Chemical Reactions in Natural Systems

- Reactions in which neither protons nor electrons are exchanged
  - \(\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} = 2 \text{FeOOH}\)
- Reactions involving protons
  - \(\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-\)
- Reactions involving electrons
  - \(\text{Fe}^{2+} = \text{Fe}^{3+} + \text{e}^-\)
- Reactions in which both protons and electrons are transferred
  - \(2\text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}\)
Electrons and Protons

Electrochemical Properties

Topic Outline

- Introduction
- Oxidation-reduction reactions
- Nernst Equation
- Eh - pH relationships
- Buffering of redox potential
- Measurement of redox potentials
- Soil and water column pH
- Redox couples in wetland soils
- Redox gradients in wetland soils
- Specific conductance
- Soil oxygen demand

Walther Nernst
The Nobel Prize in Chemistry 1920
http://www.corrosion-doctors.org/Biographies/Nernst.htm
Electrochemical Properties

Learning Objectives

- Basic concepts related to oxidation-reduction reactions
- Use of Nernst Equation to calculate redox potential (Eh)
- Relationship between redox potential (Eh) and pH
- Laboratory and field measurements of redox potentials
- Diel changes in water column pH
- Redox couples and microbial metabolic activities in wetlands
- Redox gradients and aerobic/ananaerobic interfaces in wetlands
- Soil oxygen demand and nutrient fluxes


Oxidation-Reduction

Reductant $\rightarrow$ Oxidant + e$^-$

Reductant = Electron donor

[Organic matter, NH$_4^+$, Fe$^{2+}$, Mn$^{2+}$, S$^{2-}$, CH$_4$, H$_2$, H$_2$O]

Oxidant + e$^-$ $\rightarrow$ Reductant

Oxidant = Electron acceptor

[O$_2$, NO$_3^-$, MnO$_2$, Fe(OH)$_3$, SO$_4^{2-}$, CO$_2$, and some organic compounds]
Oxidation-Reduction

[Aerobic Respiration]

Oxidation

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} = 6\text{CO}_2 + 24\text{H}^+ + 24\text{e}^- \]

Reductant \quad \text{Oxidant}

Reduction

\[ 6\text{O}_2 + 24\text{H}^+ + 24\text{e}^- = 12\text{H}_2\text{O} \]

Oxidant \quad \text{Reductant}

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 & = 6\text{CO}_2 + 6\text{H}_2\text{O} \\
\end{align*}
\]

Oxidation - Reduction

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Oxidation-Reduction

[Nitrate Respiration – Dentrification]

Oxidation

\[ 5\text{C}_6\text{H}_{12}\text{O}_6 + 30\text{H}_2\text{O} = 30\text{CO}_2 + 120\text{H}^+ + 120\text{e}^- \]

Reductant \quad \text{Oxidant}

Reduction

\[ 24\text{NO}_3^- + 144\text{H}^+ + 120\text{e}^- = 12\text{N}_2 + 72\text{H}_2\text{O} \]

Oxidant \quad \text{Reductant}

\[
\begin{align*}
5\text{C}_6\text{H}_{12}\text{O}_6 + 24\text{NO}_3^- + 24\text{H}^+ & = 12\text{N}_2 + 30\text{CO}_2 + 42\text{H}_2\text{O} \\
\end{align*}
\]

Oxidation - Reduction
**Oxidation-Reduction**

[Sulfate Respiration]

**Oxidation**

\[ C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \]

**Reduction**

\[ 3SO_4^{2-} + 24H^+ + 24e^- \rightarrow 3S^{2-} + 12H_2O \]

\[ C_6H_{12}O_6 + 3SO_4^{2-} \rightarrow 3S^{2-} + 6CO_2 + 6H_2O \]

**UPLAND SOILS**

- \( O_2 \)
- \( NO_3^- \)
- \( Mn^{4+} \)
- \( Fe^{3+} \)
- \( SO_4^{2-} \)
- \( CO_2 \)
- \( PO_4^{3-} \)
- \( H_2O \)

**FLOODED SOILS**

- \( H_2O \)
- \( N_2 \)
- \( NH_4^+ \)
- \( Mn^{2+} \)
- \( Fe^{2+} \)
- \( S^{2-} \)
- \( CH_4 \)
- \( PH_3 \)
- \( H_2 \)

Reduction

Oxidation

6/22/2008 WBL
Nernst Equation

\[ m \text{ (OXIDANT)} + m \text{ H}^+ + n \text{ e}^- = m \text{ (REDUCTANT)} \]

\[ E_h = E^0 - \left[ \frac{0.059}{n} \right] \log \left[ \frac{\text{Reductant}}{\text{Oxidant}} \right] - 0.059 \left[ \frac{m}{n} \right] \text{pH} \]

- \( E \) = Electrode potential (volts)
- \( E^0 \) = Standard electrode potential (volts)
- \( F \) = Faraday’s constant (23.061 kcal/volt mole or 96.50 kJ/volt mole)
- \( R \) = Gas constant (0.001987 kcal/mole degree or 0.008314 kJ/mole degree)
- \( T \) = Temperature (298.15 K (273.15 + 25 °C))
- \( n \) = number of electrons involved in the reaction

Wetland Soil

Drained Soil

<table>
<thead>
<tr>
<th>Anaerobic</th>
<th>Aerobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly Reduced</td>
<td>Reduced</td>
</tr>
</tbody>
</table>

Oxidation-Reduction Potential (mV)

-300 -100 0 100 300 500 700
Oxidation-Reduction

Electron donors
[Organic matter, NH$_4^+$, Fe$^{2+}$, Mn$^{2+}$, S$^{2-}$, CH$_4$, H$_2$, H$_2$O]

Electron acceptors
O$_2$ NO$_3^-$ Mn$^{4+}$ Fe$^{3+}$ SO$_4^{2-}$ CO$_2$ H$_2$O

Electron Pressure

Oxidation-Reduction Potential (mV)

Strongly reduced

Strongly oxidized
How much energy is released during oxidation-reduction reactions?

Electrode Potentials

- CO₂
- SO₄²⁻
- Fe (III)
- N-Oxides
- Mn (IV)

Energy Yield

Ease of Reduction

- O₂

Oxidation-Reduction

Redox Potential, mV (at pH 7)

- CO₂ → CH₄
- SO₄²⁻ → S²⁻
- Fe³⁺ → Fe²⁺
- Mn⁴⁺ → Mn²⁺

- SeO₄²⁻ → SeO₃²⁻
- Se(0); Se²⁻ → Se(IV)
- NO₃⁻ → N₂
- O₂ → H₂O

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Iron Redox Couple and Eh-pH

Oxidation-Reduction

Uplands
- Electron acceptor non-limiting
- Electron donor limiting

Wetlands and Aquatic Systems
- Electron acceptor limiting
- Electron donor non-limiting
Sequential Reduction of Electron Acceptors

Organic Substrate [e- donor]

SO₄²⁻ NO₃⁻ Mn²⁺ Fe²⁺ S²⁻ CH₄

O₂

Oxygen Reduction Zone

Nitrate Reduction Zone

Mn⁴⁺ Reduction Zone

Iron Reduction Zone

Sulfate Reduction Zone

Methanogenesis

Eh = > 300 mV

Eh = 100 to 300 mV

Eh = -100 to 100 mV

Eh = -200 to -100 mV

Eh = < -200 mV

Redox Zones with Depth

Aerobic

Facultative

Anaerobic
Regulators of Eh

- Water-table fluctuations.
- Activities of electron acceptors.
- Activities of electron donors.
- Temperature
- pH

Field Redox Electrodes

[Diagram showing field redox electrodes with labels for copper wire, heat shrinking tube, epoxy, platinum wire, volt meter, calomel reference, water, soil, and platinum electrodes.]
Laboratory Redox Electrodes

- Copper wire
- Heat shrinking tube
- Glass tube
- Mercury
- Epoxy
- Platinum wire
- Saturated KCl
- Platinum Glass Electrode
- Glass tube
- Calomel + Mercury
- Platinum wire
- Salt bridge
- Calomel Reference Electrode

Okeechobee Basin Wetland Soils and Stream Sediments

- Chart showing Redox Potential over time for Stream, Wetland [B], Wetland [A], and Upland environments.
Flooded Organic Soils: Everglades Agricultural Area

Flooded Paddy Soils: Louisiana
Electron Acceptors - Redox Potential

- Oxygen
- Nitrate
- Sulfate
- Bicarbonate

Time (wk)


- Low Organic Matter Soil
- High Organic Matter Soil

Time after flooding
Redox Gradients in Sediments

![Graph showing Redox Gradients in Sediments](image)


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Sediment Microbial Fuel Cell

![Diagram of Sediment Microbial Fuel Cell](image)

**Limitations of Redox Potentials**

- Most of the redox couples are not in equilibrium except in highly reduced soils.
- In biological systems, electrons are added and removed continuously.
- Platinum electrodes respond favorably to reversible redox couples.
- Redox potential is closely related to pH.
- Platinum electrode surface can be contaminated by coatings of oxides, sulfides and other impurities.
Soil and Water Column - pH

- Reactions involving protons
  - $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$
  - $\text{H}_2\text{CO}_3 = \text{H}^+ + \text{HCO}_3^-$
  - $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$

- Reactions in which both protons and electrons are transferred
  - $2\text{Fe(OH)}_3 + 3\text{H}^+ + e^- = 2\text{Fe}^{2+} + 3\text{H}_2\text{O}$

Water Column pH: Experimental Ponds – Lake Apopka Basin
Effect of Flooding on Soil pH

Effect of Flooding on Soil Porewater Ionic Strength

A

Soil

Soil Solution

B

Ionic Strength

Time after flooding

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Redox Couples in Wetlands

- $\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$ and $\text{O}_2/\text{H}_2\text{O}$
- $\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$ and $\text{NO}_3/\text{N}_2$
- $\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$ and $\text{MnO}_2/\text{Mn}^{2+}$
- $\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$ and $\text{FeOOH/Fe}^{2+}$
- $\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$ and $\text{SO}_4^{2-}/\text{H}_2\text{S}$
- $\text{H}_2/\text{H}^+$ and $\text{CO}_2/\text{CH}_4$

Aerobic Respiration and Energy Yield

\[ \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 = 6\text{CO}_2 + 6\text{H}_2\text{O} \]

$\Delta G_r = -686.4$ kcals/mole

$\text{ADP + P}_i = \text{ATP}$

$\Delta G_r = -7.7$ kcals/mole
Oxygen

- Oxygen is an electron acceptor
- Reduction [Electron acceptor]
  - \( \text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O} \)
  - Oxidant
- Oxidation [Electron donor]
  - \( \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{H}_2\text{O} = 6\text{CO}_2 + 24\text{H}^+ + 24e^- \)
  - Reductant
**Oxygen Consumption**

- Heterotrophic microbial respiration
  - \( \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 = 6\text{CO}_2 + 6\text{H}_2\text{O} \)
- Chemolithotrophic oxidation of reduced inorganic compounds
  - \( \text{NH}_4^+ + 2\text{O}_2 = \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+ \)
- Chemical oxidation of reduced inorganic compounds
  - \( 4\text{Fe}^{2+} + 10\text{H}_2\text{O} + \text{O}_2 = 4\text{Fe(OH)}_3 + 8\text{H}^+ \)

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**Oxidation-Reduction**

**Carbon**

- \( \text{CO}_2 \leftarrow \text{O}_2 + \text{CH}_4 \) (Aerobic soil)
- \( \text{OM} \rightarrow \text{CH}_4 \) (Anaerobic soil)

- \( \downarrow \text{Floodwater} \)

**Nitrogen**

- \( \text{NO}_3 \leftarrow \text{O}_2 + \text{NH}_4 \) (Aerobic soil)
- \( \text{OM} \rightarrow \text{NH}_4 \) (Anaerobic soil)

- \( \downarrow \text{Floodwater} \)
Oxidation-Reduction

**Iron**

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Floodwater</td>
<td>Fe³⁺ ⇋ O₂ + Fe²⁺</td>
<td>Aerobic soil</td>
</tr>
<tr>
<td>Anaerobic soil</td>
<td>FeOOH ⇋ Fe²⁺</td>
<td></td>
</tr>
</tbody>
</table>

**Manganese**

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Floodwater</td>
<td>Mn⁴⁺ ⇋ O₂ + Mn²⁺</td>
<td>Aerobic soil</td>
</tr>
<tr>
<td>Anaerobic soil</td>
<td>MnO₂ ⇋ Mn²⁺</td>
<td></td>
</tr>
</tbody>
</table>

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Oxidation-Reduction

**Carbon**

<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>Floodwater</td>
<td>CO₂ ⇋ O₂ + OM</td>
<td>Aerobic soil</td>
</tr>
<tr>
<td>Anaerobic soil</td>
<td>CO₂ ⇋ O₂ + OM</td>
<td></td>
</tr>
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</table>

**Sulfur**

<table>
<thead>
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<th>O₂</th>
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<tbody>
<tr>
<td>Floodwater</td>
<td>SO₄ ⇋ O₂ + H₂S</td>
<td>Aerobic soil</td>
</tr>
<tr>
<td>Anaerobic soil</td>
<td>SO₄ ⇋ H₂S</td>
<td></td>
</tr>
</tbody>
</table>
Low organic matter soil

Oxygen Consumption during chemical oxidation

High organic matter soil

Oxygen Consumption during biological oxidation

Time (hours)

6/22/2008 45WBL

Aerobic Respiration

Dissolved organic C, mg/kg

Oxygen consumption, mg/kg/day

Unimpacted Everglades, FL
Impact Everglades, FL
Talladega, AL
Salt marsh, LA
Belhaven, NC
Lake Apopka marsh, FL
Prairie pothole, ND
Crowley, LA

Crowley, LA

Houghton Lake marsh, MI

y = 1036 + 200 ln(x)
R² = 0.84

6/22/2008 46WBL
Oxygen - Periphyton

S. Hagerty, SFWMD unpublished results
**Lake Apopka Marsh**

- **Soluble P, mg L⁻¹**
- **Dissolved Fe, mg L⁻¹**

**Mobile and Immobile Iron**

- **Fe²⁺**
- **Insoluble Fe**
- **Anaerobic**
- **Aerobic**
OXYGEN: Sources and Sinks

Soil Oxygen

Plants and Algae -> Water -> Air

Release by Plant Roots

Oxidation of Reductants

Chemical oxidation

Chemolithotrophic oxidation

Respiration

Electrochemical Properties & Soil Oxygen Demand

Summary

- Oxidation-reduction reactions regulate several elemental cycles
- Wetland soils are limited by electron acceptors and have abundant supply of electron donors.
- Upland soils are usually limited by electron donors, and have abundant supply of electron acceptors (primarily oxygen).
- Nernst Equation is used to calculate redox potential (Eh)
- Redox potentials (Eh) are inversely related to pH (59 mV/pH unit)
- Redox potential of soils are affected by (i) activities of electron donors (ii) activities of electron acceptors and (iii) temperature
- Laboratory and field electrodes can be used to measure redox potentials of soils
Electrochemical Properties & Soil Oxygen Demand

Summary

- Distinct Eh gradients are present at (i) the soil-floodwater interface, (ii) root-zone of wetland plants, and (iii) around soil aggregates in drained portions of wetlands during low water-table depths.
- Water column pH is affected by photosynthesis
- Soil pH is affected by reduction of electron acceptors
- The rate of oxygen consumption is related to the concentration of reductants
- Oxygen consumption at the soil-floodwater interface regulates nutrient fluxes