Cycling of Iron and Manganese

Lecture Outline

- Introduction
- Major components of metal cycle
- Reduction of Iron and Manganese
- Oxidation of Iron and Manganese
- Mobility of Iron and Manganese
- Ecological significance
  - Nutrient regeneration/immobilization
  - Ferromanganese modules
  - Root plaque formation
  - Ferrolysis
  - Methane emissions
- Summary

Fe (III) Mn (IV) Fe (II) Mn (II)
Cycling of Iron and Manganese

Learning Objectives

- Understand the stability of iron and manganese solid phases as function of Eh and pH
- Role of Fe (III) and Mn(IV) reduction in organic matter decomposition and nutrient regeneration
- Adverse effects of reduced Fe (II) and Mn (II)
- Alteration soil pH and alkalinity
- Suppression of sulfate reduction and methanogenesis
- Formation of minerals (e.g., siderite, vivianite, pyrite, and others)
- Mottling and gleying serve as indicators of hydric soils
- Oxidation of toxic organic contaminants

Iron (Fe) and Manganese (Mn)

**Iron**
- 4th most abundant element in the Earth’s crust, (average concentration of 4.3 %, in soils and sediments 0.1-10%)

**Manganese**
- On average 60 time less abundant than Fe (In soils and sediments 0.002-0.6%)

- Fe & Mn are generally considered to be trace elements in open-water aquatic systems, but major elements in soils and sedimentary environments
Iron (Fe) and Manganese (Mn)

• Required by organisms as **nutrients**
  – Fe is a major component of cytochromes and other oxidation-reduction proteins
  – Mn is a cofactor for various enzyme systems. Plants assimilate 20-500 mg/kg in dry matter

• Although abundant in the Earth’s crust, unlike other elements (e.g. C, N, S), they are often not readily available for organisms (**oxides have low solubility**)
  – Plants and microorganisms produce chelating agents (siderophores) which facilitate solubilization and uptake of Fe/Mn from insoluble minerals

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Fe-Containing Minerals

- Siderite FeCO₃
- Goethite FeOOH
- Siderite FeCO₃
- Vivianite Fe₅(PO₄)₂
- Hematite Fe₂O₃
Mn-Containing Minerals

Rhodocrosite MnCO₃

Rhodonite
(Mn,Fe,Mg,Ca)SiO₃

Importance of Fe and Mn in wetlands

• Role in decomposition of organic matter
• Precipitation of sulfides
  – Adverse effects of sulfide on plant growth
  – Reduces available phosphorus
  – Toxic to plants at high levels
• Suppression of sulfate reduction and, methanogenesis
• Alteration of pH/alkalinity conditions
• Mobilization/immobilization of trace metals
• Formation minerals (siderite, vivianite, magnetite)
Oxidation States of Iron and Manganese

- MnO₂  +4
- Mn²⁺  +2
- FeOOH  +3
- Fe(OH)₃  +3
- FePO₄  +3
- FeS₂  +2
- FeCO₃  +2
- Fe²⁺  +2

Forms of Iron and Manganese

- Water soluble (dissolved, pore water)
- Exchangeable (sorbed on cation exchange complex)
- Reducible (insoluble ferric compounds)
- Residual (crystalline stable pool)

Forms of Fe and Mn compounds

- Amorphous
- Crystalline
Soil pH effects on Metals (Me)

Low (acid) pH conditions:
- $Me^{2+}$
- $Me^{2+}$
- $Me^{2+}$
- $Me^{2+}$

Near neutral to alkaline pH conditions:
- $Me^{2+}$
- $Me^{2+}$
- $Clay$

Metals in solution: Increased solubility leads to more bioavailability
Precipitation: Decreased solubility leads to less bioavailability
Adsorption:

Oxidation-Reduction

Reducing or Acid Conditions:
- $2Fe^{2+} + 3H_2O$

Oxidized Conditions:
- $Fe_2O_3 + 6H^+ + 2e^-$
Iron cycle

Water

\[ \text{O}_2 + \text{Fe}^{2+} \rightarrow \text{FeOOH} \rightarrow \text{OM-Fe}^{2+} \]

Aerobic

Soil

Anaerobic

\[ \text{FeOOH} \rightarrow \text{Fe}^{2+} \rightarrow \text{OM-Fe}^{2+} \]

\[ +\text{S}^2- \rightarrow \text{FeS} \rightarrow \text{FeS}_2 \]

Manganese cycle

Water

\[ \text{O}_2 + \text{Mn}^{2+} \rightarrow \text{MnOOH} \rightarrow \text{OM-Mn}^{2+} \]

Aerobic

Soil

Anaerobic

\[ \text{MnOOH} \rightarrow \text{Mn}^{2+} \rightarrow \text{OM-Mn}^{2+} \]

\[ \text{OM-Mn}^{2+} \rightarrow \text{Mn}^{2+} \rightarrow \text{OM-Mn}^{2+} \]
Sequential Reduction of Electron Acceptors

Organic Substrate [e⁻ donor]

Relative Concentration

Oxygen Nitrate Iron Manganese Sulfate Methanogenesis

Time

Sequential Reduction of Electron Acceptors

Oxidation-Reduction

Redox Potential, mV (at pH 7)
**Redox Zones with Depth**

- **Oxygen Reduction Zone**
  - $Eh = > 300 \text{ mV}$

- **Nitrate Reduction Zone**
  - $Eh = 100 \text{ to } 300 \text{ mV}$
  - **Mn$^{4+}$ Reduction Zone**
  - $Eh = 100 \text{ to } 300 \text{ mV}$

- **Fe$^{3+}$ Reduction Zone**
  - $Eh = -100 \text{ to } 100 \text{ mV}$

- **Sulfate Reduction Zone**
  - $Eh = -200 \text{ to } -100 \text{ mV}$

- **Methanogenesis**
  - $Eh = < -200 \text{ mV}$

**Redox Potential and pH**

- Eh values range from $-600$ to $1000$ mV
- pH values range from 0 to 12
Stability of Fe - Eh and pH

Stability of Mn - Eh and pH
Reduction of Iron (III) and Manganese (IV)

- Microbial communities
- Biotic and abiotic reduction
- Forms of iron and manganese

Iron (III) and Manganese (IV) Reducers

- Fermentative Fe(III) and Mn(IV) reducers
  - Bacillus; Ferribacterium; Clostridium; Desulfovibrio;
  - Escherichia Geobacter;
- Sulfur-oxidizing Fe(III) and Mn(IV) reducers  
  - Thiobacillus spp., Sulfolobus spp
- Hydrogen-oxidizing Fe(III) and Mn(IV) reducers 
  - Pseudomonas spp., Shewanella spp
- Organic acid-oxidizing Fe(III) and Mn(IV) reducers
- Aromatic compound-oxidizing Fe(III) reducers
  - Geobacter spp
Reduction of Iron (III) and Manganese (IV)

- Oxidized forms are solid phases under most conditions
- Bacterial reduction depends on the ability of bacteria to:
  - Solubilize solid phases
  - Attach directly to substrate and directly transfer electrons
  - Transport the substrates directly into cells as solid

Reduction of Iron (III) and Manganese (IV)

Bacterial reduction of Fe(III) and Mn(IV) depends on:

- The amount of bioavailable reductant (organic and inorganic substances) for microbial utilization
- The amount of bioavailable oxidant (manganese or iron) for microbial utilization.
Iron Respiration

Detrital Matter

Complex Polymers
Cellulose, Hemicellulose,
Proteins, Lipids, Waxes, Lignin

Enzyme
Hydrolysis

Monomers
Sugars, Amino Acids
Fatty Acids

Uptake

Glucose
Glycolysis

Pyruvate
Substrate level
phosphorylation

Organic Acids
[acetate, propionate, butyrate, lactate, alcohols, H₂, and CO₂]

TCA Cycle

Oxidative phosphorylation

ATP, Substrate level
phosphorylation

Iron Reducing Bacterial Cell

Fermenting Bacterial Cell

CO₂
Mn⁴⁺, Fe³⁺

Uptake

Mn²⁺, Fe²⁺

CO₂

Acetate
Lactate

6/22/2008
WBL

% of Aerobic Energy Yield

Electron Acceptors

O₂
NO₃⁻
MnO₂
Fe(OH)₃
SO₄²⁻

120
100
80
60
40
20
0

6/22/2008
WBL
Abiotic reduction of Fe (III) and Mn (IV)

- Microbial end products
  - Citrate
  - Malate
  - Oxalate
  - Pyruvate (oxidized to acetate with non enzymatic Mn(IV) reduction)
- Sulfides
- Nitrite
- NH₄⁺ (oxidized to N₂ or NO₂⁻ with Mn (IV))
- Humic acids (electron shuttles)

Humic Electron Shuttling

- Process may have important implications for controls on rate and extent of Fe(III) oxide reduction - depending on concentration and reactivity of humic substances in soils and sediments

Lovley et al. (1996)
Fe (III) Reduction

Patrick and Henderson, 1981 SSSAJ 45:35-38

Mn (IV) Reduction

Patrick and Henderson, 1981 SSSAJ 45:35-38
Oxidation of Iron (II) and Manganese (II)

- Microbial communities
- Biotic and abiotic reduction

Iron hydroxide precipitate in a Missouri stream receiving acid drainage from surface coal mining.

Fe(II) oxidizing bacteria

- **Mesophiles (< 40 °C):**
  - *Thiobacillus*,
  - *Leptospirillum*,
- **Moderate thermophiles (40-60 °C):**
  - *Sulfobacillus*,
  - *Acidimicrobium*,
  - *Ferroplasma* (an extreme acidophile which grows at pH 0!)
- **Extreme thermophiles (> 60 °C)**
  - *Acidianus*,
  - *Sulfurococcus*
Electron donor | Bacteria
---|---
Fe (II) | **Obligate Lithotrophs**
FeSO₄ | *Thiobacillus ferrooxidans*
FeS₂ | *Ferrobasillus ferrooxidans*
Fe₃(PO)₄ | [pH = 2 to 3.5]
Carbon source = CO₂

FeCO₃ | **Facultative Lithotrophs**
FeS₂ | *Leptothrix*

Organic complexes of Fe | **Heterotrophs**
Organic matter

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**Eh-pH Iron Stability – Iron Bacteria**

![Eh-pH Iron Stability Graph](image)
### Manganese

<table>
<thead>
<tr>
<th>Electron donor</th>
<th>Bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II)</td>
<td><strong>Obligate Lithotrophs</strong></td>
</tr>
<tr>
<td>MnCO₃</td>
<td><em>Arthrobacter; Bacillus;</em></td>
</tr>
<tr>
<td></td>
<td><em>Leptothrix; Metallogenium;</em></td>
</tr>
<tr>
<td></td>
<td><em>Flavobacterium;</em></td>
</tr>
<tr>
<td></td>
<td><em>Pseudomonas</em></td>
</tr>
<tr>
<td>Organic complexes of Mn</td>
<td><strong>Heterotrophs</strong></td>
</tr>
</tbody>
</table>

### Oxidation of Fe and Manganese

- Can occur under aerobic and anaerobic conditions
  - Fe(II) oxidized where sulfate reduction and methanogenesis occur.

**Iron oxidizing bacteria**
- Neutrophilic: *(Leptothrix spp.; Gallionella spp.; Ferroglobus spp.)*

\[ e^\cdot D: \text{FeCO}_3; \text{FeS}_2 \]
\[ e^\cdot A: \text{Oxygen} \]

**Manganese oxidizing bacteria**
- *Arthrobacter spp.; Bacillus spp.; Leptothrix spp.; Flavobacterium spp.; Pseudomonas spp.*

\[ e^\cdot D: \text{Mn(II); MnCO}_3 \]
\[ e^\cdot A: \text{Oxygen} \]
Pyrite Oxidation

\[
\text{FeS}_2 + 3.5 \text{O}_2 + \text{H}_2\text{O} = \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+
\]

\[
\text{Fe}^{2+} + 0.25 \text{O}_2 + \text{H}^+ = \text{Fe}^{3+} + 0.5 \text{H}_2\text{O}
\]

\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} = \text{Fe(OH)}_3(\text{s}) + 3 \text{H}^+
\]

\[
\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} = 15 \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16 \text{H}^+
\]

\[
\text{O}_2 
\]

\[
\text{FeS}_2 + 15 \text{O}_2 + 2 \text{H}_2\text{O} = 2 \text{Fe}_2(\text{SO}_4)_3 + 2 \text{H}_2\text{SO}_4
\]

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Oxidation of Iron (II) and Manganese (II)

Oxidation of Fe(II) and Mn(II) is regulated by:

- Soil or sediment pH and redox potential
- Oxygen flux and thickness of aerobic layer
- Presence of oxidants with higher reduction potentials
- Flux of soluble Fe(II) and Mn(II)
- Soil cation exchange capacity
- Metal-dissolved organic matter complexation
Iron and Manganese Fluxes-
Soil and Water Column

Aerobic/Oxic

FeOOH [s]
Fe(OH)$_3$ [s]
Fe$_2$O$_3$ [s]

MnOOH [s]
MnO$_2$ [s]

Mn(II)

(CHO)$_n$

Anaerobic/Anoxic

Fe(II)

CO$_2$

Mobile and Immobile Iron

Depth below soil surface

Fe$^{2+}$

Aerobic

Insoluble Fe

Anaerobic

% Fe

0 1 2 3

0 2 4 6 8
Solid-Phase Fe(II)
(0.5M HCl Extraction)

Talladega Wetland, North Central AL
[E. Roden, 2002]

Amorphous Fe(OH)_3
(0.5M HCl Extraction)

Lake Apopka Marsh

Soluble P, mg L\(^{-1}\)
Dissolved Fe, mg L\(^{-1}\)

Phosphorus
Iron

Water
Soil
Stratification of Electron Acceptors – Black Sea

Ecological and Environmental Significance of Oxidation-Reduction of Iron and Manganese

- Nutrient regeneration/immobilization
- Ferromanganese modules
- Root plaque formation
- Ferrolysis
- Methane emissions
Nutrient regeneration/immobilization

Organic Matter decomposition

- 35-65% CO₂ by Fe (III) reduction (Lovley, 1987)
- Positive relationship between iron oxide reduction and organic nitrogen mineralization in tropical wetland soils (Sahrawat, 2004)

Extractable Iron

(Mississippi River Floodplain Soils)
Organic Matter and Fe and Mn Reduction

\[ \text{Organic Matter} = H^+ + e^- + CO_2 + H_2O \]

\[ \text{Fe(OH)}_3 + 3 H^+ + e^- = \text{Fe}^{2+} + H_2O \]

\[ \text{Eh} = 1.06 - 0.059 \log \text{Fe}^{2+} + 0.177 \text{pH} \]

Organic matter decomposition and nutrient release

Electron Donor: \((\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)_{1}\)

<table>
<thead>
<tr>
<th>Electron Acceptor or Oxidant [EA]</th>
<th>Molar Ratio (\text{EA/}NH_3)</th>
<th>Molar Ratio (\text{EA/}H_3\text{PO}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{O}_2)</td>
<td>6.6</td>
<td>106</td>
</tr>
<tr>
<td>(\text{NO}_3^-)</td>
<td>5.3</td>
<td>85</td>
</tr>
<tr>
<td>(\text{MnO}_2)</td>
<td>13.3</td>
<td>202</td>
</tr>
<tr>
<td>(\text{Fe(OH)}_3)</td>
<td>26.5</td>
<td>424</td>
</tr>
<tr>
<td>(\text{SO}_4^{2-})</td>
<td>3.3</td>
<td>53</td>
</tr>
</tbody>
</table>
Phosphorus Release and Retention

$$\text{FePO}_4 \cdot 2 \text{H}_2\text{O} + 2 \text{H}^+ + \text{e}^- = \text{Fe}^{2+} + \text{H}_2\text{PO}_4^- + 2 \text{H}_2\text{O}$$

$$\text{Eh} = \text{E}^o - 0.059 \log [\text{Fe}^{2+}] - 0.059 \log [\text{H}_2\text{PO}_4^-] - 0.118 \text{pH}$$

Iron solubility - pH and Eh
Iron

- Reduction capacity Fe minerals decreases with increasing crystalinity
- FePO$_4$ > Fe(OH)$_3$ > FeOOH > Fe$_2$O$_3$

Iron -Phosphorus Interactions under Anaerobic Soil Conditions

- SO$_4^{2-}$ + H$_2$S $\rightarrow$ FePO$_4$
- FePO$_4$ $\rightarrow$ Fe$_3$(PO$_4$)$_2$
- FePO$_4$ $\rightarrow$ Strengite
- FePO$_4$ $\rightarrow$ Vivianite

Strengite: Fast forming
Vivianite: Stable, Slow forming
Oxidation – Reduction of Iron-Phosphate Minerals

**Anaerobic**

- **Vivianite**
  - $Fe_3(PO_4)_2 \cdot 8 H_2O$
  - [Slow] Crystallization
- **Am Ferric Phosphate**
  - $Fe_3(PO_4)_2 \cdot n H_2O$
  - [Slow] Crystallization

**Aerobic**

- **Kertschemite**
  - (hydrated $Fe^{2+}, Fe^{3+}, PO_4^{3-}$)
  - [Fast]
- **Am Ferric Phosphate**
  - $Fe(PO_4) \cdot 4 H_2O$
  - [Fast]

Ferromanganese nodules

Concretions, nodules, or mottles rich in iron and manganese

Photo © Antonio Borrelli
Root plaque formation

- Protection from reduced phytotoxins
- Interference with nutrient uptake

Methane emissions

![Graph showing methane emissions over time](image)

**Inhibition of methanogenesis**

- Fe(II), Fe(III) (μmol cm⁻³)
- CO₂ (μmol cm⁻³)
- CH₄ (μmol cm⁻³)

Time (d): 0 5 10 15 20 25
**Ferrolysis**

- During flooding...reduction of Fe$^{3+}$ to Fe$^{2+}$
- Accumulation of Fe$^{2+}$ displaces base cations from CEC
- Drainage of these soils removes base cations during leaching
- Oxidation of Fe$^{2+}$ to Fe$^{3+}$ releases H$^+$ (acid conditions)
- H$^+$ saturated clay is unstable..results in high aluminum concentration
- Repeated cycles of flooding and draining decreases base saturation
- Ferrolysis occurs in surface soil horizons with abundant supply of bioavailable organic matter to support microbial reduction of Fe(III) oxides.

\[
\begin{align*}
\text{Fe}^{3+} & \quad \text{FeS + H}_2\text{O} & \quad \text{Fe(OH)}_3 + \text{H}_2\text{SO}_4 \\
\text{Flooded} & & \text{Drained}
\end{align*}
\]

**Iron and Manganese**

- Fe forms more stable organic-metal bonds than Mn
- Stable organic-metal complexes will protect Fe from precipitation
- Extent of complexation is greater under anaerobic conditions
- Significant amounts of Fe$^{2+}$ can be present under aerobic conditions for several days.. Due to complexation with organics
Iron and Manganese

Summary

Reduction of Fe (III) and Mn (IV) results in:

- Concentration of water soluble Fe and Mn increases
- pH of acid soil increases
- Cation exchange capacity of soil is occupied by Fe and Mn
- Solubility of phosphorus increases
- Breakdown of OM and nutrient release
- New minerals are formed

Iron and Manganese

Summary

Oxidation of Fe (II) and Mn (II) results in:

- Bioavailability of metals decreases
- Co-Precipitation of other metals
- pH of soil decreases to acidic conditions
- Solubility of phosphorus decreases
- Oxidized Fe and Mn serves as electron acceptor upon flooding
General Chemical Transformations of Metals

- Water soluble metals
  - Soluble free ions, e.g., Fe²⁺
  - Soluble as inorganic complexes
  - Soluble as organic complexes
- Exchangeable metals
- Metals precipitated as inorganic compounds
- Metals complexed with large molecular weight humic materials
- Metals adsorbed or occluded to precipitated hydrous oxides
- Metals precipitated as insoluble sulfides

http://wetlands.ifas.ufl.edu
http://soils.ifas.ufl.edu