

# Biogeochemical Interactions between Fe(II)/(III) Species Cycles and Transformation of Reducible Substrates in Subtropical Soils

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## Abstract

This study provides fundamental information on the interactions between iron cycles and transformation of reducible substrates. We introduce five important topics including (1) Fe(II) adsorbed on minerals and dissimilatory iron reduction; (2) interactions between the iron cycle and dechlorination of pesticides; (3) interactions between the iron cycle and nitrogen cycles; (4) interactions between the iron cycle and the transformation of heavy metals; and (5) humic acids as electron shuttles. We proposed the mechanism of interaction between iron redox cycle and reductive dechlorination, nitrate reduction, heavy metal reduction and carbon cycles. This contribution demonstrates the important role of DIRB and iron cycles on the transformation of reducible substrates under anaerobic environments, and provides scientific information for in-situ bioremediation of reducible pollutants in Fe(III)-rich environments.

## Key Words

Iron cycle, dissimilatory iron-reducing bacteria (DIRB), reducible transformation, subtropical soil, dechlorination, nitrate reduction, heavy metal

## Introduction

Iron is the most abundant transition metal in soil, and is also an essential plant nutrient. Many subtropical soils contain large amounts of free iron oxides with special biogeochemistry. The iron cycle in subtropical soils is very important to both biological and chemical environmental processes. In the presence of dissolved organic matters (DOM), iron oxides can be reduced. In rhizosphere soils, root exudates including various forms of DOM can enhance the dissolution of iron oxides, resulting in the formation of various dissolved or adsorbed Fe(III)/Fe(II) species. DIRB can drive the reductive dissolution of iron oxides, and then generate biogenic Fe(II) species with lower redox potential (Lovley 1987; 2004). Therefore, the transformation of reducible substrates may strongly depend on the biogeochemistry of iron species. In particular, the iron cycle plays a vital role in cycles of nitrogen and carbon, the availability of heavy metal (Clementa *et al.* 2005; Jickells *et al.* 2005). The aims of the study are to investigate and discuss the roles of Fe(II) species and DIRB in reductive transformation of pesticides, nitrate and heavy metal; and then to consider the implication of iron cycles in the field of soil science.

## Materials and Methods

We have reported the experimental procedure in detail (Li *et al.* 2008; 2009b; 2009c).

## Results and Discussion

### *Fe(II) adsorbed on minerals and dissimilatory iron reduction*

Fe(II) adsorption onto minerals is an important environmental process because the surface-complex Fe(II) enables a facile reductive transformation of organic/inorganic pollutants in contaminated soils (Stumm and Sulzberger 1992). Adsorbed Fe(II) is known to be very reactive, acting as a reductant for elements including As(V), U(VI), Cr(VI) and Cu(II). Adsorbed Fe(II) is far more easily oxidized if bound by mineral surfaces than dissolved Fe(II). A general consensus is that the mineral surface provides hydroxyl groups to stabilize Fe(II), leading to the formation of surface-complex Fe(II) species such as  $\equiv\text{SOFe}^+$  and  $\equiv\text{SOFeOH}^0$  with lower redox potential compared to aqueous Fe(II) species. The negative shift of the redox potential proved to be indicative of the enhancement of Fe(II) reactivity. However, despite of the above well-recognized conclusion, there is a lack of experimental evidence regarding the magnitude of redox potential response to the variation in the identity of surface-complex Fe(II) species. In order to investigate these insights, we have established an electrochemical system to characterize the redox behavior of the adsorbed Fe(II) in the interfacial phase by cyclic voltammetry (CV). The redox potential of Fe(II) adsorbed on alumina, titanic and silica is 0.190, 0.140, 0.265, respectively at pH=6.7, while that on lepidrocite, goethite and hematite is 0.255, 0.229, 0.203, respectively at pH=6.5 in 0.2 M NaCl and 28 mM MOPS solution (Li *et al.* 2009a). At circumneutral pH values, iron exists primarily as insoluble, solid-phase minerals. Dissimilatory iron

reduction is an important pathway to form adsorbed Fe(II) bound on minerals. Microbial iron reduction includes assimilatory and dissimilatory iron reduction. Recently, dissimilatory iron reduction has been paid great attention (Weber *et al.* 2006). Both Fe(III) oxides and a variety of complexed Fe(III) species can be used as terminal electron acceptor in dissimilatory iron reduction. At a circumneutral pH, dissimilatory iron redox cycling can significantly affect the geochemistry of hydromorphic soil and sediments, leading to DOM mineralization, mineral dissolution and weathering and the mobilization or immobilization of heavy metals.

#### *Interactions between iron cycle and dechlorination of pesticides*

The system of DIRB *S12*, goethite and chlorinated pesticides (DDT and pentachlorophenol) showed an interactions between reduction of iron oxides and dechlorination of DDT driven by dissimilatory Fe(III)-reducing bacterium (Li *et al.* 2009b; 2009c; 2009d). The results showed that DDT can be degraded by DIRB and DDT removal was more effective in the system of DIRB and  $\alpha$ -FeOOH, though  $\alpha$ -FeOOH can not degrade DDT. The enhanced degradation of DDT was mainly attributable to biogenic Fe(II) on the surface of  $\alpha$ -FeOOH. The cyclic voltammetry results provided evidence of a decrease in redox potential of Fe(II) in the system, which contributed to the enhancement of Fe(II) reactivity and a subsequent increase of DDT degradation. DDT was only degraded to DDD by DIRB alone, while in the system of DIRB and  $\alpha$ -FeOOH, DDT degradation followed a sequential reductive dechlorination process as DDT to DDD to DDMS to DBP. Interactions among *CY01*, and reduction of iron oxides and reduction of 2,4- dichlorophenoxyacetic acid (2, 4-D) were also reported by our group (Wu *et al.* 2009). This case demonstrated the ability of *Comamonas koreensis* CY01 to obtain energy for microbial growth by coupling the oxidation of electron donors to dissimilatory Fe(III) reduction, and also the enhanced 2,4-D biodegradation by the presence of Fe(III) oxides under anaerobic conditions. The results suggested that the anaerobic respiration of strain CY01 can utilize ferrihydrite, goethite, lepidocrocite or hematite as the terminal electron acceptor. Under anaerobic conditions, dissimilatory Fe(III) reduction and 2,4-D biodegradation occurred simultaneously. The presence of Fe(III) (hydr)oxides would significantly enhance 2,4-D biodegradation, probably due to that the reactive mineral-bound Fe(II) species generated from dissimilatory Fe(III) reduction abiotically reducing 2,4-D. With the demonstrated ability of reducing both Fe(III) (hydr)oxides and 2,4-D, strain CY01 was proven to be a new bacterial strain for studying the interaction between reductive dechlorination and dissimilatory Fe(III) reduction.

Theses contributions demonstrated the important role of DIRB and iron oxide in pesticides transformation under anaerobic environments, and provided scientific support and information for in-situ bioremediation of chlorinated organic pollutants in Fe(III)-rich environments.

#### *Interactions between iron cycle and nitrogen cycles*

Interactions between iron redox cycle and nutrient cycles have been paid great attention (Clementa *et al.* 2005; Jickells *et al.* 2005). It had been reported that there was a biological process that uses Fe(III) as an electron acceptor while oxidizing ammonium to nitrite for energy production. Ammonium oxidation under iron reducing anaerobic conditions is thermodynamically feasible and might potentially be a critical component of N cycle in sediments (Clementa *et al.* 2005). However, it had been reported that ferrous iron as an electron donor was capable of reducing nitrate in anaerobic, sedimentary environments (Jørgensen *et al.* 2009). Reduction of nitrate to ammonia can proceed at appreciable rates in abiotic systems in the presence of green rust compounds [ $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \cdot y\text{H}_2\text{O}$ ] at ambient pH (Hansen *et al.* 1996). The presence of crystalline iron oxide surfaces accelerates low-temperature reduction of  $\text{NO}_3^-$  coupled to Fe(II) oxidation at pH values greater than 8.0 (Ottley *et al.* 1997). Microbially catalyzed nitrate reduction coupled to Fe(II) oxidation under anaerobic environment has also been reported (Straub *et al.* 1996; Weber *et al.* 2001), and the role of biogenic Fe(II) was taken into consideration for nitrogen cycling (Weber *et al.* 2001)). Our group found the potential for microbially catalyzed  $\text{NO}_3^-$  reduction with iron oxide by using *Klebsiella pneumoniae* strain L17 under anaerobic conditions. The results showed that L17 had the capacity of nitrate/nitrite reduction, and  $\alpha$ -FeOOH can increase the reduction rate significantly, but the biogenic adsorbed Fe(II) was not enough to reduce so much nitrogen. And a hypothesis mechanism was proposed as that iron oxide mediated electron transfer from cells to nitrate/nitrite. This study could be helpful to deeply understand the relationship between the redox cycles of Fe and N in subsurface sedimentary environments.

#### *Interactions between iron cycle and the transformation of heavy metals*

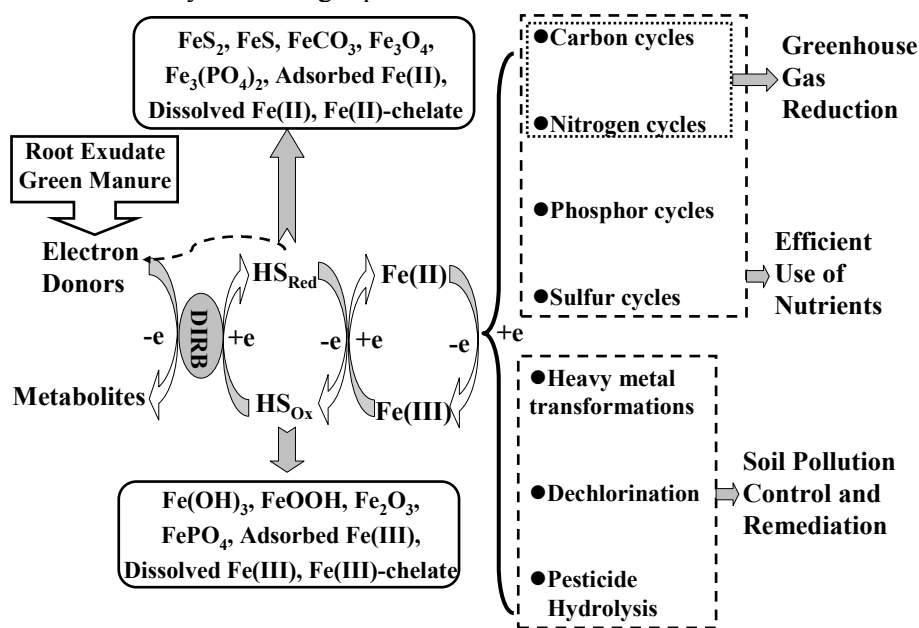
Accumulation and persistence of heavy metals in the soil environment has been paid great interest in the possible long-term changes in solubility of metals adsorbed and coprecipitated by minerals. Iron oxides can act as a kind of important adsorbent of heavy metals. Abiotic and biotic iron redox cycle can immobilize

heavy metals (As, Hg, Cu(II), Cr(VI)) and radionuclides (U(VI)) and prevent their transport by sorption and precipitation processes, and redox state transformations (Amstaetter *et al.* 2009; Burkhardt *et al.* 2009). In particular, members of the Fe(III)-reducing bacteria family have been demonstrated to be important for bioremediation at contaminated subsurface sites. Therefore, iron oxides can have a significant role in heavy metal retention, mobility, and bioavailability. Our study showed that Cu(II) was transformed into Cu(I) in the presence of Fe(II), and into Cu(I) and Cu metal in the presence of Fe(II) and DIRB. Kinetic measurements demonstrated that 2-NP reductive transformation rate was highly sensitive to the ratio of Cu(II)/Fe(II), and had a optimum Cu(II) concentration.

#### Humic acids as electron shuttles

Humic substances (HS) can accelerate dissimilatory Fe(III) oxide reduction, since HS can serve to shuttle electrons from DIRB to Fe(III) oxides in anaerobic soils and sediments. And this electron shuttling permits DIRB to indirectly reduce Fe(III) oxides. We observed an increase in cell numbers of DIRB in the presence of HS (Li *et al.* 2009c). This suggests that Fe(III) oxide reduction by DIRB may be favored in natural environment where HS are present. Quinone molecules also can act as electron transfer shuttles, like HS (Uchimiya and Stone 2009).

Finally, we proposed the mechanism of interaction between iron redox cycle and reductive dechlorination, nitrate reduction, heavy metal reduction and carbon cycle as showed in Figure 1. Recent studies have proposed that the interaction between HS and iron cycle should involve in carbon cycle, and inhibit CH<sub>4</sub> discharge (Keller *et al.* 2009). And the effect of nitrate on the iron cycle reduced arsenic uptake by rice grain (Chen *et al.* 2008). Therefore, the interaction among iron cycles, nutrient cycles and heavy metal transformation should be a very interesting topic.



**Figure 1. The mechanism of interaction between iron redox cycle and reductive dechlorination, nitrate reduction, heavy metal reduction and carbon cycle.**

#### Conclusion

The iron cycle is an important physical - chemical - biological process in subtropical soils and is driven by iron-reducing bacteria. Fe(II) species are important reductants with low redox potential. DIRB act as a driver of reduction of Fe(III) and reducible substrates. Humic acid acts as an electron shuttle. In particular, the interaction between the iron cycle and nitrogen cycle, sulfur cycles, heavy metal transformation in soil is an important issue.

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