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Biogeochemical Redox Processes and their Impact on Contaminant Dynamics

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Life and element cycling on Earth is directly related to electron transfer (or redox) reactions. An understanding of biogeochemical redox processes is crucial for predicting and protecting environmental health and can provide new opportunities for engineered remediation strategies. Energy can be released and stored by means of redox reactions via the oxidation of labile organic carbon or inorganic compounds (electron donors) by microorganisms coupled to the reduction of electron acceptors including humic substances, iron-bearing minerals, transition metals, metalloids, and actinides. Environmental redox processes play key roles in the formation and dissolution of mineral phases. Redox cycling of naturally occurring trace elements and their host minerals often controls the release or sequestration of inorganic contaminants. Redox processes control the chemical speciation, bioavailability, toxicity, and mobility of many major and trace elements including Fe, Mn, C, P, N, S, Cr, Cu, Co, As, Sb, Se, Hg, Tc, and U. Redox-active humic substances and mineral surfaces can catalyze the redox transformation and degradation of organic contaminants. In this review article, we highlight recent advances in our understanding of biogeochemical redox processes and their impact on contaminant fate and transport, including future research needs.

Introduction

The biogeochemical cycles of many major and trace elements are driven by redox processes. Examples include the cycles of carbon (C), nitrogen (N), sulfur (S), iron (Fe), and manganese (Mn), as well as those of redox-sensitive trace elements such as arsenic (As), chromium (Cr), copper (Cu), and uranium (U). The chemical speciation, bioavailability, toxicity, and mobility of these elements in the environment are directly affected by reduction and oxidation. In addition, the biogeochemical behavior of other not redox-active elements and compounds may be indirectly coupled to redox transformations of natural organic matter (NOM) and mineral phases, in particular (hydr)oxides of iron (Fe) and manganese (Mn), Fe-bearing clay minerals, and Fe sulfides. Redox-active functional groups associated with humic substances and mineral surfaces can further catalyze the oxidation or reduction of ions and molecules, including many organic contaminants (*1*−*6*). Redox processes may also provide new opportunities for engineered remediation strategies, such as the in situ microbial degradation of organic solvents and reductive sequestration of U from groundwater (*6*). Thus, understanding the biogeochemical processes at environmental redox interfaces is crucial for predicting and protecting water quality and ecosystem health (e.g., (*1*)).

In this article, we present an overview of important biogeochemical redox processes that impact contaminant dynamics, highlighting recent developments and future research needs in this field.

Major Elements, Minerals, and Humic Substances

All life on Earth derives energy from redox processes. Biomass production further requires the transfer of electrons to bring carbon, macronutrients (N and S), and micronutrients (e.g., Fe, Mn) into the proper oxidation states for incorporation in biomolecules. Over Earth's history, biological redox activity has caused the appearance of a highly oxidizing surface environment overlying a sedimentary cover rich in highly reduced biogenic products, such as organic matter, sulfide minerals, and methane. Along this global redox gradient, the numerous potential combinations of electron donors, electron acceptors, and carbon sources have given rise to a tremendous ecological and metabolic diversity of microorganisms, which we are still in the process of discovering (*7*). Redox gradients in time and space can be found, for example, in poorly drained or groundwater-fed soils, riparian zones, coastal marshes, shallow aquifers, contaminant plumes, lakes, and estuaries. The sequence of redox reactions that occurs along redox gradients in time or space depends on chemical

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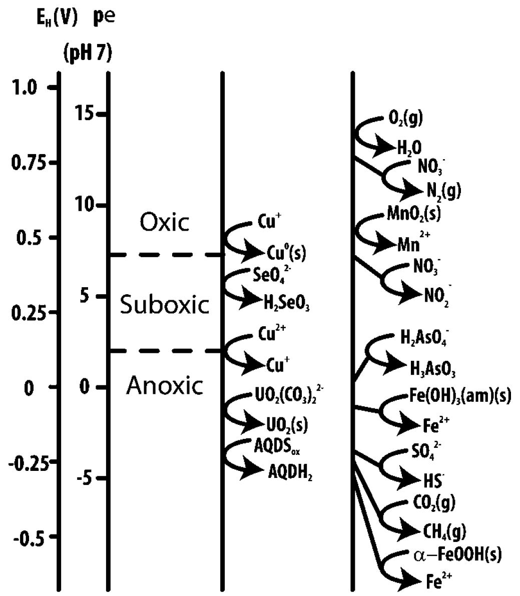

FIGURE 1. Redox ladder showing examples of environmentally relevant redox couples. Couples were calculated at pH 7 using standard techniques. Concentrations of all dissolved constituents in each half reaction are 1 M except for Fe^{2+} (1×10^{-5} M), U^{6+} (1×10^{-6} M), and CO_3^{2-} (3×10^{-3} M).

composition, microbial activity, and the reduction potentials of relevant redox couples, for which some examples are illustrated in Figure 1.

The carbon cycle is driven by oxygenic photosynthesis, which fixes CO_2 by removing electrons from water, thereby producing O_2. Anoxygenic photosynthesis and chemolithoautotrophic carbon fixation may be locally important sources of biomass, especially in more extreme environments (*8, 9*). Sequestration of organic matter and other biologically derived reduced materials, for example the mineral pyrite (FeS_2), in sedimentary deposits and their subsequent uplift and oxidative weathering at the Earth's surface are key processes controlling the composition of the atmosphere, and hence Earth's climate, on geological time scales (*10*).

The behavior of N and P in the environment is closely linked to redox processes of carbon. Nitrogen exhibits a variety of oxidation states; many of its redox transformations, e.g., nitrogen fixation, nitrification, denitrification, dissimilatory nitrate reduction to ammonium and anammox, are carried out by microorganisms. These microbial processes affect nitrogen availability, and therefore organic matter production and recycling, from local to global scales (*11*). Links also exist between the redox cycle of N and those of Fe, S, P, and trace elements. For example, denitrification coupled to pyrite oxidation can be an important nitrate removal pathway in fertilizer-impacted aquifers (*12*). However, the sulfate produced by this process may fuel microbial sulfate reduction, which, in turn, may lead to the reductive dissolution of Fe(III) (hydr)oxides by sulfide, thereby releasing sorbed phosphate. When the phosphate-rich groundwater subsequently discharges into a surface water body, it may cause eutrophication (*13*). This example illustrates the highly coupled nature of biogeochemical redox cycles.

As the most abundant transition metal on the Earth's surface, iron plays a particularly important role in environmental biogeochemistry. The oxidized form of iron (Fe(III)) is soluble under extremely acidic conditions but Fe(III) precipitates as Fe(III) (hydr)oxides in near-neutral pH environments. Many nutrients, trace elements, and contaminants strongly sorb to these Fe(III) minerals. Surfaces of Fe(III) (hydr)oxides also catalyze many environmentally important redox transformations (Table 1). Under reducing conditions, Fe(III) (hydr)oxides can be reduced abiotically, e.g., by sulfide (*14*), thereby releasing potentially harmful sorbates. In addition, Fe(III) minerals may serve as terminal electron acceptors to dissimilatory iron-reducing bacteria. These organisms, which are ubiquitous in freshwater and marine environments, are able to couple the cytoplasmic oxidation of organic compounds or hydrogen to the extracellular reduction of poorly soluble Fe(III) minerals, hence gaining energy for growth via electron transport phosphorylation (*15*). Reduction of Fe(III) minerals produces soluble Fe(II) and a wide range of secondary minerals, including Fe(II) minerals (e.g., vivianite ($Fe_3(PO_4)_2$) and siderite ($FeCO_3$)), Fe(III) minerals (e.g., goethite), and mixed Fe(II)−Fe(III) minerals (e.g., magnetite (Fe_3O_4) and green rusts (Fe(II)−Fe(III) layered double hydroxides)). Dissolved, adsorbed, and solid-state Fe(II) can act as powerful reductants in a variety of abiotic redox processes (*16, 17*).

Oxidation of Fe(II) may be mediated by aerobic and anaerobic bacteria. Microbial Fe(II) oxidation is common in low pH environments where chemical oxidation is not favorable. Under near-neutral pH conditions, aerobic Fe(II)-oxidizing bacteria have to compete with the rapid chemical oxygenation of Fe(II). Therefore, they thrive mainly at the low levels of oxygen typically encountered at oxic−anoxic interfaces (*18*), e.g., around plant roots in waterlogged soils. Phototrophic and nitrate-dependent Fe(II)-oxidizing bacteria mediate Fe(II) oxidation in neutrophilic, anoxic environments, where nitrite and Mn(IV) oxides can serve as chemical oxidants for Fe(II) (*19*).

Manganese oxide minerals commonly occur in the environment as coatings and fine-grained aggregates (*20*). Because of their large surface areas they exert chemical influences far out of proportion to their abundance. Manganese oxides are potent sorbents of heavy metals and nutrients, serving as natural sinks for contaminants. Additionally, they participate in a wide variety of environmental redox reactions; for example, birnessite (δ-MnO_2) directly oxidizes Se(IV) to Se(VI), Cr(III) to Cr(VI), and As(III) to As(V) (*20*). Mn(II) oxidation occurs in a wide array of environments and may be catalyzed by a variety of bacteria and fungi (*21, 22*). The initial products of biological Mn(II) oxidation are generally poorly crystalline, layered Mn(IV) oxide minerals, although the final mineral form is often determined by the geochemical conditions during and after Mn(II) oxidation (*23*). Biologically mediated Mn(II) oxidation is thought to be the major source of environmental manganese oxides (*24, 25*).

The structure and reactivity of Fe(III) and Mn(III, IV) mineral surfaces in natural waters are influenced by inorganic sorbates and natural organic matter (NOM) (*2, 26, 27*). Humic substances are redox-active and can be reduced by microorganisms. They can stimulate microbial reduction of poorly soluble Fe(III) minerals by acting as electron shuttles between cell and mineral (*28*). Strong adsorption of NOM, phosphate, and bicarbonate to Fe(III) and Mn(IV) mineral surfaces may cause a release of sorbed pollutants, but may also restrict access of the minerals to microorganisms, thereby protecting the solid phases against enzymatic reduction (*27*). Humic substances further influence the formation (biomineralization) of Fe and Mn minerals, through complexation and solubilization of the metal ions and by sorption to the mineral surface, generally causing less crystalline minerals to form (*29, 30*).

Impact on Trace Elements

Trace Metals. Metal mining, smelting, industrial processing, and waste disposal result in trace metal inputs into the environment. In particular, mine drainage and wastewater discharge have caused widespread contamination of redox-dynamic aquatic environments such as river floodplains. Some trace metals, such as Cr, Cu, Co, Ag, Tc, and Hg, may exist in several oxidation states (Table 1). Their reductive transformation may proceed chemically, for example Cu(II) reduction to Cu(I) by Fe^{2+} (*31*) or H_2S (*32*) and reduction of Cu(II), Ag(II), and Hg(II) to elemental forms by Fe(II)-bearing green-rust (*33*). Alternatively, microorganisms may directly reduce a wide range of even highly toxic metals (e.g., Cr, Hg, U) via dissimilatory or detoxification pathways (*34*). For instance, recent work based on the use of XAS and TEM has shown the formation of metallic Cu in a contaminated riparian soil during flooding, possibly as a result of bacterial detoxification (*35, 36*). The reduction of trace metals may either cause a decrease in mobility, as in the case of the reduction of soluble Cr(VI) to sparingly soluble Cr(III), or an increase, as in the case of Hg(II) reduction to volatile Hg(0) (*34*).

Microbial respiration indirectly influences the speciation of trace metals via changes in sorption and precipitation equilibria as well as solid-solution partitioning of metal-binding NOM. As documented for the microbial reduction of Co(III)- and Ni(II)-containing goethite (*37*), the reductive dissolution of metal oxides may result in the loss of sorption capacity. At the same time, the released Fe^{2+} may compete with trace metal cations for sorption to mineral and organic sorbents (*36*). Such mobilizing effects may be counteracted by trace metal adsorption or coprecipitation with newly formed Fe(II)-bearing precipitates, including siderite, vivianite (*37*), and green rust (*38*), whose formation is promoted by increasing Fe^{2+}, carbonate, or phosphate concentrations resulting from microbial respiration (*27, 39, 40*).

Microbial sulfate reduction may lead to the precipitation of chalcophilic metals as poorly soluble metal sulfides (*39*). In sulfur-rich sediments, trace metals may either coprecipitate with Fe-sulfides or form distinct metal sulfides (*41*). In contaminated freshwater wetlands, however, the availability of chalcophile metals may often exceed that of reducible sulfate, and trace metal dynamics may be strongly affected by competitive precipitation with biogenic sulfide (*36*). In contrast to the precipitation of poorly soluble metal sulfides, the formation of metal sulfide clusters may significantly enhance metal mobility in anoxic environments and, due to their kinetic stability, may persist in oxic water bodies (*42*). Sulfate reduction in a contaminated riparian soil was recently shown to mobilize Cu, Pb, and Cd through the formation of Cu-rich sulfide colloids (*35*), supporting the notion that colloidal metal sulfides may enhance contaminant mobility in aquatic and subsurface environments (*43*).

Biogeochemical oxidation processes are driven by O_2 entering anoxic systems. Certain oxidation processes such as Fe(II) oxidation by O_2 at neutral to alkaline pH proceed rapidly abiotically, but many slower processes are driven by chemotrophic microorganisms. Precipitation of Fe-, Mn-, and Al-(hydr)oxides may efficiently capture dissolved trace metals (*44*). If the precipitates formed during oxidative precipitation are nanoparticulate and colloidal, they may greatly enhance the mobility of associated trace metals in aquatic (*45*) and subsurface environments (*46*). In light also of the recent identification of the potential importance of colloidal metal sulfides, it appears that periodic generation of metal-bearing colloids may strongly affect trace metal mobility in redox-dynamic environments.

Metalloids. Biogeochemical redox processes strongly influence the environmental fate of metalloids such as arsenic (As) and antimony (Sb). Whereas As has by far received the most attention during the last two decades due to the worldwide health impacts of As contaminated drinking water and soils (*47*), Sb may locally represent an important contaminant, for instance in the vicinity of copper and lead ore smelters (*48*) or at shooting range sites due to the weathering of bullets (*49*). Oxidation of Sb(0) to Sb(III) or Sb(V), as well as sorption to Fe (hydr)oxides, controls the toxicity and mobility of Sb at these sites (*50*).

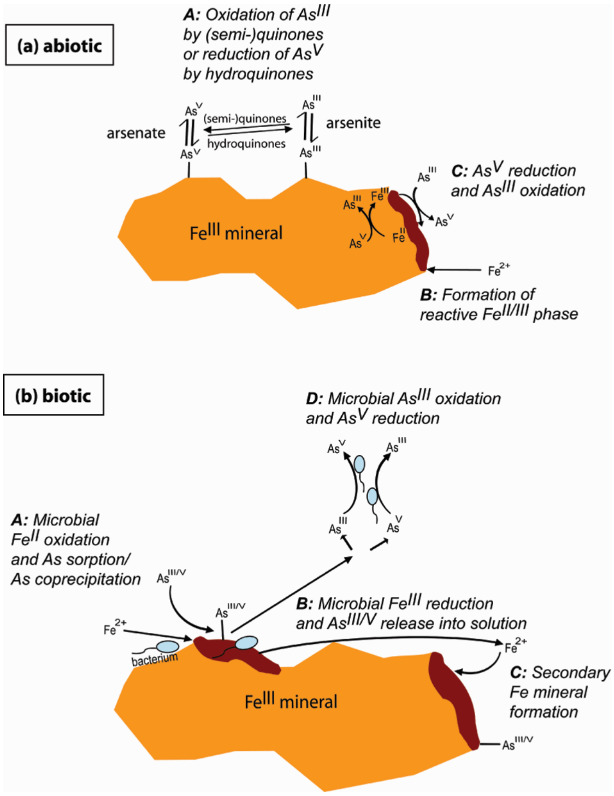

FIGURE 2. Conceptual model showing selected (a) abiotic and (b) biotic redox processes that influence the fate of arsenic in the environment. Abiotic processes include (A) oxidation of As^{III} and reduction of As^{V} (dissolved or surface-bound) by semiquinones and hydroquinones, respectively (as present, e.g., in humic substances) and (B) formation of reactive $Fe^{II/III}$ mineral phases (e.g., by microbially produced Fe^{2+}) that can lead to As^{V} reduction or As^{III} oxidation as illustrated in (C). Biotic processes include (A) microbial oxidation of Fe^{II} leading to Fe^{III} mineral formation and sorption or coprecipitation of As^{III} or As^{V} to/with these Fe^{III} minerals (oxidation of Fe^{II} can also occur abiotically), (B) microbial reduction of As-loaded Fe^{III} minerals leading to release of As^{III} or As^{V} into solution, (C) formation of secondary Fe minerals by reaction of microbially released Fe^{2+} with remaining Fe^{III} minerals leading to sorption/coprecipitation of As, and finally (D) direct microbial oxidation of As^{III} or reduction of As^{V} for either dissimilation or detoxification.

The drilling of millions of shallow tube wells in Bangladesh and West Bengal may have induced hydrological and biogeochemical changes in shallow aquifers, potentially contributing to As release into the groundwater. However, the exact release mechanisms of As in aquifers are still a subject of current research. The mobility, bioavailability, toxicity, and environmental fate of As are controlled by biogeochemical transformations that either form or destroy As-bearing carrier phases, or modify the redox state and chemical speciation of As (Figure 2, Table 1 and (*51*)). Dissolved arsenic concentrations in the groundwater are intimately related to the presence of poorly soluble iron (hydr)oxides that strongly sorb both arsenite (As(III)) and arsenate (As(V)) (*52*). The simultaneous presence of high dissolved As and Fe(II) concentrations in anoxic groundwater has led to the conclusion that reductive dissolution of As-rich Fe(III) (hydr)oxides mobilizes geogenic As (Figure 2 and (*53*)). More recently, it has been shown in laboratory experiments that microbial sulfide formation in As−ferrihydrite systems leads to transformation and dissolution of the As-

TABLE 1. Overview of Elements/Compounds Covered in This Article, Their Major Oxidation States, and Common Reduction/Oxidation Pathways

element	oxidation states[a,b,c]	common oxidation mechanism[d]	common reduction mechanism[d]	element-specific comments
nonmetals				
S	−2, −1, 0, 4, 6^{c}	A, B	B (Dis) by sulfate-reducing bacteria	essential nutrient for all organisms, forms sulfide minerals with chalcophile metals
Se	−2, 0, 4^{b}, $6^{b,c}$	A (e.g., Mn oxides), B (slow)	A (e.g., Fe(II)), B (Dis, Det)	analog of S. Essential nutrient for animals and humans, but not all plants. ^{79}Se is important in long-lived radioactive waste
transition metals				
Fe	2^{c}, 3	A (mainly at neutral and alkaline pH), B (at low and neutral pH; under oxic and anoxic conditions)	A (in presence of sulfide or reduced humics), B (Dis)	Fe(III/II)-(hydr)oxides are important sorbents and surface catalysts of redox reactions
Mn	2, 3, 4	A (mainly at alkaline pH), B (acidic to neutral pH)	B (Dis)	Mn(IV/III)-(hydr)oxides are important sorbents and surface catalysts of redox reactions
Co	$2^{b,}$ 3	A (e.g., Mn oxides)	B (Dis)	can be component of radionuclide contamination
Cu	0, 1, 2	A	A (e.g., Fe^{2+}, organic acids), B (Cu(I) in cells, Cu(0) biomineralization)	mostly Cu(II) in oxic environments, essential nutrient; rather toxic for microorganisms; used as biocide
Cr	3, $6^{b,c}$	A (MnO_2)	A (Fe(II), Fe^{2+}, S^{2-}, reduced organics), B (Dis)	often an industrial byproduct; Cr(III) is naturally enriched in serpentinites
Hg	$0^{b,c,}$ $1^{b,c,}$ $2^{b,c}$	A	A, B	highly toxic, especially methyl mercury, which bioaccumulates in the food chain
Tc	4^{b}, $7^{b,c}$	A (O_2, NO_3^-, Mn(IV) oxides)	A (Fe(II), Fe^{2+}, S^{2-}, reduced organics), B (Dis)	most common at (former) nuclear weapon production sites
metalloids				
As	−3, −2, −1, 0, 1, $3^{b,c}$, 5^{b}	A (O_2/MnO_2; O_2/Fe(II); Fe(IV) via H_2O_2 Fenton reactions), B (O_2, NO_3^-, phototrophic	A (sulfide, mainly at moderately acidic conditions), B (Det, Dis)	a major drinking water contaminant in southeast Asia
Sb	0, 3^{b}, $5^{b,c}$	A, B (similar to As)	A (e.g., by green rust, magnetite, thiol-compounds), B (during biomethylation)	common contaminant at firing ranges, used in flame retardants
actinides				
U	4^{b}, $6^{b,c}$	A (O_2, NO_3^-, Mn(IV) oxides, Fe (hydr)oxides), B (NO_3^-)	A (Fe(II), S^{2-}, reduced organics), B (Dis)	most common at mining sites and nuclear weapon production sites
Pu	$3^{b,c}$, 4^{b}, 5^{b}, $6^{b,c}$	A (Mn(IV) oxides)	A (Fe(II), S^{2-}, reduced organics), B (Dis)	most common at (former) nuclear weapon production sites
organics				
carbon tetrachloride	NA	A (photocatalytic)	A (e.g., reduced humics, sulfide, FeS, Fe(II)/Fe(III) systems, zerovalent iron), B	common groundwater contaminant
nitrobenzene	NA	A (ozone; photocatalytic; Fenton), B (aerobic)	A (e.g., Fe(II)/Fe(III) systems, reduced clays, zerovalent iron), B	common at former monition productions sites

[a] Only major oxidation states relevant for the environment. [b] Generally most toxic. [c] Generally most mobile. [d] Abiotic (A), biotic (B), detoxification (Det), dissimilatory (Dis).

bearing ferrihydrite (*54*). During this process, the arsenic repartitioned among secondary mineral phases and was associated with magnetite and residual ferrihydrite but not with green rust and iron sulfide. Direct reduction of Fe(III) by microorganisms can lead to As sequestration by sorption of As onto secondary Fe minerals (Figure 2 and (*40*)). When the aquifer sediment is rich in Fe(III) hydroxides, only sustained, long-term reducing conditions are likely to lead to complete depletion of sorbent phases, with subsequent As mobilization.

Abiotic and microbial Fe(II) oxidation under oxic conditions at circumneutral pH produces poorly soluble Fe(III) minerals that efficiently sequester metalloids such as arsenic (Figure 2 and (*55*)). However, anoxygenic phototrophic, as well as nitrate-reducing, Fe(II)-oxidizing bacteria are also able to tolerate high As concentrations and provide alternative pathways for the coprecipitation of As with Fe(III) minerals of variable crystallinity (*56*). Overall, the mobility of arsenic appears to be controlled by a fine balance between the biogeochemical redox transformations of Fe(III) and Fe(II).

The mobility and toxicity of arsenic is not only influenced by the presence of suitable sorbents, but also by its redox speciation, with arsenite generally considered to be more mobile and toxic than its oxidized counterpart arsenate. Microbial reduction of As(V) to As(III) has been proposed to contribute to arsenic mobilization (*57*) although this may not be universally true (*58*). Several biogeochemical processes can directly or indirectly lead to redox transformations of arsenic (Figure 2). Abiotic oxidation of As(III) has, for example, been observed at reactive iron barriers (*59*), in Fe(II)-goethite systems (*60*), or in the presence of Fe(IV) formed by H_2O_2-dependent Fenton reactions (*61*). Bacteria can also control arsenic mobility and toxicity directly by changing the redox state of arsenic via As(V) reduction and As(III) oxidation. These microbially catalyzed arsenic redox transformations can be part of dissimilatory processes or reflect microbial detoxification mechanisms (*62, 63*). Microorganisms may further indirectly induce As(III) oxidation or As(V) reduction. In particular, they can produce reactive organic or inorganic compounds that subsequently undergo redox reactions with As(V) or As(III). It was recently demonstrated that semiquinone radicals and hydroquinones in humic substances and humic−quinone model compounds can oxidize As(III) to As(V) and reduce As(V) to As(III), respectively (*64, 65*). Such semiquinone and hydroquinone species are produced during microbial reduction of humic substances, a process that plays an important role in electron shuttling during microbial Fe(III) mineral reduction. Additionally, it is conceivable that the As redox state can be changed by reactive Fe(II)−Fe(III) mineral systems as observed, for example, in As(III) oxidation by Fe(II)-goethite systems (*60*). These reactive Fe-phases can form when Fe(II) produced during microbial Fe(III) mineral reduction sorbs to remaining Fe(III) minerals. Such reactive systems were shown to be able to reductively transform metal ions such as U(VI) (*66*).

Radionuclides. Radionuclides represent a serious long-term environmental problem (*67, 68*). In the United States alone, radionuclide contamination is spread across 120 sites in 36 states and territories, with more than 3 million cubic meters of buried waste and an estimated 475 billion gallons of affected groundwater plus 75 million cubic meters of contaminated sediments (*67*). Globally, more than 2×10^9 tons of U contaminated mine-tailings pose a massive, long-term threat to human health (*69*). Uranium contamination of ground and surface waters has been detected at numerous locations, including agricultural evaporation ponds (*70*), nuclear weapons manufacturing areas, and mine tailings sites (*68*). Additional radionuclides of concern include technetium (Tc) and plutonium (Pu).

In oxic environments, uranium is generally present in the hexavalent oxidation state as the uranyl [$U(VI)O_2^{2+}$] species, which under most environmental conditions is quite soluble. The solubility of U(VI) is particularly enhanced by complexation with carbonate, a common groundwater ligand (*71*). Conversely, U(IV) is sparingly soluble, even in the presence of common groundwater ligands such as carbonate, and thus tends to be relatively immobile. In fact, in situ transformation of mobile U(VI) species into immobile uraninite ($U^{IV}O_2$) is being explored as a possible uranium remediation technique (*6, 72, 73*).

In low-temperature geochemical environments, the abiotic reduction of U(VI) may proceed via several pathways, albeit typically under a limited set of conditions (Table 1). In contrast, numerous common dissimilatory metal-reducing and sulfate-reducing microorganisms couple the oxidation of organic matter and H_2 to the reduction of U(VI), resulting in U(IV) and the subsequent precipitation of uraninite (*74*), a sparingly soluble phase. However, the presence of nitrate or Fe(III) (hydr)oxides as alternate electron acceptors and potential U(IV) oxidants impedes biological U(VI) reduction (*75*).

Potential UO_2 oxidants include molecular oxygen, nitrate, nitrate reduction intermediates, Mn(IV) (hydr)oxides, and Fe(III) (hydr)oxides (Figure 1). Oxidation of UO_2 may further be catalyzed by biological activity. Nitrate, a common co-contaminant with uranium (*68*), not only impedes biological uranium reduction (*76*), but may potentially oxidize U(IV). Uraninite oxidation by nitrate is thermodynamically favorable under typical environmental conditions, but tends to be kinetically limited (*76*). The biological transformation of NO_3^- into NO_2^-, NO, and N_2O increases the oxidation rate; however, the rate remains quite slow compared to U(IV) oxidation by Fe(III) and O_2. Although *Thiobacillus denitrificans* and *Geobacter metallireducens* are capable of catalyzing nitrate-dependent U(IV) oxidation, it is currently unknown if the bacteria obtain energy from this process (*77*). Furthermore, the indirect oxidation of U(IV) by nitrite through production of Fe(III) (hydr)oxides also increases the reaction rate. The redox couples for U(IV)/U(VI) and Fe(III) (hydr)oxide/Fe(II) occur at similar redox potentials under common groundwater conditions; therefore, small changes in aqueous and solid-phase chemistry can result in UO_2 oxidation by Fe(III) (hydr)oxide oscillating between thermodynamic viability and nonviability (*78*).

In contrast to U, the biogeochemical cycling of Pu and Tc remains poorly characterized. In environmental systems, technetium exists as either highly soluble Tc(VII) or relatively immobile Tc(IV). Under anoxic conditions many bacteria are capable of enzymatic reduction of Tc(VII) to Tc(IV), forming Tc(IV) oxides (*79*). Additionally, dissolved and adsorbed Fe(II) generated as a result of microbial iron respiration is a powerful Tc(VII) reductant; however, reoxidation of Tc(IV) by molecular oxygen may present a major obstacle to its reductive immobilization (*79*).

In the environment, Pu is commonly present as either Pu(III), Pu(IV), Pu(V), or Pu(VI) (*80*). Tetravalent Pu is generally considered to be the least mobile species and tri- and hexavalent Pu are the most mobile species, whereas Pu(V) is generally an ephemeral environmental species. Plutonium oxidation in the environment occurs predominantly by reaction with Mn(IV) minerals, which rapidly oxidize Pu(III), Pu(IV), and Pu(V) to Pu(VI) (*81*). Similarly to U, oxidized Pu(VI, V) species may be reduced to Pu(IV) or Pu(III), either chemically or by metal-reducing bacteria such as *Geobacter metallireducens* and *Shewanella oneidensis* (*80*).

Impact on Organic Contaminants

Organic contaminants are widely distributed in the environment and can come from various sources such as energy production (petroleum hydrocarbons), agriculture (pesticides), chemical industry (chlorinated solvents), or weapons production and use (explosives) (*82*). In addition, the "emerging" contaminants (e.g., pharmaceuticals, personal care products, and steroid hormones) have recently received a lot of attention (*83*).

Manganese and iron minerals as well as humic substances may significantly impact the fate of a multitude of organic pollutants via oxidative and reductive transformation processes. The pathways and rates of these processes depend on mineral type, solution chemistry, and microbial activity. The processes can also be engineered into remediation strategies, such as permeable reactive barriers (PRBs) to mitigate the spread of organic (and inorganic) contaminants in groundwater.

Several studies have demonstrated that, in contrast to pure aqueous Fe^{2+}, Fe(III) oxide phases such as hematite that have been reacted with Fe(II) can dramatically enhance the transformation rates of many reducible contaminants (*84*) such as nitroaromatics (*85, 86*), chlorinated solvents (*87*), pesticides (*88*), and disinfectants (*89*). The enhanced reactivity of Fe(III) oxide surfaces reacted with Fe(II) is poorly understood. In contrast to earlier suggestions of various surface complexation theories for the Fe(II) reactivity (*84*) it has now been shown that Fe(II) is oxidized to Fe(III) upon adsorption (*90*−*92*). Vikesland and Valentine examined the kinetics of the reactions between Fe(II) and monochloramine in the presence of a variety of iron oxide surfaces. The identity of the iron oxides was found to play a significant role in the rate of these reactions (*89*). In addition, the reduction of nitrobenzene by Fe(II)-reacted goethite only takes place in the presence of aqueous Fe(II) (*93*). Enhanced Fe(II) redox reactivity is not only observed in the presence of oxides, but also in the presence of other major iron minerals. Surface-area-normalized reaction rates for hexachloroethane and 4-chloronitrobenzene were found to increase in the order Fe(II) + siderite < Fe(II) + iron oxides < Fe(II) + iron sulfides (*84*). The particle size and aggregation state of magnetite have further been found to influence the reductive transformation of carbon tetrachloride (*94*). Finally, a recent study indicated that the Fe(II):Fe(III) stoichiometry of magnetite likely alters the bulk redox properties of the magnetite particle to make reduction of, for instance, nitrobenzene more favorable (*95*).

Bacteria are capable of reducing electron shuttles (e.g., humic substances) coupled to the anaerobic oxidation of organic contaminants such as toluene and vinyl chloride (*96*). Reduced electron shuttles can also transfer electrons to several distinct electron-withdrawing compounds, such as azo dyes, polyhalogenated compounds, and nitroaromatics (*96*). Reduced humic acids and model compounds (e.g., AQDS) of the hydroquinone moieties in organic matter have been reported to influence not only the reduction kinetics but also the degradation pathways of nitroaromatic compounds (*86, 96*).

In addition to transformation of contaminants by metal oxides and organic matter naturally occurring in the environment, PRBs represent a tested environmental remedial technology for treatment of polluted groundwater (*97*). Zero-valent iron (ZVI)-based PRBs have proven to be effective for removing multiple contaminants including halogenated organic solvents by reductive dechlorination (*98*). ZVI oxidation results in decreased PRB reactivity with time due to formation of passivating Fe (hydr)oxides. However, recent studies have shown the potential for improving the PRB performance by bioaugmentation with iron-reducing bacteria since they are able to solubilize precipitate layers by reducing ferric iron corrosion products to ferrous iron compounds, resulting in a reactivation of passivated iron surfaces (*99*).

In contrast to reductive treatment of organic contaminants by ZVI, permanganate is commonly used for in situ chemical oxidation of organic chemicals due to its stability, effectiveness over a wide pH range, ease of handling, and relatively low cost. Permanganate is capable of oxidizing a wide variety of organic contaminants such as 1,4-dioxane, methyl *t*-butyl ether, methyl ethyl ketone, explosives (e.g., TNT), pesticides (e.g., aldicarb and dichlorvos), substituted phenols (e.g., 4-nitrophenol), and chlorinated compounds (e.g., tetrachloroethene) (*100*). However, recent studies have shown that manganese oxides common in soils, such as birnessite, are also able to oxidize emerging contaminants such as antibacterial agents (i.e., phenols, fluoroquinolones, aromatic N-oxides, and tetracyclines), bisphenol A (an endocrine disrupting chemical used in plastic production), and 17α-ethynylestradiol (synthetic hormone used in contraceptive pills) (*101*−*103*).

Research Needs

Emerging interdisciplinary approaches in environmental biogeochemistry are advancing our ability to interpret and predict the fate and transport of contaminants and nutrients, in both natural and engineered systems. Despite the recent progress, we still face major challenges in unraveling and understanding the intricate and coupled environmental processes that control contaminant fate and transport. Some of these research needs are detailed below.

Instrumentation. The availability of synchrotron-based spectroscopy and mapping techniques has revolutionized the ability to study redox transformations at micrometer to molecular scales (*104*). In addition, various in situ electrode and gel probe techniques have been developed that permit the direct observation of redox gradients with minimal disturbance of the system of interest (e.g., *105, 106*). However, there is a constant need for new and improved instruments to allow detection of, for instance, redox-sensitive or ultratrace quantities of important species in the environment (e.g., (*107*)) or to provide means to unravel the fundamental mechanisms driving redox biogeochemistry, such as electron transfer pathways between microbial cells and minerals (*108, 109*).

Electron Transfer Mechanisms. The transfer of electrons from a donor to an acceptor is the basis for any redox process. However, the mechanisms and rates of electron transfer between microbes and minerals remain poorly characterized. The three major mechanisms are (i) direct transfer to mineral surface centers via outer-membrane cytochromes or, potentially, via conductive pili, (ii) electron shuttling, and (iii) ligand-mediated solubilization, as demonstrated for Fe(III) reduction by *Geothrix* species (*110*). An improved understanding of the microbial and environmental factors controlling the relative importance of these mechanisms will help in development of bioremediation strategies and prediction of natural attenuation processes.

Redox Activity of Humic Substances. It is known that many microorganisms can reduce humics substances and that reduced humics can transfer electrons to poorly and highly crystalline Fe(III) minerals (*26*). It remains unknown, however, if other minerals, such as Mn-oxides or clays, can be reduced by humics and thus indirectly serve as electron sink for microorganisms that can reduce humic substances. Additionally, it is unknown whether only dissolved NOM or also solid phase NOM can accept and transfer electrons. Particularly in organic-rich environments, such as soils, humic substances could be involved in extensive redox reaction networks to a far greater degree than currently recognized.

Contaminant Fate in Redox-Dynamic Systems. Much research has been dedicated to the development of the quantitative understanding of contaminant fate in fully oxic soils or permanently reducing subsurface environments. Far less research has addressed the biogeochemical functioning of environments characterized by fluctuating redox conditions. (Micro)biological communities, mineral assemblages, and transient redox species (e.g., molecular clusters) may be inherently different from those encountered in permanently oxic or anoxic environments. Therefore, the effects of transient redox changes at different time scales on contaminant transformations and transport warrant further study.

Scaling up of Molecular Level Processes. Advanced analytical tools allow for more detailed investigations at the (sub)cellular, molecular, and atomistic level, and thereby offer mechanistic insights into processes that affect contaminant fate at larger scales. However, a key research question remains how such detailed mechanistic knowledge can help advance quantitative models describing contaminant fate and transport at the field scale. The major challenge is to link detailed mechanistic studies to field observables. This will require multiscale sampling and monitoring of carefully selected field sites.

Modeling Complex Biogeochemical Environments. The increasing detail and resolution with which redox processes and microbial activity can be analyzed creates new challenges for the quantitative modeling of the biogeochemical functioning of environmental systems (*111*). The scaling up of microscale processes and reaction parameters is a crucial requirement if the newly acquired experimental knowledge is to be applied in the design and performance assessment of remediation technologies at the field scale. New developments in reactive transport modeling, for example, the use of pore-scale network models, or the application of homogenization theory, may help close the gap between laboratory and field investigations (*112, 113*).

Climate Change. Few studies have addressed the potential impact of climate change on the biogeochemical cycling of redox sensitive elements. Increased precipitation or flooding is expected to lead to a potential change in soil redox conditions. Intensification of the hydrologic regime will likely have important impacts on biogeochemical processes, contaminant behavior, and ecosystem services, but quantifying these impacts experimentally remains a key challenge.

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Literature Cited

(1) Polizzotto, M. L.; Kocar, B. D.; Benner, S. G.; Sampson, M.; Fendorf, S. Near-surface wetland sediments as a source of arsenic release to ground water in Asia. *Nature* **2008**, *454*, 505–508.

(2) Borch, T.; Fendorf, S. Phosphate interactions with iron (hydr)oxides: Mineralization pathways and phosphorus retention upon bioreduction. In *Adsorption of Metals by Geomedia II: Variables, Mechanisms, and Model Applications*, 1st ed.; Barnett, M. O., Kent, D. B., Eds.; Elsevier: Amsterdam, The Netherlands, 2008; Vol. 7, pp 321−348.

(3) Ginder-Vogel, M.; Borch, T.; Mayes, M. A.; Jardine, P. M.; Fendorf, S. Chromate reduction and retention processes within arid subsurface environments. *Environ. Sci. Technol.* **2005**, *39*, 7833–7839.

(4) Moberly, J.; Borch, T.; Sani, R.; Spycher, N.; Şengör, S.; Ginn, T.; Peyton, B. Heavy metal-mineral associations in Coeur d'Alene river sediments: A synchrotron-based analysis. *Water, Air Soil Pollut.* **2009**, *201*, 195–208.

(5) Kappler, A.; Haderlein, S. B. Natural organic matter as reductant for chlorinated aliphatic pollutants. *Environ. Sci. Technol.* **2003**, *37*, 2714–2719.

(6) Wu, W. M.; Carley, J.; Gentry, T.; Ginder-Vogel, M. A.; Fienen, M.; Mehlhorn, T.; Yan, H.; Caroll, S.; Pace, M. N.; Nyman, J.; Luo, J.; Gentile, M. E.; Fields, M. W.; Hickey, R. F.; Gu, B.; Watson, D.; Cirpka, O. A.; Zhou, J.; Fendorf, S.; Kitanidis, P. K.; Jardine, P. M.; Criddle, C. S. Pilot-scale in situ bioremedation of uranium in a highly contaminated aquifer. 2. Reduction of U(VI) and geochemical control of U(VI) bioavailability. *Environ. Sci. Technol.* **2006**, *40*, 3986–3995.

(7) DeLong, E. F.; Pace, N. R. Environmental diversity of bacteria and archaea. *Syst. Biol.* **2001**, *50*, 470–478.

(8) Overmann, J.; Manske, A. K., Anoxygenic phorotrophic bacteria in the Black Sea chemocline. In *Past and Present Water Column Anoxia*; Neretin, L. N., Ed.; Springer: Dordrecht, 2006.

(9) D'Hondt, S.; Rutherford, S.; Spivack, A. J. Metabolic activity of subsurface life in deep-sea sediments. *Science* **2002**, *295*, 2067–2070.

(10) Berner, R. A. A new look at the long-term carbon cycle. *GSA Today* **1999**, *9*, 1–6.

(11) Howarth, R. W. The Nitrogen Cycle. In *Encyclopedia of Global Environmental Change, Vol. 2, The Earth System: Biological and Ecological Dimensions of Global Environmental Change*; Wiley: Chichester, 2002; Vol. 2.

(12) Postma, D.; Boesen, C.; Kristiansen, H.; Larsen, F. Nitrate reduction in an unconfined sandy aquifer - water chemistry, reduction processes, and geochemical modeling. *Water Resour. Res.* **1991**, *27*, 2027–2045.

(13) Lucassen, E.; Smolders, A. J. P.; Van der Salm, A. L.; Roelofs, J. G. M. High groundwater nitrate concentrations inhibit eutrophication of sulphate-rich freshwater wetlands. *Biogeochemistry* **2004**, *67*, 249–267.

(14) Afonso, M. D.; Stumm, W. Reductive dissolution of iron(III) (hydr)oxides by hydrogen-sulfide. *Langmuir* **1992**, *8*, 1671–1675.

(15) DiChristina, T. J.; Fredrickson, J. K.; Zachara, J. M., Enzymology of electron transport: Energy generation with geochemical consequences. In *Molecular Geomicrobiology*; Mineralogical Society of America: Chantilly, VA, 2005; Vol. 59, pp 27−52.

(16) Liger, E.; Charlet, L.; Van Cappellen, P. Surface catalysis of uranium(VI) reduction by iron(II). *Geochim. Cosmochim. Acta* **1999**, *63*, 2939–2955.

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

(18) Druschel, G. K.; Emerson, D.; Sutka, R.; Suchecki, P.; Luther, G. W., III. Low-oxygen and chemical kinetic constraints on the geochemical niche of neutrophilic iron(II) oxidizing microorganisms. *Geochim. Cosmochim. Acta* **2008**, *72*, 3358–3370.

(19) Kappler, A.; Straub, K. L. Geomicrobiological cycling of iron. *Rev. Mineral. Geochem.* **2005**, *59*, 85–108.

(20) Post, J. E. Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 3447–3454.

(21) Miyata, N.; Tani, Y.; Maruo, K.; Tsuno, H.; Sakata, M.; Iwahori, K. Manganese(IV) oxide production by Acremonium sp strain KR21-2 and extracellular Mn(II) oxidase activity. *Appl. Environ. Microbiol.* **2006**, *72*, 6467–6473.

(22) Hastings, D.; Emerson, S. Oxidation of manganese by spores of a marine Bacillus - kinetic and thermodynamic considerations. *Geochim. Cosmochim. Acta* **1986**, *50*, 1819–1824.

(23) Webb, S. M.; Tebo, B. M.; Bargar, J. R. Structural characterization of biogenic Mn oxides produced in seawater by the marine bacillus sp strain SG-1. *Am. Mineral.* **2005**, *90*, 1342–1357.

(24) Tebo, B. M.; Bargar, J. R.; Clement, B. G.; Dick, G. J.; Murray, K. J.; Parker, D.; Verity, R.; Webb, S. M. Biogenic manganese oxides: Properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* **2004**, *32*, 287–328.

(25) Nealson, K. H.; Tebo, B. M.; Rosson, R. A. Occurrence and mechanisms of microbial oxidation of manganese. *Adv. Appl. Microbiol.* **1988**, *33*, 279–318.

(26) Bauer, I.; Kappler, A. Rates and extent of reduction of Fe(III) compounds and O_2 by humic substances. *Environ. Sci. Technol.* **2009**, *43*, 4902–4908.

(27) Borch, T.; Masue, Y.; Kukkadapu, R. K.; Fendorf, S. Phosphate imposed limitations on biological reduction and alteration of ferrihydrite. *Environ. Sci. Technol.* **2007**, *41*, 166–172.

(28) Kappler, A.; Benz, M.; Schink, B.; Brune, A. Electron shuttling via humic acids in microbial iron(III) reduction in a freshwater sediment. *FEMS Microbiol. Ecol.* **2004**, *47*, 85–92.

(29) Eusterhues, K.; Wagner, F. E.; Hausler, W.; Hanzlik, M.; Knicker, H.; Totsche, K. U.; Kögel-Knabner, I.; Schwertmann, U. Characterization of ferrihydrite-soil organic matter coprecipitates by X-ray diffraction and Mössbauer spectroscopy. *Environ. Sci. Technol.* **2008**, *42*, 7891–7897.

(30) Jones, A. M.; Collins, R. N.; Rose, J.; Waite, T. D. The effect of silica and natural organic matter on the Fe(II)-catalysed transformation and reactivity of Fe(III) minerals. *Geochim. Cosmochim. Acta* **2009**, *73*, 4409–4422.

(31) Matocha, C. J.; Karathanasis, A. D.; Rakshit, S.; Wagner, K. M. Reduction of copper(II) by iron(II). *J. Environ. Qual.* **2005**, *34*, 1539–1546.

(32) Pattrick, R. A. D.; Mosselmans, J. F. W.; Charnock, J. M.; England, K. E. R.; Helz, G. R.; Garner, C. D.; Vaughan, D. J. The structure of amorphous copper sulfide precipitates: An X-ray absorption study. *Geochim. Cosmochim. Acta* **1997**, *61*, 2023–2036.

(33) O'Loughlin, E. J.; Kelly, S. D.; Kemner, K. M.; Csencsits, R.; Cook, R. E. Reduction of Ag^{I}, Au^{III}, Cu^{II}, and Hg^{II} by Fe^{II}/Fe^{III} hydroxysulfate green rust. *Chemosphere* **2003**, *53*, 437–446.

(34) Lovley, D. R. Dissimilatory metal reduction. *Annu. Rev. Microbiol.* **1993**, *47*, 263–290.

(35) Weber, F.-A.; Voegelin, A.; Kaegi, R.; Kretzschmar, R. Contaminant mobilization by metallic copper and metal sulphide colloids in flooded soil. *Nature Geosci.* **2009**, *2*, 267–271.

(36) Weber, F.-A.; Voegelin, A.; Kretzschmar, R. Multi-metal contaminant dynamics in temporarily flooded soil under sulfate limitation. *Geochim. Cosmochim. Acta* **2009**, *73*, 5513–5527.

(37) Zachara, J. M.; Fredrickson, J. K.; Smith, S. C.; Gassman, P. L. Solubilization of Fe(III) oxide-bound trace metals by a dissimilatory Fe(III) reducing bacterium. *Geochim. Cosmochim. Acta* **2001**, *65*, 75–93.

(38) Parmar, N.; Gorby, Y. A.; Beveridge, T. J.; Ferris, F. G. Formation of green rust and immobilization of nickel in response to bacterial reduction of hydrous ferric oxide. *Geomicrobiol. J.* **2001**, *18*, 375–385.

(39) Kirk, G. *The Biogeochemistry of Submerged Soils*; John Wiley & Sons, Ltd: Chichester, 2004; p 282.

(40) Tufano, K. J.; Fendorf, S. Confounding impacts of iron reduction on arsenic retention. *Environ. Sci. Technol.* **2008**, *42*, 4777–4783.

(41) Morse, J. W.; Luther, G. W., III. Chemical influences on trace metal-sulfide interactions in anoxic sediments. *Geochim. Cosmochim. Acta* **1999**, *63*, 3373–3378.

(42) Luther III, G. W.; Rickard, D. T. Metal sulfide cluster complexes and their biogeochemical importance in the environment. *J. Nanoparticle Res.* **2005**, *7*, 389–407.

(43) Deonarine, A.; Hsu-Kim, H. Precipitation of mercuric sulfide nanoparticles in NOM-containing water: Implications for the natural environment. *Environ. Sci. Technol.* **2009**, *43*, 2368–2373.

(44) Lee, G.; Bigham, J. M.; Faure, G. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Appl. Geochem.* **2002**, *17*, 569–581.

(45) Hassellöv, M.; von der Kammer, F. Iron oxides as geochemical nanovectors for metal transport in soil-river systems. *Elements Mag.* **2009**, *4*, 401–406.

(46) Novikov, A. P.; Kalmykov, S. N.; Utsunomiya, S.; Ewing, R. C.; Horreard, F.; Merkulov, A.; Clark, S. B.; Tkachev, W.; Myasoedov, B. F. Colloid transport of plutonium in the far-field of the Mayak production association, Russia. *Science* **2006**, *314*, 638–641.

(47) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568.

(48) Krachler, M.; Zheng, J.; Koerner, R.; Zdanowicz, C.; Fisher, D.; Shotyk, W. In *Increasing Atmospheric Antimony Contamination in the Northern Hemisphere: Snow and Ice Evidence from Devon Island, Arctic Canada, 2005*; Royal Society of Chemistry: London, 2005; pp 1169−1176.

(49) Ackermann, S.; Giere, R.; Newville, M.; Majzlan, J. Antimony sinks in the weathering crust of bullets from Swiss shooting ranges. *Sci. Total Environ.* **2009**, *407*, 1669–1682.

(50) Scheinost, A. C.; Rossberg, A.; Vantelon, D.; Xifra, I.; Kretzschmar, R.; Leuz, A. K.; Funke, H.; Johnson, C. A. Quantitative antimony speciation in shooting-range soils by EXAFS spectroscopy. *Geochim. Cosmochim. Acta* **2006**, *70*, 3299–3312.

(51) Polizzotto, M. L.; Harvey, C. F.; Sutton, S. R.; Fendorf, S. Processes conducive to the release and transport of arsenic into aquifers of Bangladesh. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 18819–18823.

(52) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: Implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182–4189.

(53) Islam, F. S.; Gault, A. G.; Boothman, C.; Polya, D. A.; Charnock, J. M.; Chatterjee, D.; Lloyd, J. R. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. *Nature* **2004**, *430*, 68–71.

(54) Kocar, B. D.; Borch, T.; Fendorf, S. Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite. *Geochim. Cosmochim. Acta* **2010**, http://dx.doi.org/10.1016/j.gca.2009.10.023.

(55) Neubauer, S. C.; Emerson, D.; Megonigal, J. P. Microbial oxidation and reduction of iron in the root zone and influences on metal mobility. In *Biophysico-Chemical Processes of Heavy Metals and Metalloids in Soil Environments*; Violante, A., Huang, P. M., Gadd, G. M., Eds.; John Wiley and Sons: Hoboken, NJ, 2008; pp 339−371.

(56) Hohmann, C.; Winkler, E.; Morin, G.; Kappler, A. Anaerobic Fe(II)-Oxidizing Bacteria Show As Resistance and Immobilize As during Fe(III) Mineral Precipitation. *Environ. Sci. Technol.* **2009**; DOI: 10.1021/es900708s.

(57) Tufano, K. J.; Reyes, C.; Saltikov, C. W.; Fendorf, S. Reductive Processes Controlling Arsenic Retention: Revealing the Relative Importance of Iron and Arsenic Reduction. *Environ. Sci. Technol.* **2008**, *42*, 8283–8289.

(58) Campbell, K. M.; Root, R.; O'Day, P. A.; Hering, J. G. A gel probe equilibrium sampler for measuring arsenic porewater profiles and sorption gradients in sediments: II. Field application to Haiwee Reservoir sediment. *Environ. Sci. Technol.* **2008**, *42*, 504–510.

(59) Su, C. M.; Puls, R. W. Significance of iron(II, III) hydroxycarbonate green rust in arsenic remediation using zerovalent iron in laboratory column tests. *Environ. Sci. Technol.* **2004**, *38*, 5224–5231.

(60) Amstaetter, K.; Borch, T.; Larese-Casanova, P.; Kappler, A. Redox Transformation of Arsenic by Fe(II)-Activated Goethite (α-FeOOH). *Environ. Sci. Technol.* **2010**; DOI: 10.1021/es901274s.

(61) Hug, S. J.; Leupin, O. Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction. *Environ. Sci. Technol.* **2003**, *37*, 2734–2742.

(62) Oremland, R. S.; Stolz, J. F. Arsenic, microbes and contaminated aquifers. *Trends Microbiol.* **2005**, *13*, 45–49.

(63) Kulp, T. R.; Hoeft, S. E.; Asao, M.; Madigan, M. T.; Hollibaugh, J. T.; Fisher, J. C.; Stolz, J. F.; Culbertson, C. W.; Miller, L. G.; Oremland, R. S. Arsenic(III) fuels anoxygenic photosynthesis in hot spring biofilms from Mono Lake, California. *Science* **2008**, *321*, 967–970.

(64) Redman, A. D.; Macalady, D. L.; Ahmann, D. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **2002**, *36*, 2889–2896.

(65) Jiang, J.; Bauer, I.; Paul, A.; Kappler, A. Arsenic redox changes by microbially and chemically formed semiquinone radicals and hydroquinones in a humic substance model quinone. *Environ. Sci. Technol.* **2009**, *43*, 3639–3645.

(66) Jeon, B. H.; Dempsey, B. A.; Burgos, W. D.; Barnett, M. O.; Roden, E. E. Chemical reduction of U(VI) by Fe(II) at the solid−water interface using natural and synthetic Fe(III) oxides. *Environ. Sci. Technol.* **2005**, *39*, 5642–5649.

(67) Ginder-Vogel, M.; Fendorf, S. Biogeochemical Uranium Redox Transformation: Potential Oxidants of Uraninite. In *Adsorption of Metals by Geomedia II: Variables, Mechanisms, and Model Applications*; Barnett, M. O., Kent, D. B., Eds.; Elsevier: Amsterdam, The Netherlands, 2008; Vol. 7, pp 293−320.

(68) Riley, R. G.; Zachara, J. M. *Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research*; U.S. Dept. of Energy; U.S. Government Printing Office: Washington, DC, 1992.

(69) Diehl, P. WISE Uranium Project; http://www.wise-uranium.org/index.html.

(70) Bradford, G. R.; Bakhtar, D.; Westcot, D. Uranium, vanadium, and molybdenum in saline waters of California. *J. Environ. Qual.* **1990**, *19*, 105–108.

(71) Guillaumont, R.; Fanghanel, T.; Neck, V.; Fuger, J.; Palmer, D. A.; Grenthe, I.; Rand, M. H. *Update on the Chemical Thermodynamics of Uranium, Neptumium, Plutonium, Americium, and Technetium*; Elsevier: Amsterdam, The Netherlands, 2003.

(72) Wu, W. M.; Carley, J.; Fienen, M.; Mehlhorn, T.; Lowe, K.; Nyman, J.; Luo, J.; Gentile, M. E.; Rajan, R.; Wagner, D.; Hickey, R. F.; Gu, B.; Watson, D.; Cirpka, O. A.; Kitanidis, P. K.; Jardine, P. M.; Criddle, C. S. Pilot-scale in situ bioremediation of uranium in a highly contaminated aquifer. 1. Conditioning of a treatment zone. *Environ. Sci. Technol.* **2006**, *40*, 3978–3985.

(73) Wu, W. M.; Carley, J.; Luo, J.; Ginder-Vogel, M. A.; Cardenas, E.; Leigh, M. B.; Hwang, C.; Kelly, S. D.; Ruan, C.; Wu, L.; VanNostrand, J.; Gentry, T.; Lowe, K.; Mehlorn, T.; Carroll, S.; Luo, W.; Fields, M. W.; Gu, B.; Watson, D.; Kemner, K. M.; Marsh, T.; Tiedje, J.; Zhou, J.; Fendorf, S.; Kitanidis, P. K.; Jardine,

P. M.; Criddle, C. S. In situ bioreduction of uranium (VI) to submicromolar levels and reoxidation by dissolved oxygen. *Environ. Sci. Technol.* **2007**, *41*, 5716–5723.

(74) Gorby, Y. A.; Lovley, D. R. Enzymatic uranium precipitation. *Environ. Sci. Technol.* **1992**, *26*, 205–207.

(75) Stewart, B. D.; Nico, P. S.; Fendorf, S. Stability of uranium incorporated into Fe (Hydr)oxides under fluctuating redox conditions. *Environ. Sci. Technol.* **2009**, *43*, 4922–4927.

(76) Senko, J. M.; Mohamed, Y.; Dewers, T. A.; Krumholz, L. R. Role for Fe(III) minerals in nitrate-dependent microbial U(IV) oxidation. *Environ. Sci. Technol.* **2005**, *39*, 2529–2536.

(77) Beller, H. R. Anaerobic, nitrate-dependent oxidation of U(IV) oxide minerals by the chemolithoautotrophic bacterium *Thiobacillus denitrificans. Appl. Environ. Microbiol.* **2005**, *71*, 2170–2174.

(78) Ginder-Vogel, M.; Criddle, C. S.; Fendorf, S. Thermodynamic constraints on the oxidation of biogenic UO$_2$ by Fe(III) (hydr)oxides. *Environ. Sci. Technol.* **2006**, *40*, 3544–3550.

(79) Fredrickson, J. K.; Zachara, J. M.; Kennedy, D. W.; Kukkadapu, R. K.; McKinley, J. P.; Heald, S. M.; Liu, C.; Plymale, A. E. Reduction of TcO$_4$- by sediment-associated biogenic Fe(II). *Geochim. Cosmochim. Acta* **2004**, *68*, 3171–3187.

(80) Icopini, G. A.; Lack, J. G.; Hersman, L. E.; Neu, M. P.; Boukhalfa, H. Plutonium(V/VI) reduction by the metal-reducing bacteria *Geobacter metallireducens* GS-15 and *Shewanella oneidensis* MR-1. *Appl. Environ. Microbiol.* **2009**, *75*, 3641–3647.

(81) Powell, B. A.; Duff, M. C.; Kaplan, D. I.; Fjeld, R. A.; Newville, M.; Hunter, D. B.; Bertsch, P. M.; Coates, J. T.; Eng, P.; Rivers, M. L.; Sutton, S. R.; Triay, I. R.; Vaniman, D. T. Plutonium oxidation and subsequent reduction by Mn(IV) minerals in Yucca Mountain tuff. *Environ. Sci. Technol.* **2006**, *40*, 3508–3514.

(82) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley-Interscience: NJ, 2003; p 1313.

(83) Richardson, S. D. Water Analysis: Emerging Contaminants and Current Issues. *Anal. Chem.* **2009**, *81*, 4645–4677.

(84) Elsner, M.; Schwarzenbach, R. P.; Haderlein, S. B. Reactivity of Fe(II)-bearing minerals toward reductive transformation of organic contaminants. *Environ. Sci. Technol.* **2004**, *38*, 799–807.

(85) Heijman, C. G.; Holliger, C.; Glaus, M. A.; Schwarzenbach, R. P.; Zeyer, J. Abiotic reduction of 4-chloronitrobenzene to 4-chloroaniline in a dissimilatory iron-reducing enrichment culture. *Appl. Environ. Microbiol.* **1993**, *59*, 4350–4353.

(86) Borch, T.; Inskeep, W. P.; Harwood, J. A.; Gerlach, R. Impact of ferrihydrite and anthraquinone-2,6-disulfonate on the reductive transformation of 2,4,6-trinitrotoluene by a gram-positive fermenting bacterium. *Environ. Sci. Technol.* **2005**, *39*, 7126–7133.

(87) Amonette, J. E.; Workman, D. J.; Kennedy, D. W.; Fruchter, J. S.; Gorby, Y. A. Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environ. Sci. Technol.* **2000**, *34*, 4606–4613.

(88) Hakala, J. A.; Chin, Y. P.; Weber, E. J. Influence of dissolved organic matter and Fe(II) on the abiotic reduction of pentachloronitrobenzene. *Environ. Sci. Technol.* **2007**, *41*, 7337–7342.

(89) Vikesland, P. J.; Valentine, R. L. Iron oxide surface-catalyzed oxidation of ferrous iron by monochloramine: Implications of oxide type and carbonate on reactivity. *Environ. Sci. Technol.* **2002**, *36*, 512–519.

(90) Handler, R. M.; Beard, B. L.; Johnson, C. M.; Scherer, M. M. Atom exchange between aqueous Fe(II) and goethite: An Fe isotope tracer study. *Environ. Sci. Technol.* **2009**, *43*, 1102–1107.

(91) Yanina, S. V.; Rosso, K. M. Linked reactivity at mineral-water interfaces through bulk crystal conduction. *Science* **2008**, *320*, 218–222.

(92) Tanwar, K. S.; Petitto, S. C.; Ghose, S. K.; Eng, P. J.; Trainor, T. P. Fe(II) adsorption on hematite (0 0 0 1). *Geochim. Cosmochim. Acta* **2009**, *73*, 4346–4365.

(93) Williams, A. G. B.; Scherer, M. M. Spectroscopic evidence for Fe(II)−Fe(III) electron transfer at the iron oxide−water interface. *Environ. Sci. Technol.* **2004**, *38*, 4782–4790.

(94) Vikesland, P. J.; Heathcock, A. M.; Rebodos, R. L.; Makus, K. E. Particle size and aggregation effects on magnetite reactivity toward carbon tetrachloride. *Environ. Sci. Technol.* **2007**, *41*, 5277–5283.

(95) Gorski, C. A.; Scherer, M. M. Influence of magnetite stoichiometry on Fe^{II} uptake and nitrobenzene reduction. *Environ. Sci. Technol.* **2009**, *43*, 3675–3680.

(96) Van der Zee, F. P.; Cervantes, F. J. Impact and application of electron shuttles on the redox (bio)transformation of contaminants: A review. *Biotechnol. Adv.* **2009**, *27*, 256–277.

(97) Gillham, R. W.; Ohannesin, S. F. Enhanced degradation of halogenated aliphatics by zero-valent iron. *Ground Water* **1994**, *32*, 958–967.

(98) O'Hannesin, S. F.; Gillham, R. W. Long-term performance of an in situ "iron wall" for remediation of VOCs. *Ground Water* **1998**, *36*, 164–170.

(99) Van Nooten, T.; Springael, D.; Bastiaens, L. Positive impact of microorganisms on the performance of laboratory-scale permeable reactive iron barriers. *Environ. Sci. Technol.* **2008**, *42*, 1680–1686.

(100) Waldemer, R. H.; Tratnyek, P. G. Kinetics of contaminant degradation by permanganate. *Environ. Sci. Technol.* **2005**, *40*, 1055–1061.

(101) Lin, K.; Liu, W.; Gan, J. Oxidative removal of bisphenol A by manganese dioxide: efficacy, products, and pathways. *Environ. Sci. Technol.* **2009**, *43*, 3860–3864.

(102) de Rudder, J.; Van de Wiele, T.; Dhooge, W.; Comhaire, F.; Verstraete, W. Advanced water treatment with manganese oxide for the removal of 17 alpha-ethynylestradiol (EE2). *Water Res.* **2004**, *38*, 184–192.

(103) Zhang, H.; Chen, W.-R.; Huang, C.-H. Kinetic modeling of oxidation of antibacterial agents by manganese oxide. *Environ. Sci. Technol.* **2008**, *42*, 5548–5554.

(104) Hunter, R. C.; Hitchcock, A. P.; Dynes, J. J.; Obst, M.; Beveridge, T. J. Mapping the speciation of iron in *Pseudomonas aeruginosa* biofilms using scanning transmission x-ray microscopy. *Environ. Sci. Technol.* **2008**, *42*, 8766–8772.

(105) Krom, M. D.; Davison, P.; Zhang, H.; Davison, W. High-resolution pore-water sampling with a gel sampler. *Limnol. Oceanogr.* **1994**, *39*, 1967–1972.

(106) Tercier-Waeber, M. L.; Taillefert, M. Remote in situ voltammetric techniques to characterize the biogeochemical cycling of trace metals in aquatic systems. *J. Environ. Monit.* **2008**, *10*, 30–54.

(107) Planer-Friedrich, B.; London, J.; McCleskey, R. B.; Nordstrom, D. K.; Wallschlager, D. Thioarsenates in geothermal waters of Yellowstone National Park: Determination, preservation, and geochemical importance. *Environ. Sci. Technol.* **2007**, *41*, 5245–5251.

(108) Gorby, Y. A.; Yanina, S.; McLean, J. S.; Rosso, K. M.; Moyles, D.; Dohnalkova, A.; Beveridge, T. J.; Chang, I. S.; Kim, B. H.; Kim, K. S.; Culley, D. E.; Reed, S. B.; Romine, M. F.; Saffarini, D. A.; Hill, E. A.; Shi, L.; Elias, D. A.; Kennedy, D. W.; Pinchuk, G.; Watanabe, K.; Ishii, S. i.; Logan, B.; Nealson, K. H.; Fredrickson, J. K. Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. *Proc. Natl. Acad. Sci., U.S.A.* **2006**, *103*, 11358–11363.

(109) Geesey, G. G.; Borch, T.; Reardon, C. L. Resolving biogeochemical phenomena at high spatial resolution through electron microscopy. *Geobiology* **2008**, *6*, 263–269.

(110) Weber, K. A.; Achenbach, L. A.; Coates, J. D. Microorganisms pumping iron: anaerobic microbial iron oxidation and reduction. *Nat. Rev. Microbiol.* **2006**, *4*, 752–764.

(111) Steefel, C. I.; DePaolo, D. J.; Lichtner, P. C. Reactive transport modeling: An essential tool and a new research approach for the Earth sciences. *Earth Planet. Sci. Lett.* **2005**, *240*, 539–558.

(112) Attinger, S.; Dimitrova, J.; Kinzelbach, W. In *Homogenization of the Transport Behavior of Nonlinearly Adsorbing Pollutants in Physically and Chemically Heterogeneous Aquifers*; Elsevier Sci Ltd: 2009; pp 767−777.

(113) Raoof, A.; Hassanizadeh, S., A New Method for Generating Pore-Network Models of Porous Media. *Transp. Porous Med.* Published online: 29 May 2009, http://dx.doi.org/10.1007/s11242-009-9412-3.

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