Dissolution of Technetium(IV) Oxide by Natural and Synthetic Organic Ligands under both Reducing and Oxidizing Conditions

4 AUTHORS:

Baohua Gu
Oak Ridge National Laboratory
160 PUBLICATIONS **6,690** CITATIONS

SEE PROFILE

Wenming Dong
Lawrence Berkeley National Laboratory
63 PUBLICATIONS **996** CITATIONS

SEE PROFILE

Liyuan Liang
Oak Ridge National Laboratory
148 PUBLICATIONS **4,756** CITATIONS

SEE PROFILE

Nathalie A Wall
Washington State University
42 PUBLICATIONS **253** CITATIONS

SEE PROFILE

Dissolution of Technetium(IV) Oxide by Natural and Synthetic Organic Ligands under both Reducing and Oxidizing Conditions

Baohua Gu,*[†] Wenming Dong,[†,‡] Liyuan Liang,[†] and Nathalie A. Wall[§]

[†]Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
[§]Chemistry Department, Washington State University, Pullman, Washington 99164, United States

S *Supporting Information*

ABSTRACT: Technetium-99 (Tc) in nuclear waste is a significant environmental concern due to its long half-life and high mobility in the subsurface. Reductive precipitation of technetium(IV) oxides $[TcO_2(s)]$ is an effective means of immobilizing Tc, thereby impeding its migration in groundwater. However, technetium(IV) oxides are subject to dissolution by oxidants and/or complexing agents. In this study we ascertain the effects of a synthetic organic ligand, ethylenediaminetetraacetate (EDTA), and two natural humic isolates on the dissolution and solubility of technetium(IV) oxides. Pure

synthetic technetium(IV) oxide (0.23 mM) was used in batch experiments to determine dissolution kinetics at pH ~6 under both reducing and oxidizing conditions. All organic ligands were found to enhance the dissolution of technetium(IV) oxides, increasing their solubility from $\sim 10^{-8}$ M (without ligands) to 4×10^{-7} M under strictly anoxic conditions. Reduced Tc(IV) was also found to reoxidize rapidly under oxic conditions, with an observed oxidative dissolution rate approximately an order of magnitude higher than that of ligand-promoted dissolution under reducing conditions. Significantly, oxidative dissolution was inhibited by EDTA but enhanced by humic acid compared to experiments without any complexing agents. The redox functional properties of humics, capable of facilitating intramolecular electron transfer, may account for this increased oxidation rate under oxic conditions. Our results highlight the importance of complex interactions for the stability and mobility of Tc and thus for the long-term fate of Tc in contaminated environments.
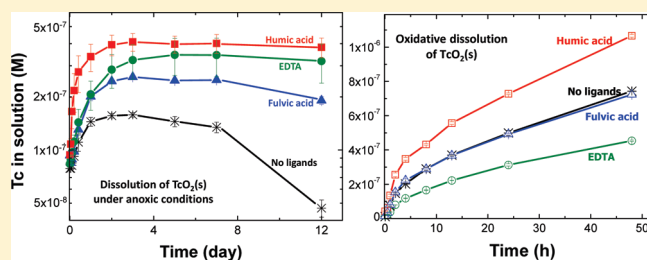
■ INTRODUCTION

Technetium-99 (Tc) is a radioactive fission product of uranium-235 and a significant environmental concern due to its long half-life (2.14×10^5 years) and high water solubility and mobility in aquatic ecosystems under oxidizing environments.[1−8] It is produced primarily as a result of nuclear weapons production during the Cold War era[1−3] and nuclear power generation nowadays.[6,9] In addition, it is a decay product of Tc-99 m, which is widely used in radiobiology and nuclear medicine.[10] Its inventory is expected to increase if nuclear power generation is emphasized in response to concerns for the use of fossil fuel and emission of atmospheric greenhouse gases.[3,6,9] Understanding Tc stability, solubility, and mobility is therefore important for assessing the behavior and impact of Tc in contaminated environments.

Depending on the redox condition, Tc exists in the environment either in oxidized [Tc(VII)] or reduced [Tc(IV) and Tc(V)] forms.[1−3] The dominant form of Tc(VII) under oxic and suboxic environments is pertechnetate (TcO_4^-) anion. It is highly soluble in water but poorly retained by sediments and thus readily transported in the subsurface.[1−4,11−15] Even in soils with relatively high organic matter content, the retention of Tc(VII) by soil is very weak, with low or negative partitioning values[15] compared with other sorbent materials.[4,16] However, under anoxic conditions, Tc(VII) can be reduced, primarily to technetium(IV) hydrous oxides, such as $TcO_2 \cdot nH_2O$ [abbreviated here as $TcO_2(s)$], which is sparingly soluble in water ($\sim 10^{-8}$ M) under circumneutral pH conditions[17−19] and is retained in the sediment.[1−3,5−7,12,20] This reduction of Tc(VII) can be mediated either chemically or biologically, and additional details can be found in a recent review by Icenhower et al.[9] For example, a wide variety of anaerobic microbes has been shown to enzymatically reduce soluble Tc(VII) to Tc(IV) solid.[21−25] Additionally, microbially produced ferrous iron and sulfide are reported to indirectly reduce Tc, hence stabilizing it against oxidation.[7,22,26−29] Consequently, stimulating the growth of anaerobic microorganisms has been proposed as one of the remedial options for contaminated soil and groundwater, because of its potential for immobilizing and impeding Tc migration in subsurface environments.[5,6,27]

Studies to date have been mostly concerned with the rates and mechanisms of reductive immobilization of Tc,[5−7,21−29] whereas the potentials of reoxidation and dissolution of Tc(IV) have been largely overlooked,[8,25,30] particularly in relation to the presence of complexing organic ligands. Natural organic ligands such as humic substances occur ubiquitously in soil and aquatic environments, whereas synthetic ligands such as EDTA, citrate, and acetate are known to coexist with toxic metals and radionuclides at many contaminated sites.[31−34] The role of organic ligands on $TcO_2(s)$ dissolution is not fully understood: in some studies, natural and synthetic ligands are shown to increase the solubility of Tc(IV) through complexation under reducing conditions,[6,35−39] whereas other studies found no significant effects.[40,41] For example, Tc(IV)−humic complexes have been suggested to be the dominant chemical species in deep groundwater containing humic substances, and the complexation reaction may control the mobility and fate of Tc under reducing environments.[35] Even microbial metabolites have been shown to form soluble complexes with reduced Tc(IV).[32] Thus, the influence of these organic ligands on the stability and mobility of Tc(IV) needs to be considered when long-term immobilization strategies are devised for soils and groundwater that are contaminated with Tc.

The present study was undertaken to examine the effects of organic ligands on the dissolution of $TcO_2(s)$. Synthesized colloidal $TcO_2(s)$ precipitates[42] were used in the dissolution experiments with selected natural and synthetic organic ligands of varying molecular size and characteristics. We quantified the influences of these ligands on the solubility and dissolution kinetics of Tc(IV) under both reducing and oxidizing conditions, and we discuss their implications for the remediation of Tc(VII) plumes through reductive immobilization techniques.

■ MATERIALS AND METHODS

Reduced Tc(IV) solids were prepared from a stock solution of Tc as ammonium pertechnetate (NH_4TcO_4) (90 mM) according to the methods of Hess et al.[42] In brief, an aliquot of NH_4TcO_4 was added to freshly prepared sodium hydrosulfite $(Na_2S_2O_4, 0.2 M)$ as a reductant, and the solution pH was adjusted to 12 to form poorly crystalline $TcO_2(s)$ colloidal precipitates in an anaerobic glovebox. After aging for 3 days, the suspension was centrifuged and washed three times with freshly prepared 0.01 M $Na_2S_2O_4$, and finally redispersed in deionized water and stored in the glovebox until use.

Three organic ligands were used to study their effects on the dissolution of $TcO_2(s)$ solids. They include a synthetic chelator, EDTA; a high-molecular weight natural soil humic acid (Elliot-HA) obtained from the International Humic Substances Society (IHSS); and a relatively low-molecular-weight soil fulvic acid (IFRC-FA) isolated from a topsoil at the background site, where the U.S. Department of Energy (DOE) Integrated Field Research Challenge (IFRC) project is conducted near Oak Ridge, TN. These humic materials were previously characterized for metal binding capabilities and chemical and structural properties.[43−46] Both natural and synthetic organic ligands were used here to represent those commonly found in soil and groundwater at many contaminated DOE sites.[31−34]

To determine dissolution of Tc(IV) solids by organic ligands, an aliquot of $TcO_2(s)$ colloid suspension was mixed with each of the organic ligand solutions in serum bottles. To ensure a strongly reducing condition, 0.01 M $Na_2S_2O_4$ was added in the solution during the experiment. The solution pH was adjusted to

6 ± 0.1, and the final volume was made up to 20 mL. The total Tc concentration was 0.23 mM, and the added ligand concentration was 2.5 mM for EDTA and 50 mg/L for the humic or fulvic acid samples. Sample bottles were then sealed with thick rubber stoppers and aluminum crimp caps and placed onto a rotary shaker for equilibration. Unless otherwise noted, all samples were prepared in duplicate, and all preparations and operations (e.g., sample filtration and centrifugation with a microultracentrifuge) were performed in a glovebox equipped with a Pd catalyst in a 98% N_2 and 2% H_2 atmosphere. Control samples were also prepared in parallel following the same procedures, except that no organic ligands were added to the Tc(IV) suspension. At given time intervals, an aliquot (1 mL) of each sample was taken with a 1-mL disposable syringe and filtered through a 0.2-μm syringe filter. The filtered sample (0.5 mL), after the first few drops were discarded, was mixed with 15 mL of scintillation cocktail (Ultima-Gold XR, Packard) and subsequently analyzed for Tc-99 β-radioactivity by means of a liquid scintillation analyzer (Tri-Carb, model 2810 TR, Packard Instruments). The measured counts per minute were converted to soluble Tc concentrations in solution by use of external calibration standards.[14]

The dissolved Tc concentration is operationally defined here as the Tc fraction that passes through a 0.2-μm filter. To assess the potential existence of Tc(IV) nanoparticles (<0.2 μm) in the filtrate solution, selected samples in a preliminary experiment were also analyzed following (1) ultracentrifugation at 13,000 rpm for 15 min or (2) ultrafiltration through the Millipore Microcon centrifugal filter device with a molecular weight cutoff (MWCO) at 30 kDa (YM-30, Millipore). Results show little contribution of nanoparticulate Tc(IV) species to the determination of dissolved Tc in solution (see Supporting Information, Figure S1).

To evaluate the potential oxidation of Tc(IV) during experiments, both oxidized Tc(VII) and reduced Tc(IV) in the filtrate solution were determined by the solvent extraction technique.[42,47] Briefly, an aliquot of the filtrate sample was acidified with 1 M HCl and mixed vigorously with tetraphenylphosphonium (TPP^+) bromide (0.05 M) in chloroform for 5 min, in which Tc(VII) (as TcO_4^-) was extracted into the organic phase, leaving the reduced Tc(IV) in the aqueous phase. This technique is specific for the extraction and quantification of TcO_4^- due to strong complexation of TcO_4^- with TPP^+ in chloroform.[42,47] The reduced Tc(IV) was then quantified by the difference between total Tc and oxidized Tc(VII) in chloroform.

In addition to the determination of dissolution of $TcO_2(s)$ by organic ligands under reducing conditions, oxidative dissolution of $TcO_2(s)$ was also investigated in the presence of organic ligands. After completion of the dissolution experiment under reducing conditions (in 20 days as described above), the same sample (2.5 mL aliquot) was transferred to a plastic vial, diluted 5 times with deionized water, and subsequently exposed to oxygen under ambient conditions. Sample vials were shaken on a rotary shaker and opened periodically to ensure that oxidizing conditions were maintained. At a given time interval, an aliquot (1 mL) of each sample was taken and filtered through a 0.2-μm syringe filter. The filtrate sample (0.5 mL) was then mixed with 15 mL of scintillation cocktail and analyzed for Tc concentrations in solution, as described earlier.

■ RESULTS AND DISCUSSION

Effects of Organic Ligands on Dissolution of Technetium-(IV) Oxide under Anoxic Conditions. Dissolution of $TcO_2(s)$
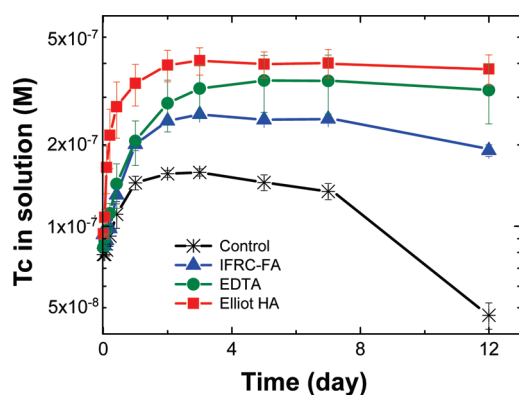
Figure 1. Dissolution kinetics of $TcO_2(s)$ in the presence of complexing organic ligands including EDTA (2.5 mM), IHSS Elliot-HA, and IFRC-FA at 50 mg/L. The experiment was performed in 10 mM sodium disulfite ($Na_2S_2O_5$) at pH 6 in an anaerobic glovebox. Total Tc concentration in suspension was 2.3×10^{-4} M.

by organic ligands was first investigated under strictly anoxic conditions in the presence of Elliot-HA, EDTA, and IFRC-FA ligands (Figure 1). The dissolution is characterized by an initial rapid increase of Tc(IV) in solution in the first day, reaching a steady-state dissolution in about 3 days, at which stage the maximum amount of solubilized Tc was about 2–3 times greater in the presence than in the absence of organic ligands (control). Without organic ligands, however, the amount of solubilized Tc(IV) decreased from $\sim 1.5 \times 10^{-7}$ M at day 3 to 4.5×10^{-8} M at day 12. We attributed this to the aging and possible crystallization of poorly crystallized $TcO_2(s)$ precipitates formed by the reduction of TcO_4^-.[17,18,36,42] This measured solubility at day 12 agrees well with the literature reported value, which is $\sim 3 \times 10^{-8}$ M for $TcO_2(s)$ under circumneutral pH.[17,18,36] However, this value is significantly lower than that reported by Maes et al.,[36] which was on the order of $\sim 10^{-6}$ M at pH ~ 8. Similarly, the increased solubility of $TcO_2(s)$ by Elliot-HA and IFRC-FA found in this study is much lower than that obtained by Maes et al.,[37] who reported values on the order of 2×10^{-6} to 10^{-4} M. This discrepancy and wide variation of the measured solubility has been partially explained by the presence of polymeric Tc(IV) species and/or nanometer-size TcO_2 particles.[37] Differences in experimental procedures may have also contributed to the difference in the measured solubility. For example, Maes et al.[37] performed the solubility measurements by reducing TcO_4^- ions directly in the presence of humic materials and clays, whereas we used synthesized $TcO_2(s)$ as starting materials and then added organic ligands to study their effects on dissolution. In their study, reduced Tc(IV) species likely form complexes immediately with humics, thus increasing the apparent solubility of $TcO_2(s)$. Additionally, the reported solubility by Maes et al. was determined at ~ 10 times the Tc concentration that we used, and at a relatively high pH (7.9–8.6). At this pH, TcO_2 and $TcO(OH)_2$ species are the dominant forms of Tc(IV), and organic ligands and humic substances are thought to be unable to competitively displace O or OH to form mononuclear Tc(IV) and humic complexes by coordination.[37] Instead, it was proposed that the association between Tc(IV) and humic substances was due to "hydrophobic sorption" of either monomeric or polynuclear $TcO(OH)_2$–$(TcO(OH)_2)_2$ neutral species by the humic substances.[36,37] Such "sorptive" interactions are likely to lead to overestimation and wider variations of apparent "solubility" of

$TcO_2(s)$ ($\sim 10^{-4}$ to 10^{-6} M),[36,37] in contrast to the intrinsic solubility observed in the present study (Figure 1).

Among various organic ligands studied, Elliot-HA and EDTA were found to be more effective than IFRC-FA in promoting the dissolution of $TcO_2(s)$ solids by forming Tc(IV)−organic complexes under anoxic conditions (Figure 1). On day 12 (Figure 1), dissolved Tc concentrations in the presence of Elliot-HA and EDTA were $\sim 4 \times 10^{-7}$ and 3.4×10^{-7} M, respectively, nearly an order of magnitude higher than that without ligands. The amount of Tc solubilized by IFRC-FA was $\sim 2.5 \times 10^{-7}$ M at day 7 but decreased slightly to 1.9×10^{-7} M at day 12. These observations indicate that while all organic ligands increased the solubilization of $TcO_2(s)$ (compared with controls), they differ in their ability to cause the dissolution of $TcO_2(s)$ due to variations in their chemical and structural properties. Previous studies have shown that carboxyl groups are among the most important functional groups for complexing Tc(IV) and other actinide ions by forming binuclear compounds.[32,39,47−50] This is demonstrated by EDTA, a well-known carboxylic chelating agent that strongly interacts with Tc(IV) under reducing conditions. EDTA shows a higher dissolution rate and capacity than IFRC-FA in dissolving $TcO_2(s)$ solids (Figure 1 and Supporting Information, Table S1). The formation of Tc(IV)−EDTA complexes has been unequivocally demonstrated by high-performance liquid chromatography analysis coupled with inductively coupled plasma mass spectrometry.[41] Furthermore, the present study shows that complexation between EDTA and Tc(IV) tends to stabilize Tc(IV) against oxidation, as described in detail below.

Previous studies also reported that oxalate and diethylenetriaminepentaacetic acid (DTPA) are effective chelators, leading to significant dissolution of Tc(IV) solids.[32,47] These chelators contain neighboring carboxyls, which have been suggested to facilitate the formation of binuclear complexes with reduced Tc(IV) species.[32,47−50] Thus, positioning of the functional groups in organic ligands may have played a role in enhancing the dissolution of $TcO_2(s)$, although we cannot rule out the possibility of hydrophobic interactions in the case of humic materials as proposed by Maes et al.[36,37] The surface of $TcO_2 \cdot nH_2O$ is hydrophilic, and the fact that EDTA and oxalate are effective in dissolving $TcO_2(s)$ and stabilizing Tc(IV) obviously does not support the hydrophobic interaction but rather points to the importance of metal−ligand complexation. Here, chelation between neighboring carboxylic functional groups of EDTA/oxalate and Tc(IV) species is responsible for the dissolution of $TcO_2(s)$. Results of geochemical speciation calculations,[40] as well as the general practice of using organic complexing ligands to stabilize Tc(IV) in diagnostic imaging applications in nuclear medicine,[10] both support this conclusion. This effect of the positioning (not merely the quantity) of the functional groups also offers a plausible explanation for the influence of humic materials. IFRC-FA is less effective in dissolving $TcO_2(s)$ (Figure 1), despite ^{13}C nuclear magnetic resonance (NMR) spectroscopic analysis revealing at least twice as many carboxylic functional groups (160−190 ppm in Figure S2, Supporting Information) in IFRC-FA as in Elliot-HA. Similarly, in a study of the interactions between soil organic matter and Tc(IV), Stalmans et al.[51] suggested that the particularly strong bonds between Tc(IV) and humics are likely formed by hydroxyls that are adjacent to carboxylic groups. These analyses thus indicate that, in addition to proposed hydrophobic interactions,[36,37] the chelation and complexation between humic substances and Tc(IV) species may have played a dominant role
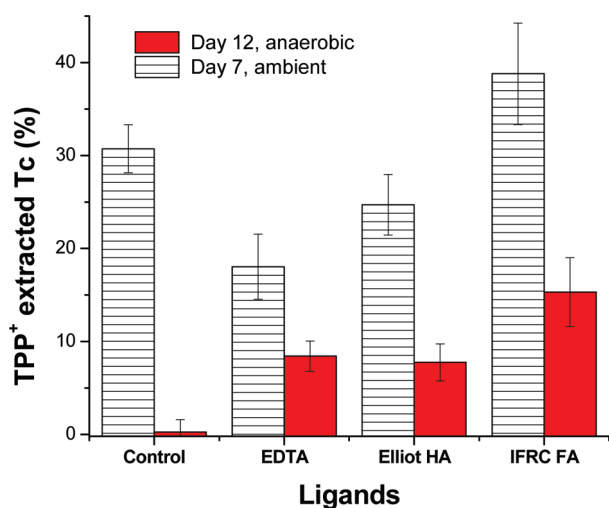
Figure 2. Tetraphenylphosphonium (TPP$^+$) solvent extraction and speciation analysis of Tc(VII)[42,47] in filtrate samples shown in Figure 1. The extraction and separation was performed by centrifugation either in an anaerobic glovebox at day 12 or outside the glovebox (ambient) at day 7.

Figure 3. Effect of organic ligands (Elliot-HA, IFRC-FA, and EDTA) on oxidative dissolution of TcO$_2$(s) following the dissolution experiment by organic ligands shown in Figure 1 (see text for details). The experiment was performed at pH ~6 under ambient aerobic conditions (open air).

in enhancing the dissolution of TcO$_2$(s) under reducing environments (Figure 1).

Effects of Organic Ligands on Oxidative Dissolution of Technetium(IV) Oxide. Reduced Tc(IV) is known to be readily oxidized in the presence of oxygen,[8,20,38] but the influence of organic ligands on Tc(IV) oxidation is poorly understood. To evaluate whether oxidation was partly responsible for the dissolution of Tc(IV) by organic ligands, the filtered samples from the above experiment (Figure 1) were further analyzed for Tc speciation [as either Tc(VII) or Tc(IV)] at days 7 and 12 by the solvent extraction technique.[42,47] The technique has been demonstrated to extract aqueous-phase TcO$_4^-$ effectively at low concentrations in the absence of organic ligands.[42,47] This is clearly illustrated in Figure 2 for the controls (solid bar) at day 12 when filtered samples were extracted under a strictly anoxic condition. A negligible amount of Tc(VII) was found in the extract in the absence of complexing organic ligands, suggesting that anoxic conditions were indeed maintained. However, in the presence of organic ligands, ~10−15% of Tc was found in the TPP$^+$ extract. Since the same anoxic condition was maintained for these samples as for the controls, the extracted Tc cannot be attributed to the oxidation of Tc(IV) (Figure 2, solid bars). Instead, this observation is likely a result of the extraction of Tc(IV) species that are associated with humic substances due to the affinity of humics for the extracting solvent (chloroform), as evidenced by lightly colored solvent after mixing with the humics. This result, however, does not affect the data presented in Figure 1 since they represent the total dissolved Tc concentration in the filtrate.

Substantially higher amounts of Tc (up to ~40%) were extracted by TPP$^+$ for samples prepared at day 7 than at day 12 (Figure 2, cross-striped bars). In particular, about 30% Tc(VII) was found in the control. The only difference for samples prepared at day 7 was that they were centrifuged for 15 min outside the anaerobic glovebox. In this case, oxygen may have permeated into the sample since the sealed vials (and polypropylene) are not completely airtight. These observations indicate that, despite a short unintentional exposure of samples
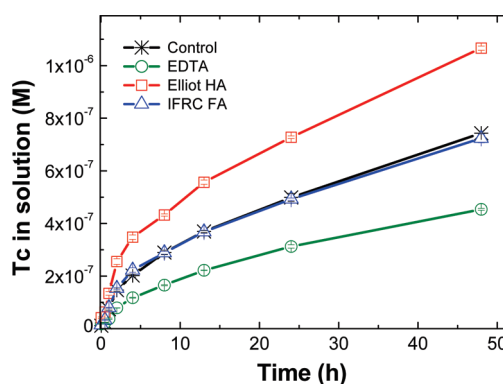
to the air, Tc(IV) is prone to oxidation, leading to rapid oxidative dissolution of TcO$_2$(s). This was further evidenced in a preliminary experiment performed exactly the same as those shown in Figure 1, except that samples were equilibrated and centrifuged outside the glovebox (Supporting Information, Figure S3). A much higher dissolution of Tc(IV) (~3 × 10^{-6} M) was observed in all samples. Importantly, the dissolution did not reach equilibrium over an extended period (40 days), and no significant differences in the dissolution of Tc(IV) by various organic ligands were observed. The latter is attributed to the complication of simultaneous dissolution by oxidative and organic ligand-induced mechanisms in the system. These observations indicate that a strictly anoxic condition is required to unambiguously determine the dissolution rates of TcO$_2$(s).[17,36,38]

To better understand the role of organic ligands in oxidative dissolution kinetics of TcO$_2$(s), samples were taken out of the glovebox following the dissolution experiment by organics (shown in Figure 1), diluted 5 times in water, and re-equilibrated under ambient air oxidizing conditions. The exposure of Tc(IV) to oxygen led to substantially increased dissolution (Figure 3), with calculated initial rates (within the first 2 h) ranging from 0.77 to 1.50 h^{-1}. These values are more than an order of magnitude higher than that of the dissolution induced by complexing organic ligands under anoxic conditions (Supporting Information, Table S1). Dissolution did not reach equilibrium after 5 days, because of continuous reactions between dissolved oxygen and TcO$_2$(s). Importantly, while both Elliot-HA and EDTA were shown to enhance the dissolution of Tc(IV) solids under reducing conditions (Figure 1), EDTA was found to inhibit dissolution under oxidizing conditions whereas Elliot-HA increased the oxidative dissolution when compared with the controls (Figure 3). The amounts of Tc dissolved by Elliot-HA were consistently higher than those in the control experiments and in the presence of EDTA (Figure 3).

Decreased oxidative dissolution of TcO$_2$(s) by EDTA may be attributed to strong complexation and stabilization of Tc(IV) by EDTA,[10,38,50] so that a higher energy would be required to break the Tc(IV)−EDTA bonds to form TcO$_4^-$ and EDTA. The fact that chelating organic ligands are often used for stabilizing reduced Tc(IV) and preventing it from oxidation supports this argument.[10,50] Using Raman spectroscopy, Gu and Ruan[38]

provided unambiguous evidence of Tc(IV) stabilization by EDTA: no significant oxidation of Tc(IV) was observed even after the samples were air-dried. On the other hand, the HA-complexed Tc(IV) was found to be more readily oxidized than that in the absence of organic ligands (Figure 3). The observation that Elliot-HA enhances both the oxidative and ligand-induced dissolution of Tc(IV) is of particular significance and can be explained by the dual functional role of humic substances. Naturally occurring humics are complex mixtures of organic compounds that contain both complexing functional groups such as carboxyls and hydroxyls[43,52] and redox-reactive moieties such as quinones and semiquinones.[44,45,53] Under reducing conditions, both Elliot-HA and IFRC-FA enhance ligand-promoted dissolution of Tc(IV) (Figure 1) because of their metal complexing/chelating capabilities. However, under oxidizing conditions, humics can act as electron acceptors, thereby increasing the oxidation rate of Tc(IV) through intramolecular electron transfer when they are exposed to oxygen (Figure 3). Elliot-HA is more effective than IFRC-FA in enhancing the oxidative dissolution of Tc(IV) because it has a much higher content of aromaticity (100−150 ppm) than IFRC-FA, as shown by ^{13}C NMR spectroscopic analysis (Supporting Information, Figure S2). These aromatic moieties in HA can act as effective electron shuttles or acceptors[44,45,53] and thus facilitate the electron transfer from Tc(IV) to HA. The role of humic substances in facilitating electron-transfer reactions is also well illustrated in previous studies in which humics are found to enhance not only the microbial reduction of metal ions such as uranium [U(VI)] and [Fe(III)] under reducing conditions[45,53,54] but also the oxidation of U(IV) and Fe(II) under oxidizing conditions.[45,55] We therefore conclude that, in addition to their metal binding capabilities for promoting ligand-induced dissolution of reduced Tc(IV), natural humic substances, particularly the HA fraction, increase the oxidation and oxidative dissolution of Tc(IV) solids under oxidizing conditions.

The complex interactions observed between Tc(IV) and organic ligands of varying chemical and structural properties are expected to have significant implications for the stability and mobility of reduced Tc(IV) species in both reducing and oxidizing environments. However, these reactions could be further complicated by the presence of mineral phases and microbial activities in soil and groundwater. For example, in a study of the effect of organic cocontaminants on Tc and rhenium speciation and solubility under reducing environments, Maset et al.[41] reported no increase in Tc(IV) solubility or mobility in the pore water when contacted by EDTA (at 1.7 mM). A careful examination of their work shows that, other than the presence of mineral phases, factors such as high organic matter (12% C) and Fe (6%) contents may have played an important role in retaining reduced Tc(IV). A low dissolved Tc(IV) found in the pore water is indicative that most reduced Tc(IV) is retained or complexed by the soil organic matter such as the high-molecular weight humin and humic acids, consistent with observations in this study (Figure 1). Furthermore, ferric ions and iron oxides are known to strongly interact with negatively charged humics[56] and EDTA and also lead to increased retention of organic ligands and/or Tc(IV)−organic complexes in soil. Similarly, despite thermodynamic model prediction of the formation of dominant anionic Tc(IV)−EDTA complexes, Begg et al.[40] reported a lack of mobilization of Tc(IV) in the presence of EDTA in soil, which could again be attributed to the presence of relatively high contents of Fe, Al, and soil organic matter. These observations

suggest that the long-term stability and mobility of reduced Tc(IV) will depend on the interplay of various organic and inorganic constituents in soil and their interactions with Tc. The present study concludes that, in soils containing low quantities of natural organic matter and oxides, the presence of soluble organic ligands will likely increase the solubility and mobility of Tc(IV) species by complexation even under strictly anoxic conditions. The presence of humic materials also increases the oxidative dissolution of Tc(IV) species under oxidizing conditions by forming soluble TcO_4^-, whereas the presence of EDTA can slow this process by forming Tc(IV)−EDTA complexes whose fate will depend on the soil and mineralogical characteristics noted earlier. Future studies are needed in complex natural systems (e.g., in the presence of minerals and microbes) to further enhance our understanding of the role of various organic ligands on the stability and mobility of Tc and thereby improve design of remediation strategies for soils and groundwater that are contaminated with Tc.

■ ASSOCIATED CONTENT

S **Supporting Information.** Additional text, three figures, and one table describing determination of particulate Tc via different separation techniques, ^{13}C NMR spectroscopic analysis, and preliminary dissolution experiments and results. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: (865)-574-7286; e-mail: gub1@ornl.gov.

Present Address
‡Lawrence Berkeley Laboratory, Berkeley, CA 94000.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Wildung, R. E.; Mcfadden, K. M.; Garland, T. R. Technetium sources and behavior in the environment. *J. Environ. Qual.* **1979**, *8* 156–161.

(2) Bondietti, E. A.; Francis, C. W. Geologic migration potentials of technetium-99 and neptunium-237. *Science* **1979**, *203*, 1337–1340.

(3) Schulte, E. H.; Scoppa, P. Sources and behavior of technetium in the environment. *Sci. Total Environ.* **1987**, *64*, 163–179.

(4) Liang, L.; Gu, B.; Yin, X. Removal of technetium-99 from contaminated groundwater with sorbents and reductive materials. *Sep. Technol.* **1996**, *6*, 111–122.

(5) Lloyd, J. R.; Macaskie, L. E. Microbially-mediated reduction and removal of technetium from solution. *Res. Microbiol.* **1997**, *148* 530–532.

(6) Abdelouas, A.; Grambow, B.; Fattahi, M.; Andres, Y.; Leclerc-Cessac, E. Microbial reduction of Tc-99 in organic matter-rich soils. *Sci. Total Environ.* **2005**, *336*, 255–268.

(7) Zachara, J. M.; Heald, S. M.; Jeon, B. H.; Kukkadapu, R. K.; Liu, C. X.; McKinley, J. P.; Dohnalkova, A. C.; Moore, D. A. Reduction of

pertechnetate [Tc(VII)] by aqueous Fe(II) and the nature of solid phase redox products. *Geochim. Cosmochim. Acta* **2007**, *71*, 2137–2157.

(8) Fredrickson, J. K.; Zachara, J. M.; Plymale, A. E.; Heald, S. M.; McKinley, J. P.; Kennedy, D. W.; Liu, C. X.; Nachimuthu, P. Oxidative dissolution potential of biogenic and ablogenic TcO₂ in subsurface sediments. *Geochim. Cosmochim. Acta* **2009**, *73*, 2299–2313.

(9) Icenhower, J. P.; Qafoku, N. P.; Zachara, J. M.; Martin, W. J. The biogeochemistry of technetium: a review of the behavior of an artificial element in the natural environment. *Am. J. Sci.* **2010**, *310*, 721–752.

(10) Hjelstuen, O. K. Tc-99m Chelators in Nuclear-Medicine - a Review. *Analyst* **1995**, *120*, 863–866.

(11) Routson, R. C.; Jansen, G.; Robinson, A. V. Am-241, Np-237 and Tc-99 sorption on two United States subsoils from differing weathering intensity areas. *Health Phys.* **1977**, *36*, 21–30.

(12) Wildung, R. E.; Garland, T. R.; McFadden, K. M.; Cowan, C. E. *Technetium sorption in surface soils*; Elsevier: London, 1986.

(13) Wolfrum, C.; Bunzl, K. Sorption and desorption of technetium by humic substances under oxic and anoxic conditions. *J. Radioanal. Nucl. Chem.* **1986**, *99*, 315–323.

(14) Gu, B.; Brown, G. M.; Bonnesen, P. V.; Liang, L.; Moyer, B. A.; Ober, R.; Alexandratos, S. D. Development of novel bifunctional anion-exchange resins with improved selectivity for pertechnetate sorption from contaminated groundwater. *Environ. Sci. Technol.* **2000**, *34*, 1075–1080.

(15) Kaplan, D. I. Influence of surface charge of an Fe-oxide and an organic matter dominated soil on iodide and pertechnetate sorption. *Radiochim. Acta* **2003**, *91*, 173–178.

(16) Gu, B.; Dowlen, K. E.; Liang, L.; Clausen, J. L. Efficient separation and recovery of technetium-99 from contaminated groundwater. *Sep. Technol.* **1996**, *6*, 123–132.

(17) Lieser, K. H.; Bauscher, C. Technetium in the hydrosphere and in the geosphere. 1. Chemistry of technetium and iron in natural-waters and influence of the redox potential on the sorption of technetium. *Radiochim. Acta* **1987**, *42*, 205–213.

(18) Cui, D. Q.; Eriksen, T. E. Reduction of pertechnetate in solution by heterogeneous electron transfer from Fe(II)-containing geological material. *Environ. Sci. Technol.* **1996**, *30*, 2263–2269.

(19) Baston, G. M. N.; De Canniere, P. R.; Ilett, D. J.; Cowper, M. M.; Pilkington, N. J.; Tweed, C. J.; Wang, L.; Williams, S. J. Technetium behaviour in Boom Clay - a laboratory and field study. *Radiochim. Acta* **2002**, *90*, 735–740.

(20) McBeth, J. M.; Lear, G.; Lloyd, J. R.; Livens, F. R.; Morris, K.; Burke, I. T. Technetium reduction and reoxidation in aquifer sediments. *Geomicrobiol. J.* **2007**, *24*, 189–197.

(21) Lloyd, J. R.; Nolting, H. F.; Sole, V. A.; Bosecker, K. Technetium reduction and precipitation by sulfate-reducing bacteria. *Geomicrobiol. J.* **1998**, *15*, 45–58.

(22) Lloyd, J. R.; Sole, V. A.; Van Praagh, C. V. G.; Lovley, D. R. Direct and Fe(II)-mediated reduction of technetium by Fe(III)-reducing bacteria. *Appl. Environ. Microbiol.* **2000**, *66*, 3743–3749.

(23) Fredrickson, J. K.; Kostandarithes, H. M.; Li, S. W.; Plymale, A. E.; Daly, M. J. Reduction of Fe(III), Cr(VI), U(VI), and Tc(VII) by *Deinococcus radiodurans* R1. *Appl. Environ. Microbiol.* **2000**, *66*, 2006–2011.

(24) Wildung, R. E.; Gorby, Y. A.; Krupka, K. M.; Hess, N. J.; Li, S. W.; Plymale, A. E.; McKinley, J. P.; Fredrickson, J. K. Effect of electron donor and solution chemistry on products of dissimilatory reduction of technetium by *Shewanella putrefaciens*. *Appl. Environ. Microbiol.* **2000**, *66*, 2451–2460.

(25) Burke, I. T.; Boothman, C.; Lloyd, J. R.; Mortimer, R. J. G.; Livens, F. R.; Morris, K. Effects of progressive anoxia on the solubility of technetium in sediments. *Environ. Sci. Technol.* **2005**, *39*, 4109–4116.

(26) Fredrickson, J. K.; Zachara, J. M.; Kennedy, D. W.; Kukkadapu, R. K.; McKinley, J. P.; Heald, S. M.; Liu, C. X.; Plymale, A. E. Reduction of TcO₄⁻ by sediment-associated biogenic Fe(II). *Geochim. Cosmochim. Acta* **2004**, *68*, 3171–3187.

(27) Wildung, R. E.; Li, S. W.; Murray, C. J.; Krupka, K. M.; Xie, Y.; Hess, N. J.; Roden, E. E. Technetium reduction in sediments of a shallow aquifer exhibiting dissimilatory iron reduction potential. *FEMS Microbiol. Ecol.* **2004**, *49*, 151–162.

(28) Peretyazhko, T.; Zachara, J. M.; Heald, S. M.; Kukkadapu, R. K.; Liu, C.; Plymale, A. E.; Resch, C. T. Reduction of Tc(VII) by Fe(II) sorbed on Al (hydr)oxides. *Environ. Sci. Technol.* **2008**, *42*, 5499–5506.

(29) Wharton, M. J.; Atkins, B.; Charnock, J. M.; Livens, F. R.; Pattrick, R. A. D.; Collison, D. An X-ray absorption spectroscopy study of the coprecipitation of Tc and Re with mackinawite (FeS). *Appl. Geochem.* **2000**, *15*, 347–354.

(30) Burke, I. T.; Boothman, C.; Lloyd, J. R.; Livens, F. R.; Charnock, J. M.; McBeth, J. M.; Mortimer, R. J. G.; Morris, K. Reoxidation behavior of technetium, iron, and sulfur in estuarine sediments. *Environ. Sci. Technol.* **2006**, *40*, 3529–3535.

(31) Francis, A. J.; Dodge, C. J.; Gillow, J. B. Biodegradation of metal-citrate complexes and implications for toxic-metal mobility. *Nature* **1992**, *356*, 140–141.

(32) Francis, A. J.; Dodge, C. J.; Meinken, G. E. Biotransformation of pertechnetate by clostridia. *Radiochim. Acta* **2002**, *90*, 791–797.

(33) Haas, J. R.; Northup, A. Effects of aqueous complexation on reductive precipitation of uranium by *Shewanella putrefaciens*. *Geochem. Trans.* **2004**, *5*, 41–48.

(34) Rihs, S.; Sturchio, N. C.; Orlandini, K.; Cheng, L. W.; Teng, H.; Fenter, P.; Bedzyk, M. J. Interaction of uranyl with calite in the presence of EDTA. *Environ. Sci. Technol.* **2004**, *38*, 5078–5086.

(35) Sekine, T.; Asai, N.; Mine, T.; Yoshihara, K. Complexation of technetium traces with humic acid. *Radiochemistry* **1997**, *39*, 309–311.

(36) Maes, A.; Bruggeman, C.; Geraedts, K.; Vancluysen, J. Quantification of the interaction of Tc with dissolved boom clay humic substances. *Environ. Sci. Technol.* **2003**, *37*, 747–753.

(37) Maes, A.; Geraedts, K.; Bruggeman, C.; Vancluysen, J.; Rossberg, A.; Hennig, C. Evidence for the interaction of technetium colloids with humic substances by X-ray absorption spectroscopy. *Environ. Sci. Technol.* **2004**, *38*, 2044–2051.

(38) Gu, B.; Ruan, C. Determination of technetium and its speciation by surface enhanced Raman spectroscopy. *Anal. Chem.* **2007**, *79* 2341–2345.

(39) Boggs, M. A.; Dong, W.; Gu, B.; Wall, N. A. Complexation of Tc(IV) with acetate at varying ionic strengths. *Radiochim. Acta* **2010**, *98*, 583–587.

(40) Begg, J. D. C.; Burke, I. T.; Morris, K. The behaviour of technetium during microbial reduction in amended soils from Dounreay, UK. *Sci. Total Environ.* **2007**, *373*, 297–304.

(41) Maset, E. R.; Sidhu, S. H.; Fisher, A.; Heydon, A.; Worsfold, P. J.; Cartwright, A. J.; Keith-Roach, M. J. Effect of organic co-contaminants on technetium and rhenium speciation and solubility under reducing conditions. *Environ. Sci. Technol.* **2006**, *40* 5472–5477.

(42) Hess, N. J.; Xia, Y. X.; Rai, D.; Conradson, S. D. Thermodynamic model for the solubility of TcO₂·xH₍₂₎O(am) in the aqueous Tc(IV)-Na⁺-Cl⁻-H⁺-OH⁻-H₂O system. *J. Sol. Chem.* **2004**, *33*, 199–226.

(43) Boggs, M. A.; Minton, T.; Lomasney, S.; Islam, M. R.; Dong, W.; Gu, B.; Wall, N. A. Interactions of Tc(IV) with humic substances. *Environ. Sci. Technol.* **2011**, *45*, 2718–2724.

(44) Chen, J.; Gu, B.; LeBoeuf, E. J.; Pan, H.; Dai, S. Spectroscopic characterization of the structural and functional properties of natural organic matter fractions. *Chemosphere* **2002**, *48*, 59–68.

(45) Gu, B.; Yan, H.; Zhou, P.; Watson, D.; Park, M.; Istok, J. D. Humics impact uranium bioreduction and oxidation. *Environ. Sci. Technol.* **2005**, *39*, 5268–5275.

(46) Luo, W.; Gu, B. Dissolution and mobilization of uranium in a reduced sediment by natural humic substances under anaerobic conditions. *Environ. Sci. Technol.* **2009**, *43*, 152–156.

(47) Xia, Y. X.; Hess, N. J.; Felmy, A. R. Stability constants of technetium(IV) oxalate complexes as a function of ionic strength. *Radiochim. Acta* **2006**, *94*, 137–141.

(48) Choppin, G. R. The role of natural organics in radionuclide migration in natural aquifer systems. *Radiochim. Acta* **1992**, *58–9*, 113–120.

(49) Schwochau, K.; Pleger, U. Basic coordination chemistry of technetium. *Radiochim. Acta* **1993**, *63*, 103–110.

4776

dx.doi.org/10.1021/es200110y |*Environ. Sci. Technol.* 2011, 45, 4771–4777

(50) Schwochau, K. *Technetium. Chemistry and radiopharmaceutical applications*; Wiley−VCH: Weiheim, Germany, 2000.

(51) Stalmans, M.; Maes, A.; Cremers, A. Chapter 9. Role of organic matter as a geochemical sink for technetium in soils and sediments. In *Technetium in the Environment*; Demet, G., Myttenaere, C., Eds.; Elsevier: London, 1986.

(52) Zhou, P.; Yan, H.; Gu, B. Competitive complexation of metal ions with humic substances. *Chemosphere* **2005**, *58*, 1327–1337.

(53) Lovley, D. R.; Blunt-Harris, E. L. Role of humic-bound iron as an electron transfer agent in dissimilatory Fe(III) reduction. *Appl. Environ. Microbiol.* **1999**, *65*, 4252–4254.

(54) Chen, J.; Gu, B.; Royer, R. A.; Burgos, W. D. The roles of natural organic matter fractions in chemical and microbial reduction of ferric iron. *Sci. Total Environ.* **2003**, *307*, 167–178.

(55) Voelker, B. M.; Sulzberger, B. Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide. *Environ. Sci. Technol.* **1996**, *30* 1106–1114.

(56) Gu, B.; Schmitt, J.; Chen, Z.; Liang, L.; McCarthy, J. F. Adsorption and desorption of different organic matter fractions on iron oxide. *Geochim. Cosmochim. Acta* **1995**, *59*, 219–229.