J Soils Sediments (2012) 12:683–693
DOI 10.1007/s11368-012-0507-z

SOILS, SEC 1 • SOIL ORGANIC MATTER DYNAMICS AND NUTRIENT CYCLING • REVIEW ARTICLE

Are the biogeochemical cycles of carbon, nitrogen, sulfur, and phosphorus driven by the “Fe^{III}–Fe^{II} redox wheel” in dynamic redox environments?

Yichun Li · Shen Yu · James Strong · Hailong Wang

Received: 8 December 2011 / Accepted: 15 March 2012 / Published online: 30 March 2012

Abstract

Purpose Iron’s fluctuation between the II (ferrous) and III (ferric) oxidation states has been coined as the “Fe^{III}–Fe^{II} redox wheel.” Numerous studies have coupled the “iron redox wheel” with the biogeochemical cycle of carbon (C), nitrogen (N), sulfur (S), or phosphorus (P) individually in soils or sediments, but evidence suggests that the Fe^{III}–Fe^{II} redox wheel drives the biogeochemical cycles interactively in a fluctuating redox microenvironment. The interactions of the Fe^{III}–Fe^{II} redox wheel with the biogeochemical cycles of C, N, S, and P in the fluctuating redox environments were reviewed in this paper.

Discussion In this review, we discuss the importance of iron with regard to each of the biogeochemical cycles individually as well as interactively. The importance of crystalline and non-crystalline Fe^{III} (hydr)oxides is highlighted as they serve as terminal electron acceptors for organic matter mineralization and N and S transformation and also act as sorbents for dissolved P compounds. Mechanically, electron transfer from organic matter to Fe^{III} (hydr)oxides via organic matter oxidation, oxidation of NH_4^+ to NO_2^-, formation and oxidation of Fe sulfide minerals in the S cycle, and P transformation were discussed to couple with the Fe^{III}–Fe^{II} redox wheel.

Conclusions The knowledge gaps are identified at the end of the review. The natural environmental relationships still require further studies that link the iron redox wheel as a driver of the biogeochemical cycles of C, N, S, and P. Anthropogenically altered environments (nutrient and metal elevation, global warming, and acidification) require intensive studies to allow for improved integrated modeling of global C, N, S, and P biogeochemical cycles driven by the Fe^{III}–Fe^{II} redox wheel.

Keywords Biogeochemical cycles · Fe^{III}–Fe^{II} redox wheel · Ferric · Ferrous · Oxidation · Reduction

1 Introduction

The iron (Fe) redox cycle refers ferrous iron (Fe^{II}) oxidation and ferric iron (Fe^{III}) reduction, referred to as the “Fe^{III}–Fe^{II} redox wheel” in this review, which is driven by ambient E_h/pH and microbial activity in a natural environment. Ferric iron (Fe^{III}) is soluble under arguably acidic conditions ($pH < 3$ or <5), but it exists as Fe^{III} (hydr)oxides at near-neutral pH (Lindsay 1979). Reduction of Fe^{III} or Fe^{III} (hydr)oxides to Fe^{II} occurs via either the abiotic or biotic pathway in a soluble, adsorbed, or solid state. The mechanisms and processes of the reductive dissolution of Fe^{III} (hydr)oxides have been reviewed from both abiotic (Stumm and Sulzberger 1992) and biotic (Lovley et al. 2004) standpoints. In a reducing environment, Fe^{III} (hydr)oxides may be reduced abiotically via surface processes (Stumm and Sulzberger 1992; Tanwar

---

Responsible editor: Thomas DeLuca

Y. Li · S. Yu (✉)
Key Laboratory of Urban Environment and Health,
Institute of Urban Environment, Chinese Academy of Sciences,
Xiamen, Fujian 361021, China
e-mail: syu@iue.ac.cn

J. Strong
LanzaTech,
24 Balfour Rd,
Auckland 1060, New Zealand

H. Wang
School of Environmental and Resource Science,
Zhejiang A&F University,
Linan, Zhejiang 311300, China

et al. 2009; Catalano et al. 2010). Alternatively, the reduction of Fe^{III} (hydr)oxides can be driven by dissimilatory iron-reducing bacteria, coupling with the oxidation of organic carbon or H_2 (Lovley et al. 2004; Lovley 2008). The Fe^{II} compounds, a group of strong reductants, can reduce Fe^{III} (hydr)oxides and form secondary minerals such as goethite, siderite, magnetite, and green rusts (Borch et al. 2010). The oxidation of Fe^{II} may occur when phyto-photosynthesis results in higher ambient O_2 concentrations or when mediated by anoxygenic photosynthetic bacteria under low O_2 concentrations (Kappler and Straub 2005).

Numeric research has pointed out that the Fe^{III}–Fe^{II} redox wheel couples with biogeochemical cycles of carbon (C), nitrogen (N), sulfur (S), or phosphorus (P) individually or interactively. The Fe^{III}–Fe^{II} redox wheel not only acts as an electron donor and acceptor coupling with the reduction–oxidation of C, N, and S but also provides adsorption surface such as secondary iron minerals, especially for P. In this review, we present an overview of the interactions of the Fe^{III}–Fe^{II} redox wheel with the C, N, S, and P biogeochemical cycles occurring in soils and sediments. We highlight recent developments and the most pressing needs in this field.

2 The roles of the Fe^{III}–Fe^{II} redox wheel within the biogeochemical cycles

2.1 Carbon cycling

A large reservoir of organic matter exists in reductive soils and sediments. This represents a thermodynamically unstable carbon source as it is susceptible to microbial decomposition. The microbial transformation releases protons and electrons, which are normally depleted through redox processes by electron acceptors (oxidants) such as O_2, NO_3^-, Fe^{III}, SO_4^{2-}, and CO_2 (Lindsay 1979; Bohn 1985). This may be illustrated with an example:

$$\mathrm{Fe(OH)_3(amorphous)} + 3\mathrm{H}^+ + \mathrm{e}^- \rightarrow \mathrm{Fe}^{II} + 2\mathrm{H_2O}, \log K = 16.58$$

(Lindsay 1979).

Sahrawat (2004a) pointed out the lack of Fe^{III} (hydr) oxides as terminal electron acceptors increases organic matter accumulation in submerged soils and sediments (Sahrawat 2004a). Roden and Wetzal (2002) confirmed that the first-order constant of Fe^{III} reduction was correlated to the initial mineralization rate (as $\sum CO_2+CH_4$) of organic matter in freshwater sediments. Thus, the Fe^{III}–Fe^{II} redox wheel is considered an important redox process that links the reduction of Fe^{III} (hydr)oxides to the oxidation (or mineralization) of organic matter.

Organic ligands may be produced via the anaerobic decomposition of organic matter when a soil or sedimentary environment becomes reductive (Sahrawat 2004a). In the presence of these organic ligands, the dissolution of Fe^{III} (hydr)oxides is thermodynamically controlled by surface processes as opposed to mass transport processes (Stumm and Sulzberger 1992). The formation of complexes (or chelates) between organic ligands (such as oxalate) with Fe^{III} on the Fe^{III} (hydr)oxides' surface can polarize the Fe^{III}–O bonds, which weaken or even break the bonds and enhance the release of Fe^{III} into the solution as organic Fe^{III} complexes (Ratering and Schnell 2000). Alternatively, reactive functional groups of these organic ligands (such as hydroxyl and carboxyl groups) may complex with the Fe^{III} (hydr)oxide surface and transfer their inner-spherical electrons and reduce Fe^{III} (hydr)oxides interstructurally. The Fe^{II}–O bonds of the reduced crystalline lattice are easily broken and release Fe^{II} into the solution (Larsen et al. 2006; Hofmann and Liang 2007; Debnath et al. 2010). On the other hand, soluble organic ligand-bound Fe^{II} can attack Fe^{III} (hydr)oxides, resulting in Fe^{III} (hydr)oxide dissolution (Suter et al. 1991). Therefore, the induced reductive dissolution of Fe^{III} (hydr)oxides can be summarized via three steps: (1) rapid adsorption or diffusion of reductive organic ligand to the oxides' surface; (2) the transfer of the inner-spherical electrons to the oxides' surface (reduction of Fe^{III} to Fe^{II}); and (3) the detachment and diffusion of Fe^{II} into the bulk solution (Stumm and Sulzberger 1992). The dissolution rate depends on the specific surface area and structure of the Fe^{III} (hydr)oxides. Another factor is the presence of Fe^{II} on the surface as this may block the active sites of the Fe^{III} (hydr) oxides and lower the reductive dissolution rate. Additionally, the dissolution rate is pH-dependent as the free energy of the electron transfer reaction decreases as the environment becomes more alkaline (Stumm and Sulzberger 1992).

Biologically, the microorganisms can enzymatically couple the oxidation of organic matter to the reduction of Fe^{III} (hydr)oxides (Christen 2001; Roden and Wetzal 2002; Lovley et al. 2004; Beal et al. 2009; Hori et al. 2010). Lovley (1995) constructed a model where the oxidation of organic matter to CO_2 occurred with Fe^{III} acting as the sole electron acceptor (Fig. 1). In this model, monomeric compounds (such as sugars and amino acids), long-chain fatty acids, and mono-aromatics were hydrolytically released by microbial enzymes. These compounds were microbially hydrolysed to short-chain fatty acids and H_2, which were further oxidized to CO_2 and H_2O by Fe^{III}-reducing microorganisms.

Humic substances may function as an electron shuttle between Fe^{III}-reducing microorganisms and insoluble Fe^{III} (hydr)oxides, thereby coupling the oxidation of organic matter to the reduction of Fe^{III} (hydr)oxides in reductive soils or sediments (Lovley et al. 1996; Kappler et al. 2004;

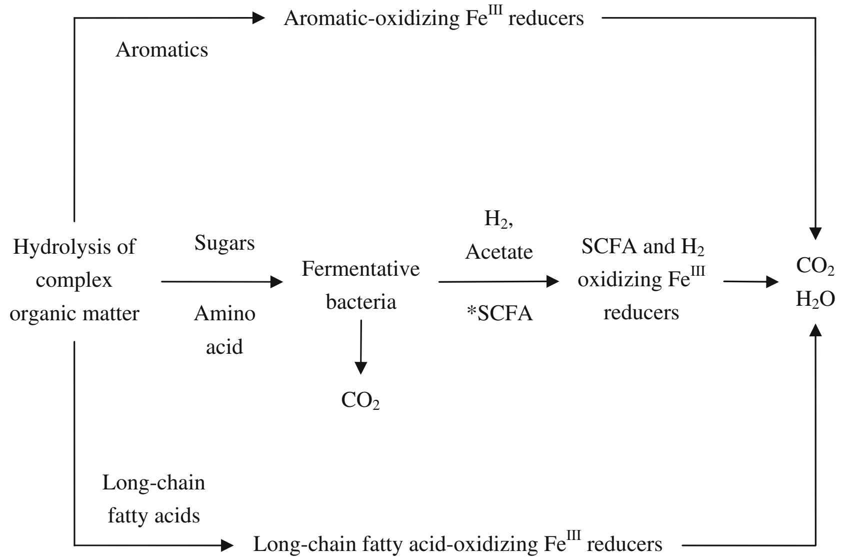

Fig. 1 Model for the microbial oxidation of organic matter in anaerobic soil/sediment with Fe^{III} serving as the electron acceptor (Lovley 1995). In this model, complex organic matter is enzymatically hydrolyzed to be sugars, amino acids, long-chain fatty acids, and aromatics. Furthermore, fermentative microorganisms ferment sugars and amino acids to be short-chain fatty acids and H_2. The fermentative products are then oxidized with the reduction of Fe^{III}. The long-chain fatty acids and aromatics are also oxidized to CO_2 and H_2O by Fe^{III} reducers. **SCFA* short-chain fatty acid

Jiang and Kappler 2008; Rakshit et al. 2009). Microorganisms may also reduce Fe^{III} through direct (Lovley et al. 1991; Lovley 1995) or indirect (Lovley et al. 1998) physical contact with insoluble Fe^{III} (hydr)oxides in the presence of dissolved humic substances. This contradicted the paradigm that suggested that humic substances derived from the decomposition of soil organic matter were inert and resisted decay in the soil for many years (Bohn 1985).

Quinone moieties act as the predominant electron acceptors within humic substances, and their reduced forms can transfer electrons to either dissolved or solid phase Fe^{III} (Scott et al. 1998; Nurmi and Trathyek 2002; Cory and McKnight 2005; Aeschbacher et al. 2010). The microbial electron transfer is dependent on the concentration of the humic substances present. Electron shuttling via humic substances to ferrihydrite would not occur in aqueous environments where dissolved humic substances occurred below a threshold of 5 mg C per liter (Jiang and Kappler 2008). The electron-carrying capacity depends upon the chemical structure of humic substances and the environmental conditions under which the humic substances are produced (Lovley and Blunt-Harris 1999; Struyk and Sposito 2001; Bauer et al. 2007). Dissolved organic matter (DOM) acts as the most viable electron shuttle in sediments and aquatic ecosystems, partly because of its ubiquity and partly due to its quinone functional groups and metal-chelating moieties (Hakala and Weber 2007; Fimmen et al. 2007; Zhang and Weber 2009).

In summary, the Fe^{III}–Fe^{II} redox wheel is interactively coupled with C cycling in a reductive environment. The integration of organic matter mineralization and the Fe^{III}–Fe^{II} redox wheel may also play an important role in the concurrent cycling of N, S, and P since organic matter mineralization is a crucial process for N, S, and P cycles.

2.2 Nitrogen cycling

The excessive N in the environment resulting from anthropogenic activity (fertilizer use and fossil fuel combustion) increases eutrophication, acid rain, and harmful algal blooms (Seitzinger 2008; Schlesinger 2009). Soils are the dominant N sink in an ecosystem, although their N content may be lowered by plant uptake (Nadelhoffer et al. 1999). Intensive research pertaining to the transformation and retention of N in soils and sediments has increased the understanding of N cycling in terrestrial and aquatic ecosystems. The Fe^{III}–Fe^{II} redox wheel has been abiotically and biotically involved within the N cycling. Microbially mediated oxidation of Fe^{II} coupling nitrate (NO_3^-) reduction has been reported within a variety of natural wetland soils and sediments (Senn and Hemond 2002; Straub et al. 2004; Weber et al. 2006; Smolders et al. 2010). The coupling process was detected via enrichment culture and the most probable number method (Straub and Buchholz-Cleven 1998). *Sideroxydans* is identified as the primary genus responsible for lithoautotrophic Fe^{II} oxidation in a lithoautotrophic NO_3^--reducing enrichment culture (Straub et al. 1996; Blöthe and Roden 2009). However, its biochemical mechanisms and the genes responsible for the NO_3^--dependent Fe^{II} oxidation remain unclear (Blöthe and Roden 2009; Byrne-Bailey et al. 2010). Furthermore, whether the NO_3^--dependent Fe^{II} oxidation and Fe^{III} (hydr)oxide reduction can concurrently occur in a reductive soil or sediment remains unknown, even though the redox condition for both processes should be similar. If they did occur coupledly, the Fe^{III}–Fe^{II} redox wheel could be proven as involving both C and N cycles.

The reduction of NO_3^- coupled to Fe^{II} oxidation may also proceed via abiotic pathways. The reduction of NO_3^- (electron acceptor) to NO_2^- with the concomitant oxidation of Fe^{II} (electron donor) to Fe^{III} is thermodynamically favorable (Ottley et al. 1997). Davidson et al. (2003) proposed the "ferrous wheel hypothesis" that Fe^{III} (hydr)oxide reduction by the carbonaceous compounds is followed by NO_3^- to nitrite (NO_2^-) reduction and Fe^{II} to Fe^{III} oxidation. The NO_2^- subsequently reacted with DOM to produce dissolved organic nitrogen complexes (Fig. 2). This was hypothesized to occur in an anaerobic microsite that contained Fe^{II} and an excess of organic carbon (Davidson et al. 2003, 2008). The reaction of NO_2^- with DOM was based upon the rapid reaction of NO_2^- with phenolic compounds (Davidson et al. 2003) instead of a rapid incorporation of NO_2^- into solid organic matter (Thorn and Mikita 2000; Fitzhugh et al. 2003). The hypothesis could explain the rapid disappearance of NO_3^- in soils and sediments (Corre et al. 2007; Burgin and Hamilton 2007; Zhu and Wang 2011). This is an evidence of the Fe^{III}–Fe^{II} redox wheel interacting with C and N biochemical cycles.

However, the rapid abiotic reaction of NO_3^- with Fe^{II} in the ferrous wheel hypothesis was questioned by Colman et al. (2007, 2008). They failed to repeat the catalytic reduction of NO_3^- to produce NO_2^- instead of NH_3 or N_2 as the end product in 45 soils. They concluded that the catalytic reduction of NO_3^- would not occur in acidic forest soils. Interestingly, an unlikely abiotic reaction of NO_2^- with natural dissolved organic carbon was reported by Schmidt and Matzner (2009). Debates on the ferrous wheel hypothesis are ongoing, but evidences from both sides support our hypothesis that the Fe^{III}–Fe^{II} redox wheel has been involved in the cycling of C and N interactively in the redox fluctuating soil or sediment systems.

The role of Fe^{III} has been demonstrated with regard to N mineralization or ammonium (NH_4^+) production in anaerobic environments (see Fig. 2). Organic matter and Fe^{III} are two important factors that control NH_4^+ production in submerged soils or sediments (Sahrawat 2004b; Coyle et al. 2009; Yin et al. 2010) and have been correlated with NH_4^+ production in paddy soils (Sahrawat and Narteh 2003). Zhang and Scherer (1999, 2000) demonstrated that the diffusion of NH_4^+ into or out of clay was promoted by the reductive dissolution of Fe^{III} (hydr)oxides which coated the clay particles. On the other hand, flooding enhances the reduction of octahedral Fe^{III} and negative charges within layers of clay minerals. These two enhanced characteristics may accelerate the diffusion of NH_4^+ into clay and its subsequent fixation in paddy soils (Scherer and Zhang 2002; Liu et al. 2008; Nieder et al. 2011).

Additionally, simultaneous production of NO_2^- and Fe^{II} may occur under strict anaerobic conditions in soil slurries (Clément et al. 2005; Burgin et al. 2011) via the coupled reduction of Fe^{III} to Fe^{II} with the subsequent oxidation of NH_4^+ to NO_2^- (see Fig. 2). The relative importance of abiotic or biotic processes involved in the coupled oxidation of NH_4^+ and reduction of Fe^{III}, as well as their ecological

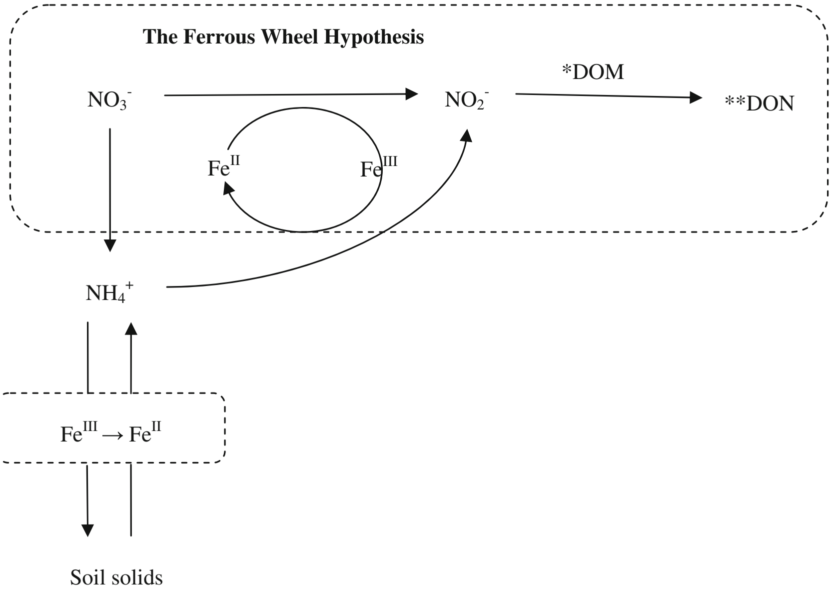

Fig. 2 Conceptual model illustrating relationships between the Fe^{III}–Fe^{II} redox wheel and N cycling in anaerobic soil/sediment. In this model, the "ferrous wheel hypothesis" established by Davidson et al. (2003) shows that carbon compounds derived from photosynthates reduce Fe^{III} in soil minerals and Fe^{II} is released into the solution. Fe^{II} further reduces NO_3^- to NO_2^-, and NO_2^- subsequently reacts with DOM to produce DON in temperate forest soils under anaerobic condition. In addition, the reduction of Fe^{III} in minerals, such as Fe^{III} (hydr)oxides and octahedral Fe^{III}, affects their surface structure and negatively charges solid phases, which induces NH_4^+ movement between aqueous and solid phases in wetland and paddy soils. The production of NO_2^- and Fe^{II} may also simultaneously occur in wetland soils from the coupled reduction of Fe^{III} to Fe^{II} with the oxidation of NH_4^+ to NO_2^-. **DOM* dissolved organic matter, ***DON* dissolved organic nitrogen

effects under field conditions, still requires further elucidation. However, studies indicated that N cycling in dynamic redox environments is related to C cycling and the Fe^{III}–Fe^{II} redox wheel abiotically and biotically.

2.3 Sulfur cycling

Iron sulfides couple S cycling with the Fe^{III}–Fe^{II} redox wheel. This has been supported by the processes and fluxes occurring in the global geochemical iron sulfide cycle and the "iron–sulfur world" hypothesis (Rickard and Luther 2007). The chemistry of S^{II} suggests that H_2S and HS^- are two main species in pore water of marine sediment profiles while S^{2-} is negligible (Rickard and Luther 2007). Aqueous iron sulfide–complexes produced by the reaction of H_2S or HS^- with Fe^{II} are prevalent in the literature (Fig. 3). Based on the stoichiometry, soluble iron–sulfide complexes, such as Fe_2S_2 (Buffle et al. 1988), $Fe_x(HS)_{2x}$ ($x \geq 2$) (Davison et al. 1998), and $[Fe_2(HS)]^{3+}$ (Luther et al. 2003), have been suggested, while some authors refer to the soluble iron–sulfide complexes as FeS_{aq} (Rickard and Morse 2005) with no implication of stoichiometry. Given the above, soluble iron–sulfide complexes may occur as aqueous FeS clusters, and their apparent stability is likely to be an average for the cluster system. More importantly, FeS_{aq} plays a key role in the geochemical dynamics of ecosystems as it removes toxic H_2S and drives hydrothermal vent ecosystems (Luther et al. 2001; Luther and Rickard 2005). FeS_{aq} is also a necessary intermediate in the formation of solid Fe sulfides, such as mackinawite and pyrite (Luther et al. 2003; Slowey and Brown 2007; Papadas et al. 2009). Oxidation of FeS_{aq} on Fe^{III} (hydr)oxides' surface releases Fe^{II} and SO_4^{2-} into the solution. Soluble Fe^{II} further reacts with another FeS_{aq} to form Fe sulfide minerals. Thus, S transformation between aqueous and solid phases is controlled by Fe^{III} (hydr)oxides (Poulton et al. 2004; Zopfi et al. 2008).

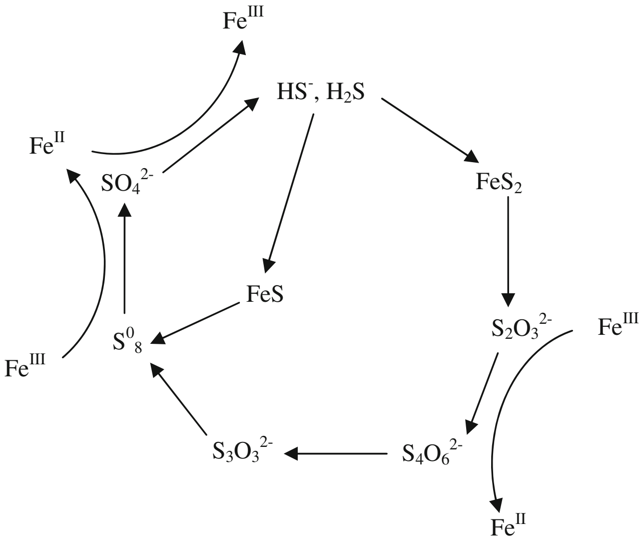

Fig. 3 Conceptual model illustrating the relationships between the Fe^{III}–Fe^{II} redox wheel and S cycling in anaerobic soil/sediment. In this model, the reduction of Fe^{III} to Fe^{II} couples with the transformation of $S_2O_3^{2-}$ to $S_4O_6^{2-}$ and S_8^0 to SO_4^{2-}, while the oxidation of Fe^{II} to Fe^{III} couples with the transformation of SO_4^{2-} to HS^- and H_2S. The formation of soluble FeS and FeS_2 also regulates the transformation of HS^- and H_2S to S_8^0 and $S_2O_3^{2-}$, respectively

The Fe sulfide minerals are the major sinks of reduced S in anaerobic subsurface environments (Rickard and Morse 2005). The formation of Fe sulfide minerals promotes the immobilization of dissolved Fe^{II} as well as toxic trace elements (Kirk et al. 2010; Johnston et al. 2010). Pyrite is one of the major iron sulfide minerals for sequestrating reduced S (Rickard and Morse 2005). Pyrite may form with (Hunger and Benning 2007) or without (Burton et al. 2011) the need of FeS precursors, such as mackinawite (FeS) and greigite (Fe_3O_4). This potentially causes a spatial decoupling between monosulfide accumulation and pyrite stability (Burton et al. 2011), indicating the complexity of Fe–S mineralization pathways in a reductive environment.

Iron sulfide minerals are likely to be oxidized when reductive soils or sediments are disturbed or resuspended into an oxic environment. The oxidation of Fe sulfide minerals may be coupled to Fe^{III} (hydr)oxide reduction (Zopfi et al. 2008; Pollok et al. 2009; Aller et al. 2010; Li et al. 2011), resulting in acidification (Boman et al. 2010; Claff et al. 2011; Keene et al. 2011) and releasing dissolved Fe^{II} and toxic trace elements (Kocar et al. 2010; Burton et al. 2011). A variety of key intermediate S compounds were observed (Burton et al. 2009; Zopfi et al. 2008) during the oxidation of Fe sulfide minerals (see Fig. 3), including elemental S (S_8^0), thiosulfate ($S_2O_3^{2-}$), trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$), and disulfane-monosulfonic acid ($HS_3O_3^-$).

In short, the Fe^{III}–Fe^{II} redox wheel not only relates to Fe–S mineralization but also is involved in the oxidation of Fe sulfides. Interestingly, CO_2/CO can be reduced by FeS_{aq} to form organic sulfides under extreme environments (Rickard and Luther 2007). It suggests that C and S cycling interacts with the Fe^{III}–Fe^{II} redox wheel.

2.4 Phosphorus cycling

The transformation of P in soils or sediments has become a significant eutrophication risk as it may be released into adjacent aquatic ecosystems (Carpenter 2008; Howarth and Paerl 2008; Conley et al. 2009; Duan et al. 2009). Phosphorus has a strong affinity toward Fe^{III} (hydr)oxide surfaces (Khare et al. 2004; Norton et al. 2009). Since Fe^{III} (hydr)oxide is redox-sensitive and its surface is variably charged, P sorption on the Fe^{III} (hydr)oxide surface becomes dependent on the redox potential and pH of the environment. The transformation and distribution of P compounds from the aqueous phase to solid phase iron oxide minerals depends on the type of iron oxide and its surface structure (Fig. 4). The reactive surface areas of amorphous Fe^{II} or Fe^{III} (hydr)oxides are much greater than those of crystalline Fe^{III} (hydr)oxides. Amorphous Fe^{III} (hydr)oxides can enhance the sorption of dissolved inorganic phosphorus (DIP) in a reductive soil (Zhang et al. 2010). The co-precipitation of P and Fe^{III} (hydr)oxides due to oxidation (via nitrate reduction or aeration) leads to a high retention of P in non-calcareous sediments (Schauser et al. 2006; Lake et al. 2007). Vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) or similar Fe^{II} phosphate minerals enhance the P sorption capacity in reductive mineral soils with high DIP (Heiberg et al. 2010). Dissolved organic phosphorus adsorption displayed a similar trend, with less sorption occurring as the crystallinity of Fe^{III} (hydr)oxides increased (Ruttenberg and Sulak 2011).

Nonetheless, the release of P from Fe–P complexes is coupled with the Fe^{III}–Fe^{II} redox wheel in the environment (see Fig. 4). The reductive dissolution of Fe^{III} (hydr)oxides at alkaline pHs has been correlated to greater P release in submerged mineral soils or sediments (Chacon et al. 2006; Mort et al. 2010; Heiberg et al. 2010). However, the presence of aluminum hydroxides ($Al(OH)_3$) lowered the P release in the aqueous phase of non-calcareous sediments—even though an in situ reductive solubilization of Fe^{III} (hydr)oxides occurred (Kopáček et al. 2005). Aluminum hydroxides are not sensitive to redox fluctuation, but pH-dependent. Aluminum hydroxides may provide additional binding sites for P if P is released from Fe^{III} (hydr)oxides at neutral pH (Kopáček et al. 2000; Rydin et al. 2000; Reitzel et al. 2005; Navratil et al. 2009). Kopáček et al. (2005) suggested that the molar Al/Fe ratio and the molar Al/P ratio were indicative parameters for predicting P release from lake sediments. This has been corroborated by Lake et al. (2007).

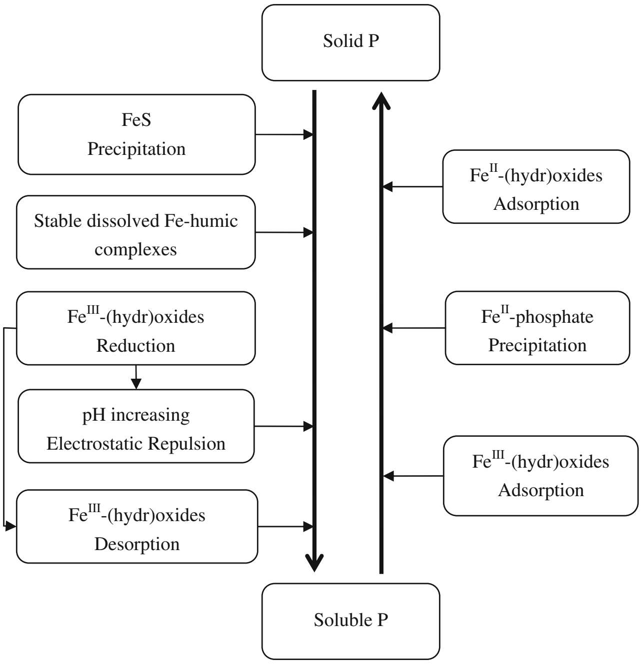

Fig. 4 Conceptual model illustrating the relationships between the Fe^{III}–Fe^{II} redox wheel and P cycling in anaerobic soil/sediment. In this model, sorption on the surface of amorphous Fe^{II} or Fe^{III} (hydr) oxides, precipitation as Fe^{II} phosphate, and co-precipitation with Fe^{III} (hydr)oxides promote the transformation of P from the soluble to the solid phase. In contrast, reductive dissolution of Fe^{III} (hydr)oxides decreases P-binding sites and increases negative charges on solid phase surface, inducing the transformation of P from the solid to the soluble phase. The formation of Fe sulfide minerals in sulfate-enriched anaerobic sediments can promote P release by preventing the formation of insoluble Fe–phosphate complexes or by hampering Fe^{II} diffusion to aerobic layers. Soluble Fe–humic complexes may also accelerate P release from the solid to the soluble phase via blocking P co-precipitating with Fe^{III} (hydr)oxides

Fe^{III} can form soluble complexes with humic (Steinmann and Shotyk 1997). The stable Fe–humic complexes resulted in P release in eutrophic fens since they prevent P from co-precipitating with Fe^{III} (hydr)oxides (Zak et al. 2004). The formation of Fe–S complexes in sulfate-enriched anaerobic sediments can also promote P release by preventing the formation of insoluble Fe–phosphate complexes or by hampering Fe^{II} diffusion to aerobic layers (Smolders et al. 2010; Hartzell and Jordan 2012). The Fe/P ratio may be used to predict P sorption capacity for a sediment. A significantly negative relationship was found between soluble P and the total Fe/P ratio in the trophogenic zone of surface sediments from Danish lakes (Jensen et al. 1992). Reductive dissolution of Fe^{III} (hydr)oxides (Section 2.1) caused by anaerobic microbial respiration can enhance P solubilization as well (Pant and Reddy 2001; Zak et al. 2004; Shenker et al. 2005; Chacon et al. 2006; Zhang et al. 2010).

Overall, the Fe^{III}–Fe^{II} redox wheel only regulates sorption surface or site for phosphorus in the environment regardless of Fe–humic complex formation or dissolution of Fe oxides. Phosphorus released from organic P mineralization coupled with Fe^{III} reduction might relate to the Fe^{III}–Fe^{II} redox wheel.

2.5 Integration of biogeochemical cycles with the Fe^{III}–Fe^{II} redox wheel concept

The Fe^{III}–Fe^{II} redox wheel plays an important role in the biogeochemical cycles of C, N, S, and P, and at least partially drives or is involved into their biogeochemical cycles at various scales. It is evident that Fe^{III} (hydr)oxides are the core for the biogeochemical cycles of C, N, S, and P in a dynamic redox micro-ecosystem, where they serve as terminal electron acceptors for organic matter mineralization and N and S transformation. They also possess a remarkably large specific surface area and act as sorbents for dissolved P compounds. With the above factors in mind, the C, N, S and P cycles were integrated with the Fe^{III}–Fe^{II} redox wheel

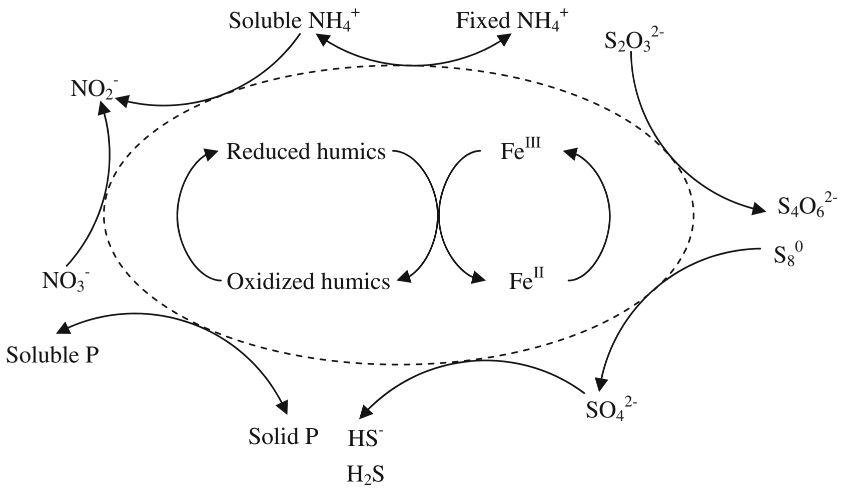

Fig. 5 Conceptual model illustrating the relationships between the Fe^{III}–Fe^{II} redox wheel and C, N, S, and P cycles in anaerobic soil/sediment. In this model, the Fe^{III}–Fe^{II} redox wheel drives the biogeochemical cycles of C, N, S, and P interactively in dynamic redox environments. Fe^{III} serves as a terminal electron acceptor for organic matter mineralization. The reduction of Fe^{III} to Fe^{II} drives the transformation of NO_3^- to NO_2^-, NH_4^+ to NO_2^-, $S_2O_3^{2-}$ to $S_4O_6^{2-}$, and S_8^0 to SO_4^{2-}, while the oxidation of Fe^{II} to Fe^{III} couples the transformation of SO_4^{2-} to HS^- and H_2S. Furthermore, the Fe^{III}–Fe^{II} redox wheel changes the surface structure of solid phase and solution chemistry, affecting the transformation of NH_4^+ and P between the soluble and solid phases in anaerobic soil/sediment

concept; the conceptual model is displayed in Fig. 5. In the model, Fe^{III} serves as terminal electron acceptors for organic matter mineralization; the reduction of Fe^{III} to Fe^{II} couples the transformation of NO_3^- to NO_2^-, NH_4^+ to NO_2^-, $S_2O_3^{2-}$ to $S_4O_6^{2-}$, and S_8^0 to SO_4^{2-}; the oxidation of Fe^{II} to Fe^{III} couples the transformation of SO_4^{2-} to HS^- and H_2S; the Fe redox processes change the surface structure of the solid phase and the solution chemistry, affecting the transformation of NH_4^+ and P between soluble and solid phases. Some evidences also indicate that the Fe^{III}–Fe^{II} redox wheel integrates with the C and N, C and S, or C and P cycles interactively, especially the C and N cycles (Davidson et al. 2003; Colman et al. 2007), in the dynamic redox environments.

Although iron is one of the most abundant elements in the earth's crust, it may be considered as limited within a microsite or micro-ecosystem for reduction or oxidation. When iron is chemically inert (due to Fe–S precipitation or Fe–humic complexation), Fe^{III} (hydr)oxides are reduced (via abiotic or biotic nitrification processes), or the specific surface area of Fe^{III} (hydr)oxides decreases (due to crystallization), the P in the aqueous phase of the micro-ecosystem may increase due to the lack of a sorption surface and the co-precipitation of Fe^{III} oxide minerals. The reverse is true that the availability of C, S or N may be lowered due to the oxidation or complexation of Fe oxides. Given the complexity of the interactive processes between the Fe^{III}–Fe^{II} redox wheel and C, N, S, and P biogeochemical cycles and the difficulty of locating certain dynamic redox environment, direct evidences are demanded in future studies.

3 Challenges and future studies

There is still a great need to understand the interactions of biogeochemical C, N, S, and P cycles with the Fe^{III}–Fe^{II} redox wheel in microenvironments under aerobic–anaerobic fluctuations, even though the complexity of coupling these relationships has been discussed in previous studies (Gauci et al. 2004; Robinson et al. 2004; Meulepas et al. 2009; Howarth et al. 2011; Burgin et al. 2011; Schlesinger et al. 2011). Nowadays, anthropogenic activities result in nutrient and metal enrichment in the environment, increase ambient temperature, and alter pH in environmental matrices. This, in turn, alters the interactions of the biogeochemical cycles and increases the complexity of predicting their interactions with the Fe^{III}–Fe^{II} redox wheel. However, these challenges must be overcome because they are crucial to process-based models that predict these cycles in anthropogenically altered ecosystems. Despite some advances, more work should be focused on the interactions of the Fe^{III}–Fe^{II} redox wheel involved in the cycles of C, N, S, and P. The major challenges are stated below:

1. Studies in anaerobic environments have demonstrated the significant role of humic substances on electron transfer from many microorganisms to crystalline and non-crystalline Fe^{III} (hydr)oxides (Section 2.1). Nonetheless, direct evidence of kinetic mechanisms of electron transfer is lacking.
2. The "ferrous wheel hypothesis" proposed by Davidson et al. (2003) requires confirmation or further refinement due to some contradictory findings (Section 2.2). The

natural dissolved organic carbon extracted from different types of soils and sediments should be used to investigate the possibility of its abiotic reaction with NO_2^- under anaerobic conditions. The rapid catalytic reduction of NO_3^- mediated by Fe^{II} adsorbed to Fe^{III} (hydr)oxide surfaces also requires confirmation.

3. So far, Fe^{II} sulfides have been defined and quantified on the basis of the source of H_2S evolved from soils and sediments by adding 1 mol l^{-1} HCl (Rickard and Morse 2005). Species of Fe^{II} sulfides and their presence in anaerobic environmental conditions require new in situ measurement techniques, as opposed to the operationally defined quantification (Section 2.3).
4. Although some studies have assessed the movement and transformation of P, the mechanisms controlling the release or retention of P in anaerobic soils and sediments remain unknown. It is well documented that some physical and chemical factors (such as pH, redox potential, available P concentration, Al hydroxides, Fe^{III} (hydr)oxides) will influence the adsorption–desorption processes of P in reducing soils or sediments (Section 2.4). But, the integrative mechanisms of these factors regulating P sorption or desorption in relation the Fe^{III}–Fe^{II} redox wheel require direct evidence.

Acknowledgments The authors thank Prof. Max Haggblom at Rutgers, the State University of New Jersey, and anonymous reviewers for valuable comments. This work was financially supported by the grants from the “Knowledge Innovation Programs” (KZCX2-YW-JC402) and the “Hundred Talent Program” (no. A0815) of the Chinese Academy of Sciences, the Ministry of Science and Technology of China (2009DFB90120), and the National Science Foundation of China (no. 40871244).

References

Aeschbacher M, Sander M, Schwarzenbach RP (2010) Novel electrochemical approach to assess the redox properties of humic substances. Environ Sci Technol 44:87–93

Aller RC, Madrid V, Chistoserdov A, Aller JY, Heilbrum C (2010) Unsteady diagenetic processes and sulfur biogeochemistry in tropical deltaic muds: implications for oceanic isotope cycles and the sedimentary record. Geochim Cosmochim Acta 74:4671–4692

Bauer M, Heitmann T, Macalady DL, Blodau C (2007) Electron transfer capacities and reaction kinetics of peat dissolved organic matter. Environ Sci Technol 41:139–145

Beal EJ, House CH, Orphan VJ (2009) Manganese- and iron-dependent marine methane oxidation. Science 325:184–187

Blöthe M, Roden EE (2009) Composition and activity of an autotrophic Fe(II)-oxidizing, nitrate-reducing enrichment culture. Appl Environ Microbiol 75:6937–6940

Bohn HL (1985) Oxidation and reduction. In: Bohn HL (ed) Soil chemistry. Wiley, New York, pp 262–289

Boman A, Fröjdö S, Backlund K, Åström ME (2010) Impact of isostatic land uplift and artificial drainage on oxidation of brackish-water sediments rich in metastable iron sulfide. Geochim Cosmochim Acta 74:1268–1281

Borch T, Kretzschmar R, Kappler A, Van Cappellen P, Ginder-vogel M, Voegelin A, Campbell K (2010) Biogeochemical redox processes and their impact on contaminant dynamics. Environ Sci Technol 44:15–23

Buffle J, de Vitre RR, Perret D, Leppard GG (1988) Combining field measurements for speciation in non perturbable waters. In: Kramer JR Jr, Allen HE (eds) Metal speciation: theory, analysis and application. Lewis Publishers, Boca Raton, pp 99–124

Burgin AJ, Hamilton SK (2007) Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Front Ecol Environ 5:89–96

Burgin AJ, Yang WH, Hamilton SK, Silver WL (2011) Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. Front Ecol Environ 9:44–52

Burton ED, Bush RT, Sullivan LA, Hocking RK, Mitchell DRG, Johnston SG, Fitzpatrick RW, Raven M, Mcclure S, Jang LY (2009) Iron-monosulfide oxidation in natural sediments: resolving microbially mediated S transformations using XANES, electron microscopy, and selective extractions. Environ Sci Technol 43:3128–3134

Burton ED, Bush RT, Johnston SG, Sullivan LA, Keene AF (2011) Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. Geochim Cosmochim Acta 75:3434–3451

Byrne-Bailey KG, Weber KA, Chair AH, Bose S, Knox T, Spanbauer TL, Chertkov O, Coates JD (2010) Completed genome sequence of the anaerobic iron-oxidizing bacterium *Acidovorax ebreus* strain TPSY. J Bacteriol 192:1475–1476

Carpenter SR (2008) Phosphorus control is critical to mitigating eutrophication. Proc Natl Acad Sci 105:11039–11040

Catalano JG, Fenter P, Park C, Zhang Z, Rosso KM (2010) Structure and oxidation state of hematite surfaces reacted with aqueous Fe (II) at acidic and neutral pH. Geochim Cosmochim Acta 74:1498–1512

Chacon N, Silver WL, Dubinsky EA, Cusack DF (2006) Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound. Biogeochemistry 78:67–84

Christen K (2001) Linking iron with carbon sequestration. Environ Sci Technol 35:98A–99A

Claff SR, Burton ED, Sullivan LA, Bush RT (2011) Metal partitioning dynamics during the oxidation and acidification of sulfidic soil. Chem Geol 286:146–157

Clément JC, Shrestha J, Ehrenfeld JG, Jaffé PR (2005) Ammonium oxidation coupled to dissimilatory reduction of iron under anaerobic conditions in wetland soils. Soil Biol Biochem 37:2323–2328

Colman BP, Fierer N, Schimel JP (2007) Abiotic nitrate incorporation in soil: is it real? Biogeochemistry 84:161–169

Colman BP, Fierer N, Schimel JP (2008) Abiotic nitrate incorporation, anaerobic microsites, and the ferrous wheel. Biogeochemistry 91:223–227

Conley DJ, Paerl HW, Howarth RW, Boesch DF, Seitzinger SP, Havens KE, Lancelot C, Likens GE (2009) Controlling eutrophication: nitrogen and phosphorus. Science 323:1014–1015

Corre MD, Brumme R, Veldkamp E, Beese FO (2007) Changes in nitrogen cycling and retention processes in soils under spruce forests along a nitrogen enrichment gradient in Germany. Glob Chang Biol 13:1509–1527

Cory RM, McKnight DM (2005) Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ Sci Technol 39:8142–8149

Coyle JS, Dijkstra P, Doucett RR, Schwartz E, Hart SC, Hungate BA (2009) Relationships between C and N availability, substrate age, and natural abundance ^{13}C and ^{15}N signatures of soil microbial biomass in a semiarid climate. Soil Biol Biochem 41:1605–1611

Davidson EA, Chorover J, Bryan Dail D (2003) A mechanism of abiotic immobilization of nitrate in forest ecosystems: the ferrous wheel hypothesis. Glob Chang Biol 9:228–236

Davidson EA, Dail DB, Chorover J (2008) Iron interference in the quantification of nitrate in soil extracts and its effect on hypothesized abiotic immobilization of nitrate. Biogeochemistry 90:65–73

Davison W, Phillips N, Tabner BJ (1998) Soluble iron sulfide species in natural waters: reappraisal of their stoichiometry and stability constants. Aquat Sci 377:193–203

Debnath S, Hausner DB, Strongin DR, Kubicki J (2010) Reductive dissolution of ferrihydrite by ascorbic acid and the inhibiting effect of phospholipid. J Colloid Interface Sci 341:215–223

Duan H, Ma R, Xu X, Kong F, Zhang S, Kong W, Hao J, Shang L (2009) Two-decade reconstruction of algal blooms in China's lake Taihu. Environ Sci Technol 43:3522–3528

Fimmen RL, Cory RM, Chin YP, Trouts TD, McKnight DM (2007) Probing the oxidation–reduction properties of terrestrially and microbially derived dissolved organic matter. Geochim Cosmochim Acta 71:3003–3015

Fitzhugh RD, Lovett G, Venterea RT (2003) Biotic and abiotic immobilization of ammonium, nitrite, and nitrate in soils developed under different tree species in the Catskill Mountains, New York, USA. Glob Chang Biol 9:1591–1601

Gauci V, Matthews E, Dise N, Walter B, Koch D, Granberg G, Vile M (2004) Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. Proc Natl Acad Sci 101:12583–12587

Hakala JACY, Weber EJ (2007) Influence of dissolved organic matter and Fe(II) on the abiotic reduction of pentachlorobenzene. Environ Sci Technol 41:7337–7342

Hartzell JL, Jordan TE (2012) Shifts in the relative availability of phosphorus and nitrogen along estuarine salinity gradients. Biogeochemistry 107:489–500. doi:10.1007/s10533-010-9548-9

Heiberg L, Pedersen TV, Jensen HS, Kjaergaard C, Hansen HCB (2010) A comparative study of phosphate sorption in lowland soils under oxic and anoxic conditions. J Environ Qual 39:734–743

Hofmann A, Liang L (2007) Mobilization of colloidal ferrihydrite particles in porous media–An inner-sphere complexation approach. Geochim Cosmochim Acta 71:5847–5861

Hori T, Müller A, Igarashi Y, Conrad R, Friedrich MW (2010) Identification of iron-reducing microorganisms in anoxic rice paddy soil by ^{13}C-acetate probing. ISME J 4:267–278

Howarth R, Paerl HW (2008) Coastal marine eutrophication: control of both nitrogen and phosphorus is necessary. Proc Natl Acad Sci 105:E103

Howarth R, Chan F, Chonley DJ, Garnier J, Doney SC, Marino R, Billen G (2011) Coupled biogeochemistry cycles: eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. Front Ecol Environ 9:18–26

Hunger S, Benning LG (2007) Greigite: a true intermediate on the polysulfide pathway to pyrite. Geochem Trans 8:1

Jensen HS, Kristensen P, Jeppesen E, Skytthe A (1992) Iron:phosphorus ratio in surface sediments in shallow lakes. Hydrobiology 235 (236):731–743

Jiang J, Kappler A (2008) Kinetics of microbial and chemical reduction of humic substances: implications for electron shuttling. Environ Sci Technol 42:3563–3569

Johnston SG, Burton ED, Bush RT, Keene AF, Sullivan LA, Smith D, Martens MA, McElnea AE, Ahern CR, Powell B (2010) Abundance and fractionation of Al, Fe and trace metals following tidal inundation of a tropical acid sulfate soil. Appl Geochem 25:323–335

Kappler A, Straub KL (2005) Geomicrobiological cycling of iron. Rev Mineral Geochem 59:85–108

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

Keene AF, Johnston SG, Bush RT, Sullivan LA, Burton ED, McElnea AE, Ahern CR, Powell B (2011) Effects of hyper-enriched reactive Fe on sulfidisation in a tidally inundation acid sulfate soil wetland. Biogeochemistry 103:263–279

Khare N, Hesterberg D, Beauchemin S, Wang SL (2004) XANES determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures. Soil Sci Soc Am J 68:460–469

Kirk MF, Roden EE, Crossey LJ, Brealey AJ, Spilde MN (2010) Experimental analysis of arsenic precipitation during microbial sulfate and iron reduction in model aquifer sediment reactors. Geochim Cosmochim Acta 74:2538–2555

Kocar BD, Borch T, Fendorf S (2010) Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite. Geochim Cosmochim Acta 74:980–994

Kopáček J, Hejzlar J, Borovec J, Porcal P, Kotorová I (2000) Phosphorus inactivation by aluminum in the water column and sediments: a process lowering in-lake phosphorus availability in an acidified watershed–lake ecosystem. Limnol Oceanogr 45:212–225

Kopáček J, Borovec J, Hejzlar J, Ulrich K, Norton SA, Amirbahman A (2005) Aluminum control of phosphorus sorption by lake sediments. Environ Sci Technol 39:8784–8789

Lake BA, Coolidge KM, Norton SA, Amirbahman A (2007) Factors contributing to the internal loading of phosphorus from anoxic sediments in six Maine, USA, lakes. Sci Total Environ 373:534–541

Larsen O, Postma D, Jakobsen R (2006) The reactivity of iron oxides towards reductive dissolution with ascorbic acid in a shallow sandy aquifer (Rømø, Demark). Geochim Cosmochim Acta 70:4827–4835

Li X, Cutter GA, Thunell RC, Tappa E, Gilhooly WP III, Lyons TW, Astor Y, Scranton MI (2011) Particulate sulfur species in the water column of the Cariaco Basin. Geochim Cosmochim Acta 75:148–163

Lindsay WL (1979) Iron. In: Lindsay WL (ed) Chemical equilibria in soils. Wiley, New York, pp 1–160

Liu YL, Zhang B, Li CL, Hu F, Velde B (2008) Long-term fertilization influences on clay mineral composition and ammonium adsorption in a rice paddy soil. Soil Sci Soc Am J 72:1580–1590

Lovley DR (1995) Microbial reduction of iron, manganese, and other metals. Adv Agron 54:175–231

Lovley DR (2008) Extracellular electron transfer: wires, capacitors, iron lungs, and more. Geobiology 6:225–231

Lovley DR, Blunt-Harris EL (1999) Role of humic-bound iron as an electron transfer agent in dissimilatory Fe(III) reduction. Appl Environ Microbiol 65:4252–4254

Lovley DR, Phillips EJP, Lonergan J (1991) Enzymatic versus nonenzymatic mechanisms for Fe(III) reduction in aquatic sediments. Environ Sci Technol 25:1062–1067

Lovley DR, Coates JD, Blunt-Harris EL, Phillips EJP, Woodward JC (1996) Humic substances as electron acceptors for microbial respiration. Nature 382:445–448

Lovley DR, Fraga JL, Blunt-Harris EL, Hayes LA, Phillips EJP, Coates JD (1998) Humic substances as a mediator for microbially catalyzed metal reduction. Acta Hydrochim Hydrobiol 26:152–157

Lovley DR, Holmes DE, Nevin KP (2004) Dissimilatory Fe(III) and Mn(IV) reduction. Adv Microb Physiol 49:219–286

Luther GW III, Rickard DT (2005) Metal sulfide cluster complexes and their biogeochemical importance in the environment. J Nanopart Res 7:713–733

Luther GW III, Rozan TF, Taillefert M, Nuzzio DB, Di Meo C, Shank TM, Lutz RA, Craig Cary S (2001) Chemical speciation drives hydrothermal vent ecology. Nature 410:813–816

Luther GW III, Glazer B, Ma S, Trouwborst R, Shultz B, Druschel G, Kraiya C (2003) Iron and sulfur chemistry in a stratified lake: evidence for iron-rich sulfide complexes. Aquat Geochem 9:87–110

Meulepas RW, Jagersma CG, Khadem AF, Buisman CJN, Stams AJM, Lens PNL (2009) Effect of environmental conditions on sulfate reduction with methane as electron donor by an Eckernförde Bay enrichment. Environ Sci Technol 43:6553–6559

Mort HP, Slomp CP, Gustafsson BG, Andersen TJ (2010) Phosphorus recycling and burial in Baltic Sea sediments with contrasting redox conditions. Geochim Cosmochim Acta 74:1350–1362

Nadelhoffer KJ, Emmett BA, Gundersen P et al (1999) Nitrogen deposition makes a minor contribution to carbon sequestration in temperate forests. Nature 398:145–148

Navratil T, Rohovec J, Amirbahman A, Norton SA, Fernandez IJ (2009) Amorphous aluminum hydroxide control on sulfate and phosphate in sediment–solution systems. Water Air Soil Pollut 201:87–98

Nieder R, Benbi DK, Scherer HW (2011) Fixation and defixation of ammonium in soils: a review. Biol Fertil Soils 47:1–14

Norton SA, Coolidge K, Amirbahman A, Bouchard R, Kopáček J, Reinhardt R (2009) Speciation of Al, Fe, and P in recent sediment from three lakes in Maine, USA. Sci Total Environ 404:276–283

Nurmi JT, Trathyek PG (2002) Electrochemical properties of natural organic matter (NOM), fractions of NOM, and model biogeochemical electron shuttles. Environ Sci Technol 36:617–624

Ottley CJ, Davison W, Edmunds WM (1997) Chemical catalysis of nitrate reduction by iron(II). Geochim Cosmochim Acta 61:1819–1828

Pant HK, Reddy KR (2001) Phosphorus sorption characteristics of estuarine sediments under different redox conditions. J Environ Qual 30:1474–1480

Papadas IT, Katerinopoulos L, Gianni A, Zacharias I, Deligiannakis Y (2009) A theoretical and experimental physicochemical study of sulfur species in the anoxic lagoon of Aitoliko-Greece. Chemosphere 74:1011–1017

Pollok K, Hellige K, Harries D, Peiffer S (2009) Redox processes at the nanoscale: a TEM perspective of iron sulphide–iron (oxyhydr)oxide reactions. Geochim Cosmochim Acta 73:A1039–A1039

Poulton SW, Krom MD, Raiswell R (2004) A revised scheme for the reactivity of iron (oxyhydr)oxide minerals towards dissolved sulfide. Geochim Cosmochim Acta 68:3703–3715

Rakshit S, Uchimiya M, Sposito G (2009) Iron(III) bioreduction in soil in the presence of added humic substances. Soil Sci Soc Am J 73:65–71

Ratering S, Schnell S (2000) Nitrate-dependent iron(II) oxidation in paddy soil. Environ Microbiol 3:100–109

Reitzel K, Hansen J, Andersen F, Hansen K, Jensen H (2005) Lake restoration by dosing aluminum relative to mobile phosphorus in the sediment. Environ Sci Technol 39:4134–4140

Rickard D, Luther GW III (2007) Chemistry of iron sulfides. Chem Rev 107:514–562

Rickard D, Morse JW (2005) Acid volatile sulfide (AVS). Mar Chem 97:141–197

Robinson C, Saunders PW, Madan NJ, Pryce-miller EJ, Pentecost A (2004) Dose nitrogen deposition affect soil microfungal diversity and soil N and P dynamics in a high Arctic ecosystem? Glob Chang Biol 10:1065–1079

Roden EE, Wetzal RG (2002) Kinetics of microbial Fe(III) oxide reduction in fresh water sediments. Limnol Oceanogr 47:198–211

Ruttenberg KC, Sulak DJ (2011) Sorption and desorption of dissolved organic phosphorus onto iron (oxyhydr)oxides in seawater. Geochim Cosmochim Acta 75:4095–4112

Rydin E, Huster B, Welch EB (2000) Amount of phosphorus inactivated by alum treatments in Washington lakes. Limnol Oceanogr 45:226–230

Sahrawat KL (2004a) Organic matter accumulation in submerged soils. Adv Agron 81:169–201

Sahrawat KL (2004b) Ammonium production in submerged soils and sediments: the role of reduction iron. Commun Soil Sci Plant 35:399–411

Sahrawat KL, Narteh LT (2003) A chemical index for predicting ammonium production in submerged rice soils. Commun Soil Sci Plant 34:1013–1021

Schauser I, Chorus I, Lewandowski J (2006) Effects of nitrate on phosphorus release: comparison of two Berlin lakes. Acta Hydrochim Hydrobiol 34:325–332

Scherer HW, Zhang YS (2002) Mechanisms of fixation and release of ammonium in paddy soils after flooding III. Effect of the oxidation state of octahedral Fe on ammonium fixation. J Plant Nutr Soil Sci 165:185–189

Schlesinger WH (2009) On the fate of anthropogenic nitrogen. Proc Natl Acad Sci 106:203–208

Schlesinger WH, Cole JJ, Finzi AC, Holland EA (2011) Introduction to coupled biogeochemical cycles. Front Ecol Environ 9:5–8

Schmidt BHM, Matzner E (2009) Abiotic reaction of nitrite with dissolved organic carbon? Testing the ferrous wheel hypothesis. Biogeochemistry 93:291–296

Scott DT, McKnight DM, Blunt-Harris EL, Kolesar SE, Lovley DR (1998) Quinone moieties act as electron acceptors in the reduction of humic substances by humics-reducing microorganisms. Environ Sci Technol 32:2984–2989

Seitzinger S (2008) Nitrogen cycle out of reach. Nature 452:162–163

Senn DB, Hemond HF (2002) Nitrate controls on iron and arsenic in an urban lake. Science 296:2373–2376

Shenker M, Seitelbach S, Brand S, Haim A, Litaor MI (2005) Redox reactions and phosphorus release in re-flooded soils of an altered wetland. Eur J Soil Sci 56:515–525

Slowey AJ, Brown GE (2007) Transformation of mercury, iron, and sulfur during the reductive dissolution of iron oxyhydroxide by sulfide. Geochim Cosmochim Acta 71:877–894

Smolders AJP, Lucassen ECHET, Bobbink R, Roelofs JGM, Lamers LPM (2010) How nitrate leaching from agricultural lands provokes phosphate eutrophication in groundwater fed wetlands: the sulphur bridge. Biogeochemistry 98:1–7

Steinmann P, Shotyk W (1997) Chemical composition, and redox state of sulfur and iron in complete vertical porewater profiles from two Sphagnum peat bogs. Geochim Cosmochim Acta 61:1143–1163

Straub KL, Buchholz-Cleven BEE (1998) Enumeration and detection of anaerobic ferrous iron-oxidizing, nitrate-reducing bacteria from diverse European sediments. Appl Environ Microbiol 64:4846–4856

Straub KL, Benz M, Schink B, Widdel F (1996) Anaerobic, nitrate-dependent microbial oxidation of ferrous iron. Appl Environ Microbiol 62:1458–1460

Straub KL, Schönhuber WA, Buchholz-Cleven BEE, Schink B (2004) Diversity of ferrous iron-oxidizing, nitrate-reducing bacteria and their involvement in oxygen-independent iron cycling. Geomicrobiol J 21:371–378

Struyk Z, Sposito G (2001) Redox properties of standard humic acids. Geoderma 102:329–346

Stumm W, Sulzberger B (1992) The cycling of iron in natural environments: considerations based on laboratory studies of heterogeneous redox processes. Geochim Coamochim Acta 56:3233–3257

Suter D, Banwart S, Stumm W (1991) Dissolution of hydrous iron (III) oxides by reductive mechanisms. Langmuir 7:809–813

Tanwar KS, Petitto SC, Ghose SK, Eng PJ, Trainor TP (2009) Fe(II) adsorption on hematite(0001). Geochim Cosmochim Acta 73:4346–4365

Thorn KA, Mikita MA (2000) Nitrite fixation by humic substances: nitrogen-15 nuclear magnetic resonance evidence for potential intermediates of chemodenitrification. Soil Sci Soc Am J 64:568–582

Weber KA, Urrutia MM, Churchill PF, Kukkadapu RK, Roden EE (2006) Anaerobic redox cycling of iron by freshwater sediment microorganisms. Environ Microbiol 8:100–113

Yin X, Lv X, Jiang M, Zou Y (2010) Research progress of the coupling process of Fe and N in wetland soils. Chin J Environ Sci 31:2254–2259 (in Chinese)

Zak D, Gelbrecht J, Steinberg CEW (2004) Phosphorus retention at the redox interface of peatlands adjacent to surface waters in northeast Germany. Biogeochemistry 70:357–368

Zhang YS, Scherer HW (1999) Ammonium fixation by clay minerals in different layers of two paddy soils after flooding. Biol Fert Soils 29:152–156

Zhang YS, Scherer HW (2000) Mechanisms of fixation and release of ammonium in paddy soils after flooding. II. Effect of transformation of nitrogen forms on ammonium fixation. Biol Fert Soils 31:517–521

Zhang HC, Weber EJ (2009) Elucidating the role of electron shuttles in reductive transformations in anaerobic sediments. Environ Sci Technol 43:1042–1048

Zhang W, Faulkner JW, Giri SK, Geohring LD, Steenhuis TS (2010) Effect of soil reduction on phosphorus sorption of an organic-rich silt loam. Soil Sci Soc Am J 74:240–249

Zhu W, Wang W (2011) Does soil organic matter variation affect the retention of $^{15}NH_4^+$ and $^{15}NO_3^-$ in forest ecosystems? Forest Ecol Manage 261:675–682

Zopfi J, Böttcher ME, Jørgensen BB (2008) Biogeochemistry of sulfur and iron in Thioploca-colonized surface sediments in the upwelling area off central Chile. Geochim Cosmochim Acta 72:827–843