transition to microbially mediated sulfate-reduction in the electron-donor–amended system (SI Figure S9), confirming that the system remained poised at Fe(III)-reduction until the end of the experiment. In the electron-donor + sulfate–amended system, effluent Fe output from the columns followed a similar trend, indicating active Fe(III)-reduction (SI Figure S8). There was also a decrease in effluent sulfate concentrations from ∼400 μM in the first 25 days to <10 μM by 80 days (SI Figure S9). Sulfate then remained at this level until the end of the bioreduction experiment. At the experimental end point, there was an increased relative abundance of sulfate-reducing bacteria (SRB) in the electron-donor + sulfate–amended system compared to fresh sediment and the electron-donor–amended system (SI Figure S2). A detectable sulfide odor and blackening of the sediment was also noted, indicating robust sulfate-reduction.

^{99}Tc was present in the effluents, presumably as $TcO_4^-{}_{(aq)}$, of both bioreducing experiments for ∼12 days, with trends in effluent ^{99}Tc output from both systems almost identical (Figure 1). The onset of ^{99}Tc removal from solution coincided with the increase in microbially mediated Mn(IV/III)- and Fe(III)-reduction (SI Figures S7 and S8), and this likely reflected Tc(VII) reduction to Tc(IV) upon reaction with biogenic Fe(II) in the sediment.[15,21,23,24] After 12 days (which was before the onset of detectable sulfate-reduction; SI Figure S9), the ^{99}Tc concentration in the effluent decreased to ≤0.16 nM, and it remained so until the end of the experiment (147 days). During 147 days of bioreduction, >90% of the added ^{99}Tc (∼400 μg) had become associated with the sediment (SI Table S2) in both systems. This equated to a minimum ^{99}Tc loading in the sediment of ∼50 μg/g, assuming homogeneous distribution throughout the columns.

3.1.2. Solid Phase Geochemistry. After 147 days of bioreduction, sediment columns from both bioreducing systems were sectioned at 0.5 cm intervals under O_2-free conditions for solid phase geochemical analyses. Sediment-associated ^{99}Tc was sequentially extracted using increasing HCl concentrations and boiling aqua regia to study trends in Tc solid phase extractability with distance from the groundwater inlet (Figure 2). The total ^{99}Tc in each sediment horizon ranged from 11–148 μg/g in the electron-donor–amended system, and 8–178 μg/g in the electron-donor + sulfate–amended system (Figure 2 and SI Table S3). The general trend for ^{99}Tc retention in both column systems (Figure 2A,B) showed that most (72–83%; SI Table S3) of the extractable ^{99}Tc was retained within 2 cm of the groundwater inlet. Only limited ^{99}Tc retention (several %) occurred >4 cm beyond the inlet. These data suggest that the bioreduced columns could continue to retain Tc over extended times while reactive Fe(II) was present.

Based on past column work with Se using the same sediment material, groundwater treatments, and time scales,[57] the sediment sections closest to the inlet develop Fe(III)- and sulfate-reducing conditions. Interestingly, the electron-donor–amended system (Figure 2A) showed increasing concentrations of sediment-associated ^{99}Tc at modest distance from the inlet until 1.0–1.5 cm. As such, stronger Fe(III)-reducing conditions likely occurred away from the inlet. Similar was observed in past column work with Se.[57] The influent groundwater provides a continual source of NO_3^- and possibly small amounts of O_2, likely creating an area of oxic/anoxic redox cycling at the inlet to the column. In contrast, the sediment-associated ^{99}Tc concentration decreased with distance from the inlet in the electron-donor + sulfate–amended system (Figure 2B), comparable to past work with Se.[57] While overall ^{99}Tc retention in the two bioreducing systems was similar (SI Table S3), ∼20% more ^{99}Tc was retained in the electron-donor + sulfate–amended system between 0 and 1.5 cm. This suggests that enhanced reducing conditions with increased Fe(II) and sulfide were stimulated close to the inlet in the electron-donor + sulfate–amended system (i.e., sulfate-reduction vs denitrifying/metal reduction), and that this increased ^{99}Tc removal.

There were significant differences in the extractability of the sediment-associated ^{99}Tc phases that formed in the different bioreducing column systems (Figure 2A,B and SI Table S3). In the electron-donor–amended system (Figure 2A), which supported sustained Fe(III)-reduction, the majority (∼60%) of the sediment-associated ^{99}Tc was removed by the weaker acid extractions (0.001–2 M HCl, 30 min extractions). This indicates the presence of proportionately more labile forms of Tc in the samples, for example, TcO_2 octahedral chains loosely bound to mineral surfaces, as suggested in past work.[23] The Tc extracted in more aggressive extraction steps likely reflected different Tc(IV) species such as TcO_2 monomers strongly sorbed to Fe(II)-minerals,[23,25] or Tc(IV) incorporated into the lattice of neo-forming Fe(II)-bearing minerals (e.g., refs 30,40).

For the electron-donor + sulfate–amended system, which had supported a sustained period of sulfate-reduction, only 23% of the sediment-associated ^{99}Tc was extracted by the weaker acid extractions (0.001–2 M HCl; SI Table S3) suggesting proportionally less labile Tc(IV) formed in this system. Instead, stronger acid was required to extract the majority of the sediment-associated ^{99}Tc (e.g., up to 51% of ^{99}Tc was extracted by boiling aqua regia; Figure 2B and SI Table S3). Under extended sulfate-reducing conditions, acid extraction results confirmed more recalcitrant Tc(IV) phases formed under sulfate reducing conditions, such as Tc(IV)-sulfides, TcO_2 monomers, and/or Fe(II)-mineral incorporated Tc(IV).[30,38,39] As both of the column systems had slowly accumulated ^{99}Tc in the sediments during bioreduction to elevated concentrations, XAS was then used to further understand ^{99}Tc speciation and fate.

3.1.3. Speciation of Sediment-Associated Technetium. Tc K-edge XAS was used to determine ^{99}Tc speciation in select sediment samples taken from both bioreducing systems after 147 days of reaction. XAS data were collected from the electron-donor–amended column at 0–0.5 cm, and from two samples sectioned from the electron-donor + sulfate–amended system at 0–0.5 cm and 3.5–4.0 cm. XANES data from the samples were compared to three reference standards (SI Section S6).

XANES data from the electron-donor−amended 0−0.5 cm sample showed a pre-edge feature characteristic of TcO_4^-. LCF indicated a 25% contribution of $Tc(VII)O_4^-$ (SI Figure S11), with the remainder attributed to $Tc(IV)O_2$. EXAFS fitting was informed by the XANES LCF and relevant past literature.[18,38,49,50,71] EXAFS data (Figure 3 and SI Table S4) for this sample were best fit with a similar contribution from TcO_4^- (0.9 O at 1.71 Å)[63] and the remainder from hydrous TcO_2 (4.5 O at 2.02 Å and 1.4 Tc at 2.55 Å).[21] The best-fit modeling suggests that the average $TcO_2{\cdot}xH_2O$ chains were between dimers and polymers of infinite length.[72] Modeling of an Fe backscattering shell at 2.6 Å, indicative of Tc(IV)-binding via an edge sharing "short" Fe octahedron, was also attempted. This was not statistically significant. As such, $TcO_2{\cdot}xH_2O$ seems to dominate Tc(IV) speciation at the influent of the column after 147 days of bioreduction, in agreement with acid extraction data and the relevant literature in Fe(III)-reducing systems.[21,23,49,72,73] The presence of significant Tc(VII) in this sample was notable. TcO_4^- is continually introduced in the groundwater, but this would account for <1% of the total Tc in the wet sediment sample. Sediment entrained TcO_4^- has been reported in the past.[18,19,49,50,74] In the work of Fredrickson et al., 2009,[74] a mixture of Tc(VII) and Tc(IV) was observed in reoxidized sediment from the Hanford site. Extensive water washing removed the Tc(VII), suggesting it was readily soluble. In the current work, we did not wash the sediment. Assuming no artifacts from oxidation during our sampling and analysis (SI Section S6.2), the presence of significant Tc(VII) at the column inlet suggests dynamic redox cycling at the column influent. As discussed, O_2 and NO_3^- are continually introduced in the groundwater at the influent, leading to dynamic redox cycling and the potential for both Tc(VII) and Tc(IV) to be present in this zone. Overall, XAS measurements at the column inlet highlight the presence of both a TcO_2-like phase, and significant Tc(VII), highlighting the complexity of the inlet environment.

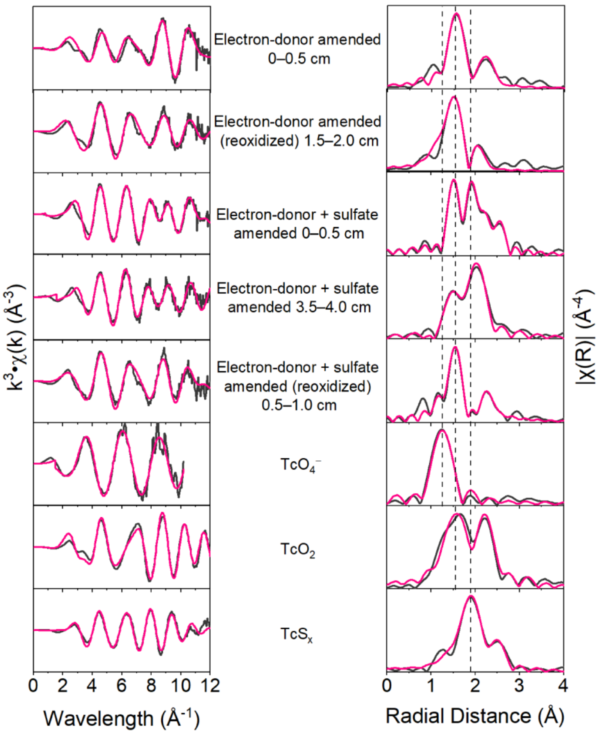

Figure 3. K-edge EXAFS data (black) and best fits (red) of column sediment samples and Tc standards, presented as k^3 weighted data (left) and their Fourier transforms (right). Dashed horizontal lines in the Fourier transforms indicate the position of the first coordination shell peak for the TcO_4^-, TcO_2, and TcS_x standards (from left to right, respectively).

Linear combination fitting of XANES data collected from the electron-donor + sulfate−amended 0−0.5 cm sample indicated contributions of 12% TcO_4^-, 34% TcO_2, and 54% TcS_x, although the Tc(VII) pre-edge feature was not as pronounced in the spectra compared to the electron donor only sample (SI Figure S11). The results of the XANES analysis and past literature were used to inform the EXAFS fitting.[18,38,49,50,71] The best fit to the EXAFS (Figure 3 and SI Table S4) was obtained with similar contributions from TcO_4^-, TcO_2, and TcS_x. For the 3.5−4.0 cm sample taken from the same column, LCF of the XANES data indicated that this sample contained only reduced Tc phases with 38% TcO_2 and 62% TcS_x (SI Figure S11). Fitting of the EXAFS for this sample also confirmed that TcS_x dominated (SI Table S4). Overall, XANES and EXAFS analyses clearly indicated the presence of significant Tc(IV)-sulfides (≥50%) in these samples. However, the difficulty of fitting different Tc-sulfides (Tc_2S_7, TcS_x, TcS_2[52,53,74]) and the lower levels of Tc in these more environmentally relevant samples, meant that it was not possible to precisely determine which Tc(IV)-sulfide phase dominated. Interestingly, in contrast to the Fe(III)-reducing column, a mix of TcO_2 (likely also present as $TcO_2{\cdot}xH_2O$ dimers/polymeric chains) and Tc(IV)-sulfides was found in all of the sulfidic column samples. This reflected the sequential extraction analyses where a larger recalcitrant Tc fraction (up to 51%) was observed, indicating that Tc-sulfides are more recalcitrant than TcO_2-like phases (Figure 2 and SI Table S3).

In contrast to earlier static microcosm studies, where TcO_2-like phases were the predominant products of Tc(VII) bioreduction, even under sulfate-reducing conditions,[15,18−22] our dynamic column approach shows that continuous electron donor supply and sustained sulfate reduction promote Tc(IV)-sulfide formation. This suggests that in contaminated environments with ample sulfate and active sulfate-reducing microbial communities, Tc(IV)-sulfides may be an important end product of Tc(VII) bioreduction.

3.2. Stability of TcO_2-Like Phases and Tc(IV)-Sulfides in Reoxidation Experiments. Due to the potential for oxidative remobilization of $Tc(IV)_{(s)}$ during redox cycling,[23] we further assessed the reoxidation behavior of the TcO_2-like and Tc(IV)-sulfide phases that formed in the bioreducing columns. Here, after 147 days of bioreduction, parallel sediment columns from the electron-donor−amended, and electron-donor + sulfate−amended systems were transitioned to oxic groundwater containing no added ^{99}Tc, electron donors, and sulfate (SI Table S1). The columns then clearly oxidized after 160 days as indicated by geochemical markers (see SI Section S5 for additional geochemical data).

A gradual increase in effluent ^{99}Tc concentrations was observed with both systems upon transition to the oxic groundwater, from below detection to a peak of ~4 μM after 13 days of oxidation (Figure 1). This initial effluent ^{99}Tc likely reflected the loss of labile Tc-bearing fractions, including any sediment-associated Tc(VII) and longer chain $TcO_2{\cdot}xH_2O$, which is considered more labile than other TcO_2 phases.[23]

Thereafter, the ^{99}Tc effluent concentration in the electron-donor−amended system was variable and higher than the parallel electron-donor + sulfate−amended system, averaging 2.0 μM during the first 100 days. Beyond this, the ^{99}Tc effluent concentration slowly decreased to ∼0.25 μM by the end of the experiment (160 days). In the electron-donor + sulfate system after 15 days of reoxidation, the ^{99}Tc effluent concentration decreased to ∼0.5 μM and stayed at this level for 65 days. Thereafter, Tc effluent concentrations slowly decreased to maintain ∼0.25 μM by the end of the experiment (160 days). The total sediment-associated ^{99}Tc lost from the electron-donor−amended system during the oxidation treatment was ∼50%, and ∼25% of that available in the electron-donor + sulfate−amended system (SI Table S2). Interestingly, while the sulfidic system did retain more Tc during the reoxidation experiment, the rate of Tc remobilization from both systems had converged by 160 days, suggesting oxidative remobilization of the same Tc(IV)-phase.

To probe potential differences in the speciation of Tc in the reoxidized sediment columns, sequential extractions and XAS analysis of samples from 160 days were completed. Sediment-associated ^{99}Tc concentrations in both column systems (Figure 2C,D) were lower than in the bioreduced equivalents (9−66 μg/g; SI Table S3), reflecting ^{99}Tc remobilization (Figure 1). Further, after reoxidation, ^{99}Tc was more evenly distributed throughout the reoxidized columns and no one sequential extraction treatment dominated (Figure 2C,D, and SI Table S3). The recalcitrant Tc phases previously observed after bioreduction (Figure 2A,B) appeared less prevalent after reoxidation.

XANES data from the reoxidized electron-donor−amended system (1.5−2.0 cm section) indicated that the sediment now contained only TcO_2-like phases (SI Figure S11). The best fit to the EXAFS (Figure 3 and SI Table S4) was again for dimeric/polymeric chain $TcO_2{\cdot}xH_2O$, which has been observed after oxidation in similar systems.[23,75] The addition of other backscattering contributions (e.g., Tc(VII)−O or Fe) was not possible. The XANES data from the oxidized electron-donor + sulfate system (0.5−1.0 cm section) indicated that the sediment contained 83% TcO_2 and 18% TcS_x, compared to 34% TcO_2 and 54% TcS_x in the freshly reduced sample. The best fit to the EXAFS for this system was also realized chiefly with dimeric/polymeric chain $TcO_2{\cdot}xH_2O$, but minor (∼10%) TcS_x could also be fitted credibly (Figure 3 and SI Table S4). Compared to the equivalent bioreduced sulfidic samples (SI Table S4), the majority of Tc(IV)-sulfides clearly underwent significant oxidation and phase transition to form sediment-associated TcO_2-like phases and $Tc(VII)_{(aq)}$, as observed in previous studies.[43,53,76,77] Potential incorporation of Tc(IV) into neo-forming Fe minerals (e.g., goethite) during oxidation of the sulfidic column was not evident in XAS data. Here, the Tc K-edge XANES (SI Figure S11) lacks the double peak indicative of Tc incorporation into Fe oxides,[30] and addition of an Fe backscatterer to the EXAFS fit was not possible. Such phases may have formed, but at levels not discernible through XAS analysis. Follow-up work investigating the potential for Tc(IV) incorporation into neo-forming Fe minerals should be conducted in more complex systems, under environmentally relevant conditions, and at low Tc concentrations.

3.3. Implications for Tc Migration in Subsurface Environments.

Dynamic column systems exploring Tc(VII)-bioreduction have revealed that different Tc(VII) bioreduction end-products form under sustained microbially mediated Fe(III)- vs sulfate-reducing conditions. Tc(IV)-sulfides appear to be the more stable end product if sulfidic, bioreducing conditions can be maintained. However, when bioreduced sediments are exposed to oxic groundwaters, Tc(IV)-sulfides oxidize to TcO_2-like phases and $Tc(VII)_{aq}$ over several months. In contaminated shallow subsurface environments where redox cycling may be expected over extended times due to groundwater recharge/seawater ingress, or in active remediation scenarios (e.g., biostimulation) where electron donor supply ceases, $TcO_2{\cdot}xH_2O$ monomers/dimers/chains will likely be more important phase(s). In deep geological disposal of radioactive wastes where there may be a supply of sulfate and electron donors, and where more stable redox conditions are likely, Tc(IV)-sulfides may dominate. Given ^{99}Tc's long half-life, these are important considerations in safety case modeling for the stewardship of ^{99}Tc contaminated nuclear sites and for radioactive waste disposal.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.5c12024.

> Details on synthetic groundwater and sediment chemistry, column design, DNA extraction and microbial community characterization, additional geochemical and spectroscopy data (and interpretation), information on XAS data collection, additional XAS data, XAS data fits, and XAS data interpretation (PDF)

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Notes

The authors declare no competing financial interest.

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