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Institute of Food and Agricultural Sciences (IFAS)

Biogeochemistry of Wetlands

Science and Applications

Electrochemical Properties

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Chemical Reactions in Natural Systems

- **Reactions in which neither protons nor electrons are exchanged**
  - $Fe_2O_3 + H_2O = 2\ FeOOH$
- **Reactions involving protons**
  - $H_2CO_3 = H^+ + HCO_3^-$
- **Reactions involving electrons**
  - $Fe^{2+} = Fe^{3+} + e^-$
- **Reactions in which both protons and electrons are transferred**
  - $2Fe(OH)_3 + 3H^+ + e^- = 2Fe^{2+} + 3H_2O$

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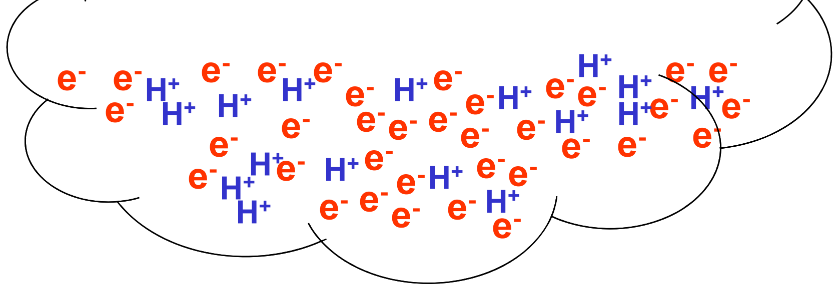
Electrons and Protons



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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

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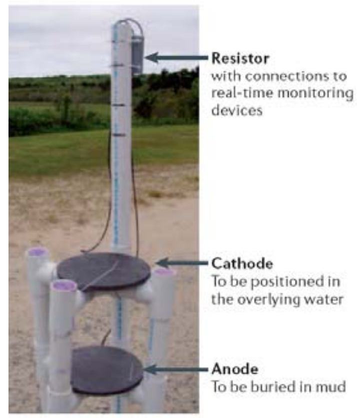
Electrochemical Properties

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/anaerobic interfaces in wetlands
- Soil oxygen demand and nutrient fluxes



Source: D. R. Lovley, 2006. Nature Reviews 4:497-508

Oxidation-Reduction

Reductant → **Oxidant + e^-**

Reductant = Electron donor

[Organic matter, NH_4^+, Fe^{2+}, Mn^{2+}, S^{2-}, CH_4, H_2, H_2O]

Oxidant + e^- → **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

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^-$$

Reductant *Oxidant*

Reduction

$$6O_2 + 24H^+ + 24e^- = 12H_2O$$

Oxidant *Reductant*

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$

Oxidation - Reduction

Oxidation-Reduction

[Nitrate Respiration – Dentrification]

Oxidation

$$5C_6H_{12}O_6 + 30H_2O = 30CO_2 + 120H^+ + 120e^-$$

Reductant *Oxidant*

Reduction

$$24NO_3^- + 144H^+ + 120e^- = 12N_2 + 72H_2O$$

Oxidant *Reductant*

$$5C_6H_{12}O_6 + 24NO_3^- + 24H^+ = 12N_2 + 30CO_2 + 42H_2O$$

Oxidation - Reduction

Oxidation-Reduction

[Sulfate Respiration]

Oxidation

$$C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^-$$

Reductant — *Oxidant*

Reduction

$$3SO_4^{2-} + 24H^+ + 24e^- = 3S^{2-} + 12H_2O$$

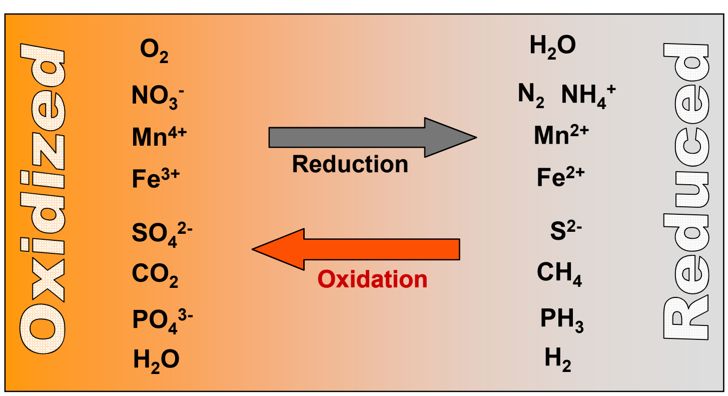
Oxidant — *Reductant*

$$C_6H_{12}O_6 + 3SO_4^{2-} = 3S^{2-} + 6CO_2 + 6H_2O$$

Oxidation - Reduction

Oxidation-Reduction

UPLAND SOILS — **FLOODED SOILS**



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Nernst Equation

m (OXIDANT) + m H^+ + n e^- = m (REDUCTANT)

$$Eh = E^o - [0.059/n] \log [Reductant/Oxidant] - 0.059 [m/n] pH$$

E = Electrode potential (volts)
E^o= 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 ^oC))
n = number of electrons involved in the reaction

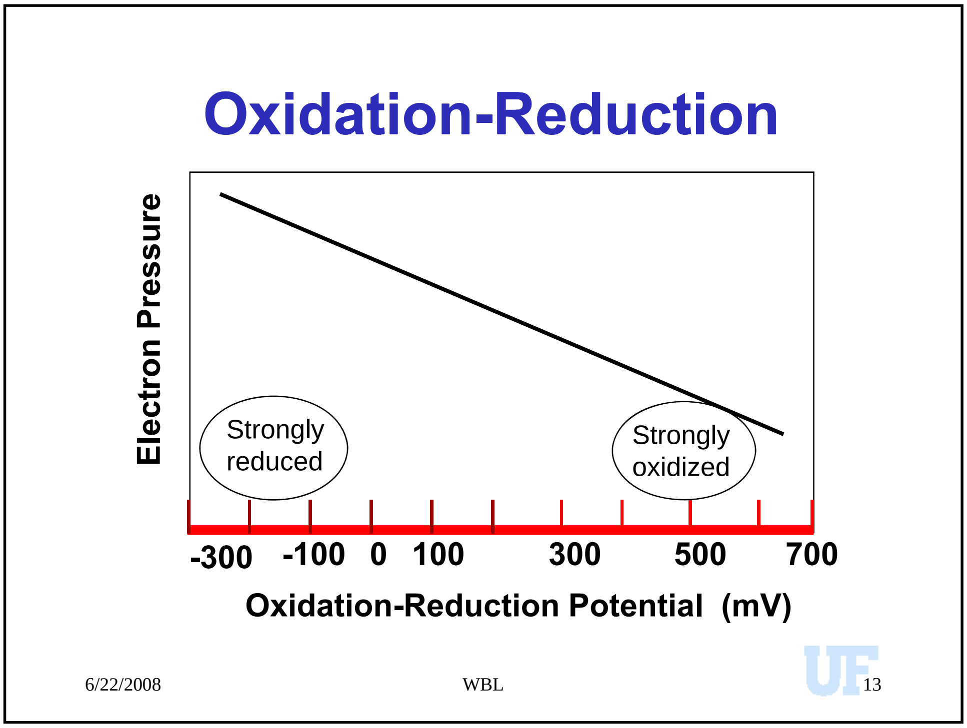
Wetland Soil

Drained Soil

Anaerobic	Aerobic
Highly Reduced / Reduced / Moderately Reduced	Oxidized

-300 -100 0 100 300 500 700

Oxidation-Reduction Potential (mV)


Oxidation-Reduction
Electron Pressure
Strongly reduced
Strongly oxidized
-300 -100 0 100 300 500 700
Oxidation-Reduction Potential (mV)
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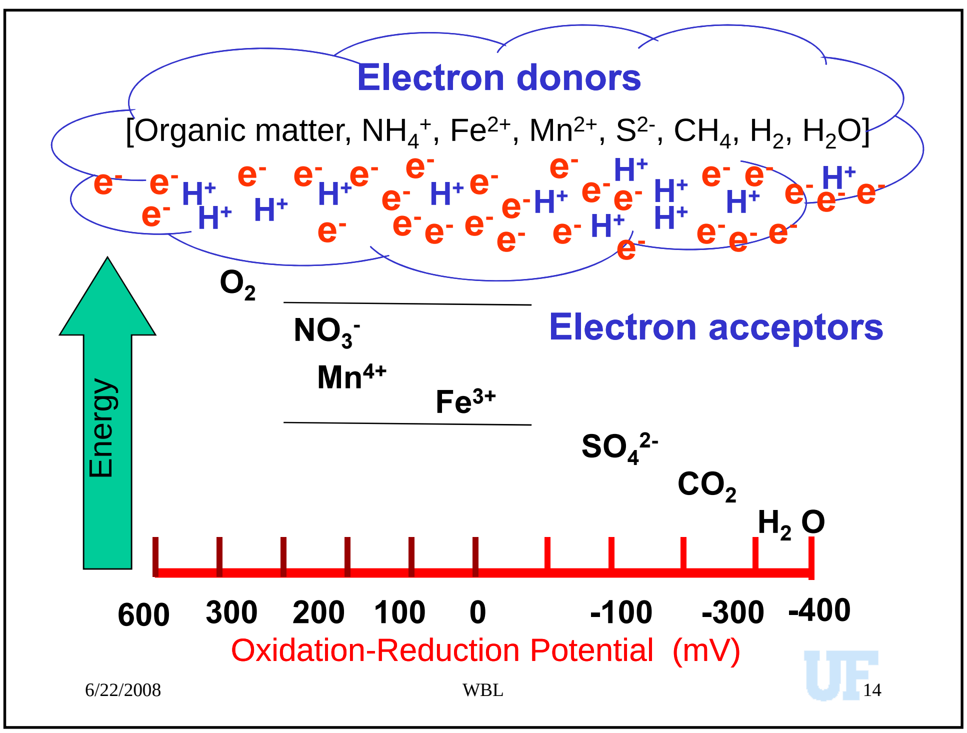
Electron donors
[Organic matter, NH_4^+, Fe^{2+}, Mn^{2+}, S^{2-}, CH_4, H_2, H_2O]
Energy
O_2
NO_3^-
Mn^{4+}
Fe^{3+}
Electron acceptors
SO_4^{2-}
CO_2
H_2O
600 300 200 100 0 -100 -300 -400
Oxidation-Reduction Potential (mV)
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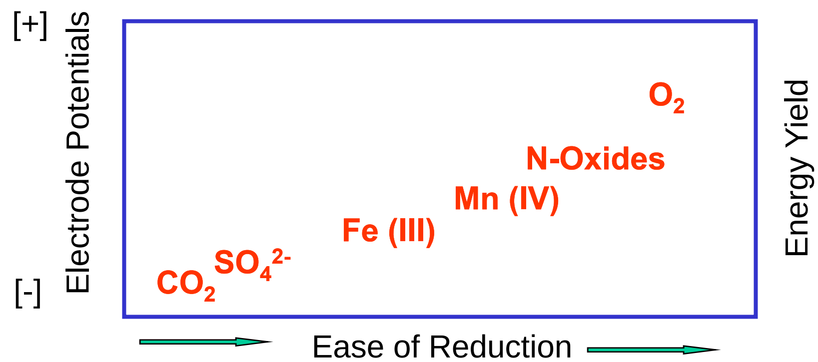
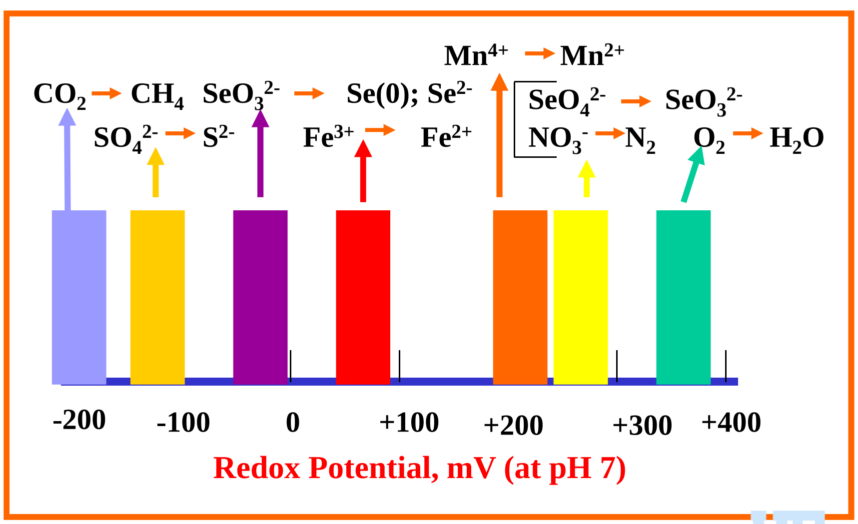
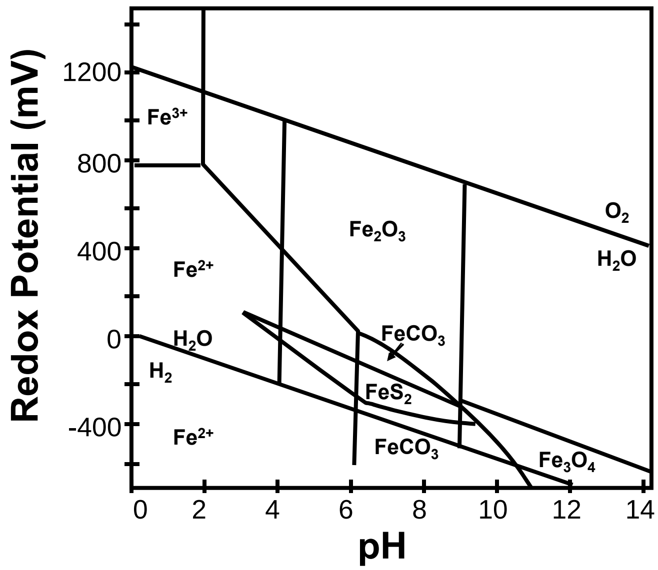
How much energy is released during oxidation - reduction reactions?



Oxidation-Reduction



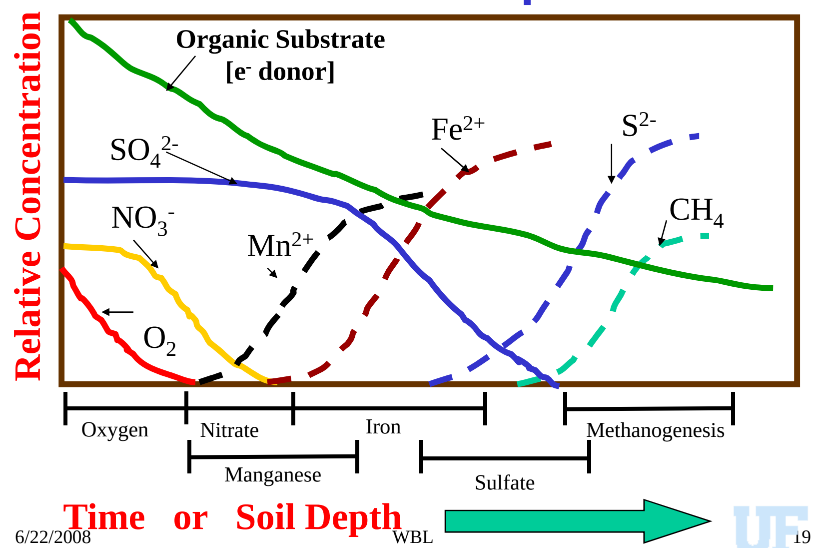
Iron Redox Couple and Eh-pH



Oxidation-Reduction

Uplands	Wetlands and Aquatic Systems
➢ **Electron acceptor non-limiting**	➢ **Electron acceptor limiting**
➢ **Electron donor limiting**	➢ **Electron donor non-limiting**

Sequential Reduction of Electron Acceptors



Redox Zones with Depth

WATER

- **Oxygen Reduction Zone**

SOIL

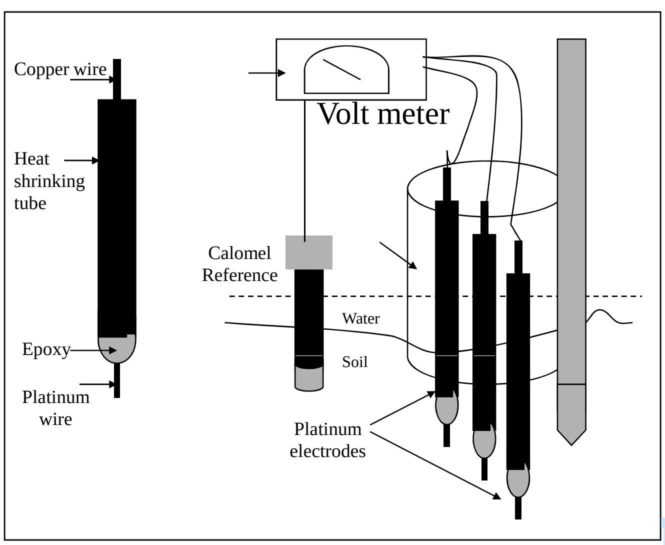
- **Oxygen Reduction Zone** — Eh = > 300 mV — **Aerobic**
- **Nitrate Reduction Zone**, **Mn^{4+} Reduction Zone** — **Eh = 100 to 300 mV** — **Facultative**
- **Fe^{3+} Reduction Zone** — Eh = -100 to 100 mV
- **Sulfate Reduction Zone** — Eh = -200 to -100 mV — **Anaerobic**
- **Methanogenesis** — Eh = < -200 mV

Depth ↓

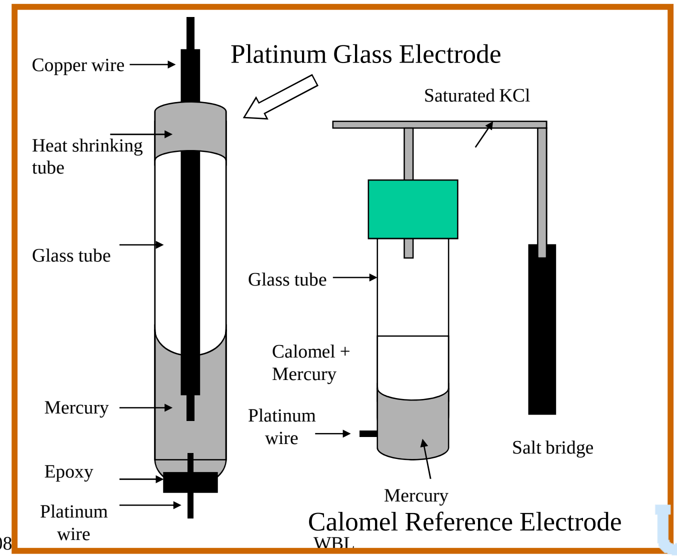
Regulators of Eh

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

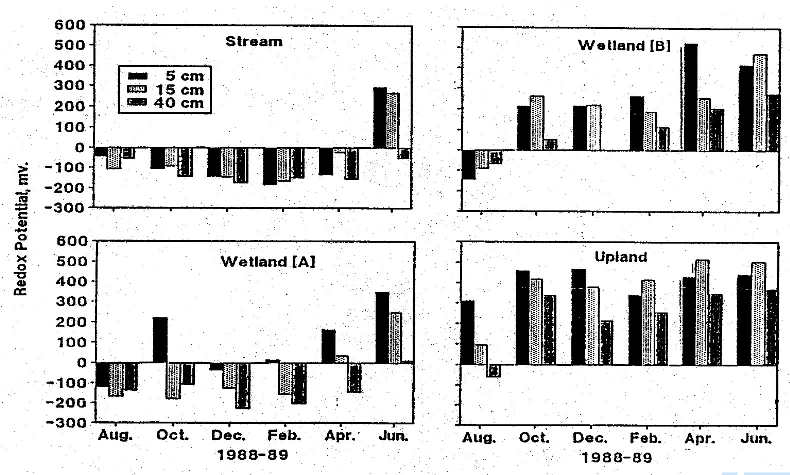
Field Redox Electrodes



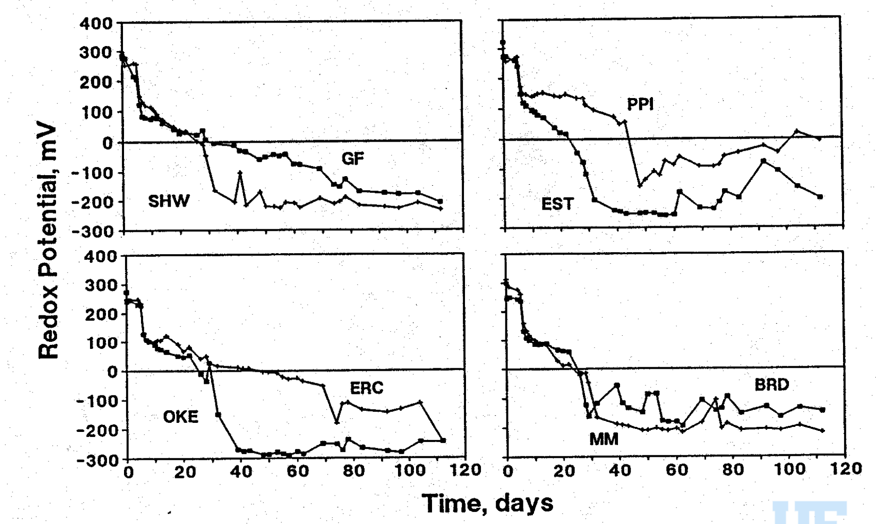
Laboratory Redox Electrodes



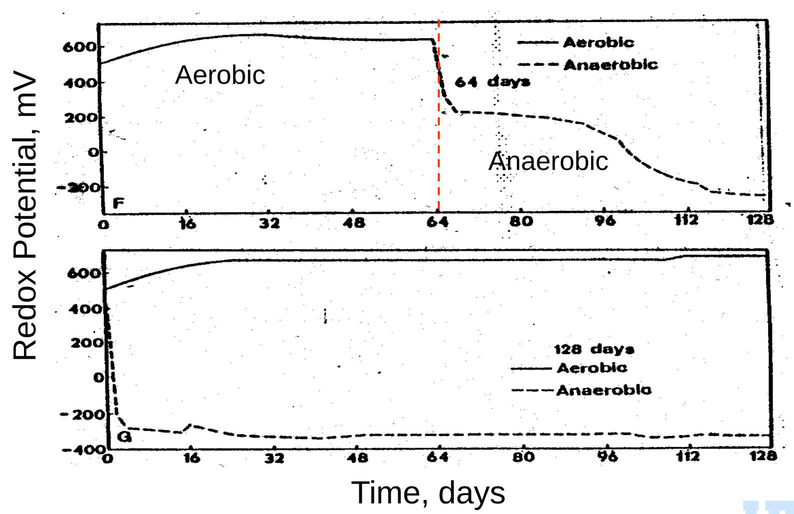
Okeechobee Basin Wetland Soils and Stream Sediments



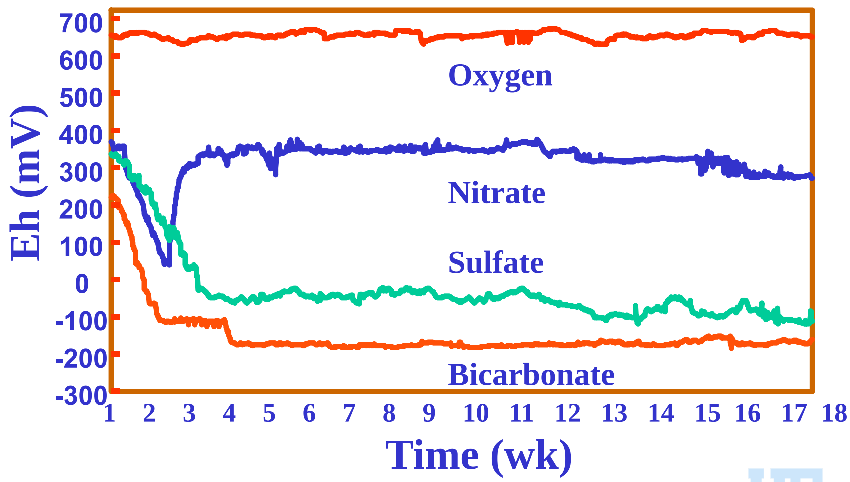
Flooded Organic Soils: Everglades Agricultural Area



Flooded Paddy Soils: Louisiana



Electron Acceptors - Redox Potential



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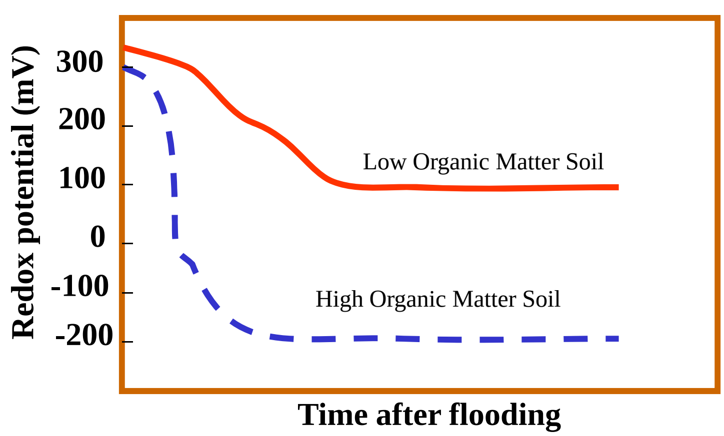
Electron Donor [Organic Matter] – Redox Potential



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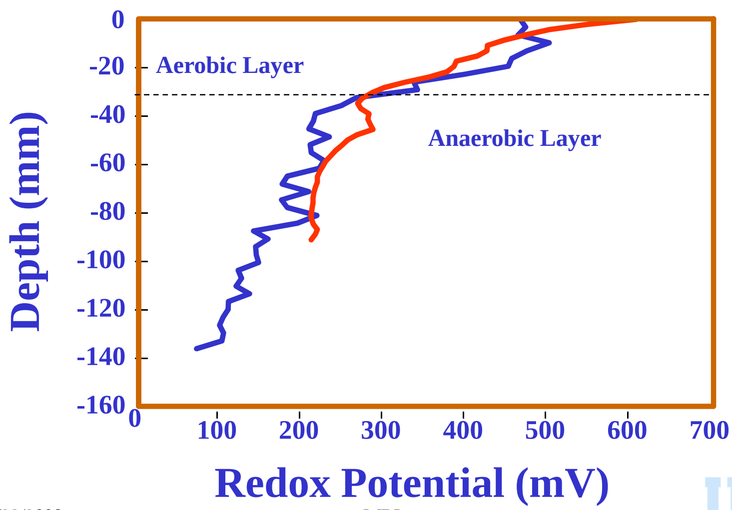
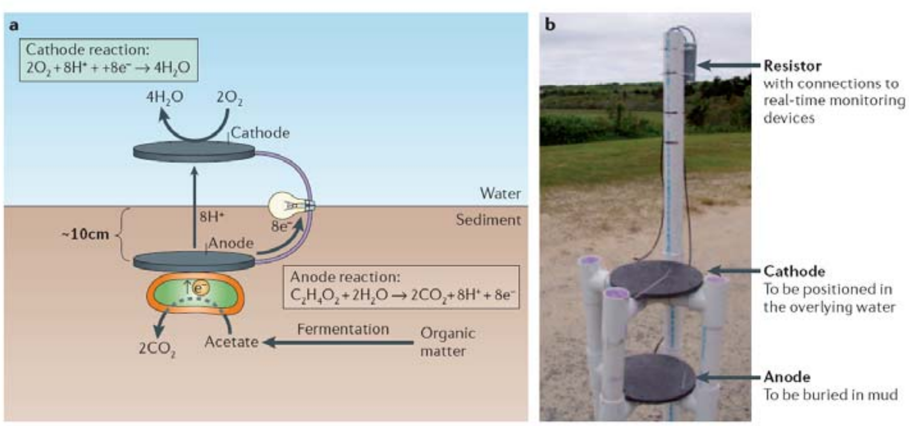
Redox Gradients in Sediments

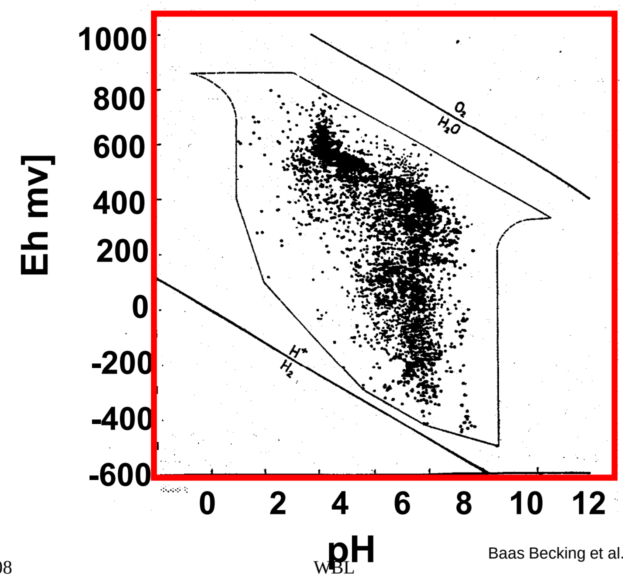


Sediment Microbial Fuel Cell



Source: D. R. Lovley, 2006. Nature Reviews 4:497-508

Redox Potential and pH



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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.

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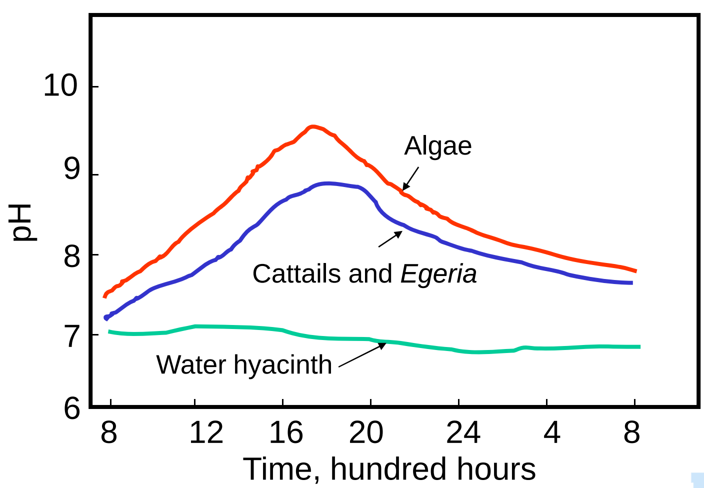
Soil and Water Column - pH

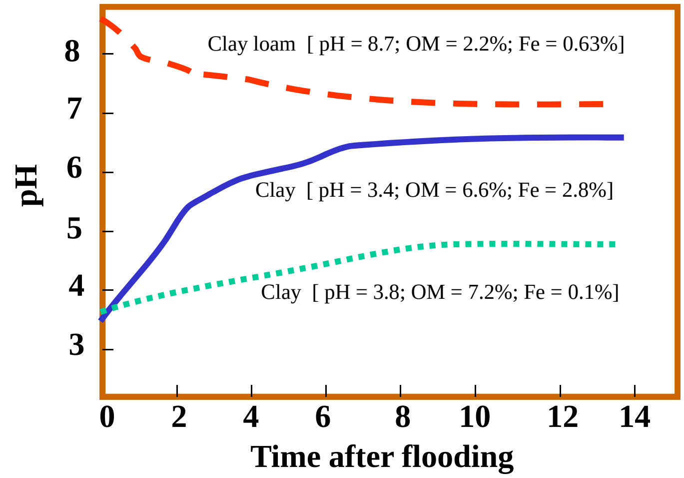
- **Reactions involving protons**
  - $CO_2 + H_2O = H_2CO_3$
  - $H_2CO_3 = H^+ + HCO_3^-$
  - $HCO_3^- = H^+ + CO_3^{2-}$

- **Reactions in which both protons and electrons are transferred**
  - $2Fe(OH)_3 + 3H^+ + e^- = 2Fe^{2+} + 3H_2O$

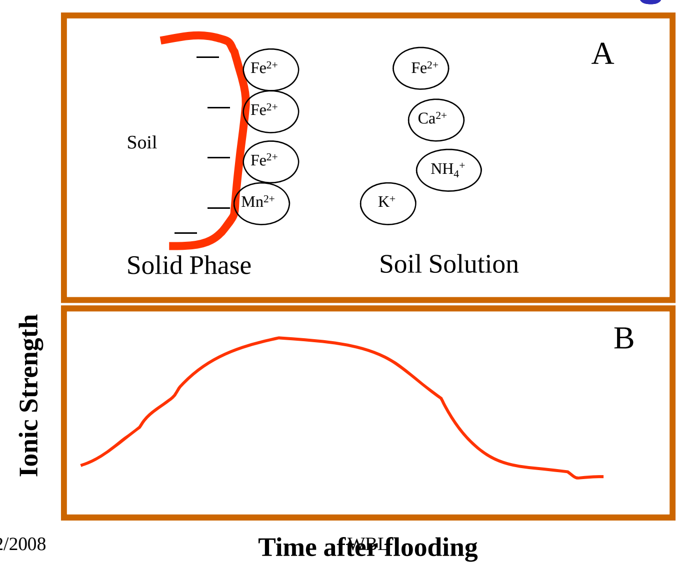
Water Column pH: Experimental Ponds – Lake Apopka Basin



Effect of Flooding on Soil pH



Effect of Flooding on Soil Porewater Ionic Strength



Redox Couples in Wetlands

- $C_6H_{12}O_6/CO_2$ and O_2/H_2O
- $C_6H_{12}O_6/CO_2$ and NO_3^-/N_2
- $C_6H_{12}O_6/CO_2$ and MnO_2/Mn^{2+}
- $C_6H_{12}O_6/CO_2$ and $FeOOH/Fe^{2+}$
- $C_6H_{12}O_6/CO_2$ and SO_4^{2-}/H_2S
- H_2/H^+ and CO_2/CH_4

Aerobic Respiration and Energy Yield

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$

ΔG_r = -686.4 kcals/mole

$$ADP + P_i = ATP$$

ΔG_r = -7.7 kcals/mole

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Soil Oxygen Demand

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Oxygen

- Oxygen is an electron acceptor
- Reduction [Electron acceptor]
  - $O_2 + 4H^+ + 4e^- = 2H_2O$:

  Oxidant
- Oxidation [Electron donor]
  - $C_6H_{12}O_6 + 6H_2O = 6CO_2 + 24H^+ + 24e^-$

  Reductant

Oxygen Consumption

- Heterotrophic microbial respiration
  - $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$
- Chemolithotrophic oxidation of reduced inorganic compounds
  - $NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$
- Chemical oxidation of reduced inorganic compounds
  - $4Fe^{2+} + 10H_2O + O_2 = 4Fe(OH)_3 + 8H^+$

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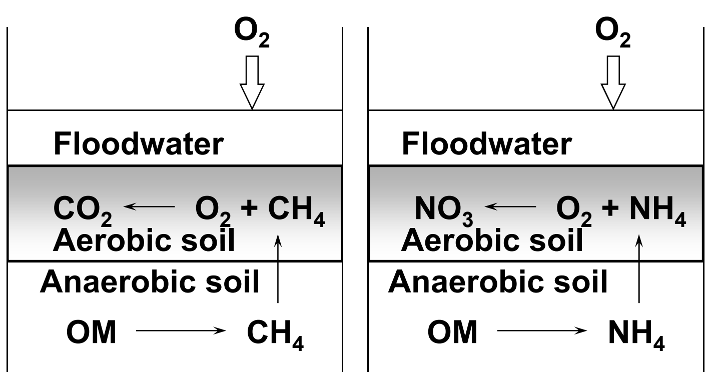
Oxidation-Reduction

Carbon **Nitrogen**



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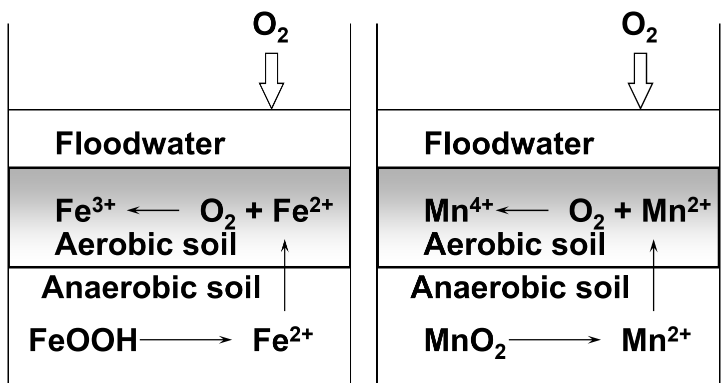
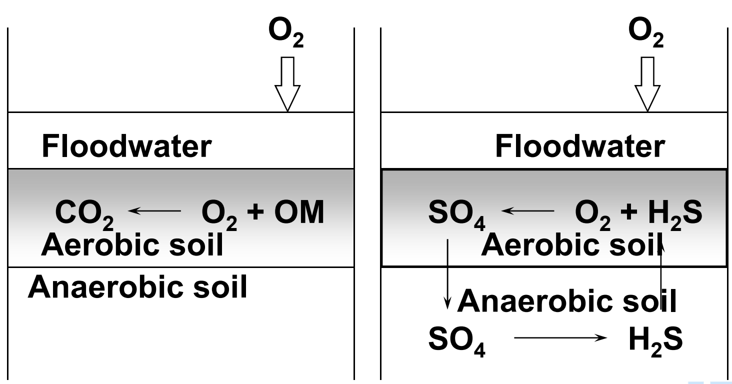
Oxidation-Reduction

Iron / Manganese

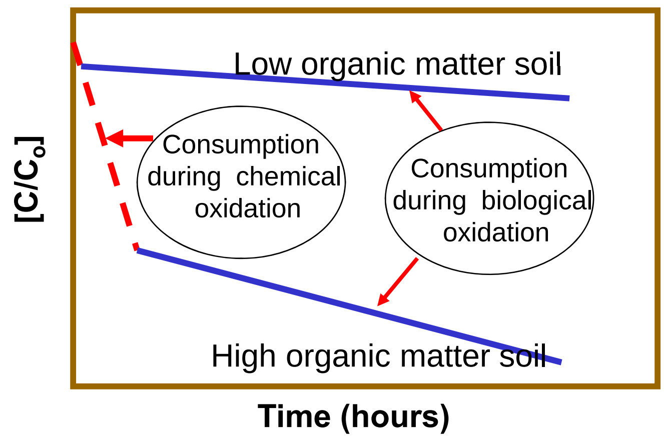


Oxidation-Reduction

Carbon / Sulfur



Oxygen Consumption



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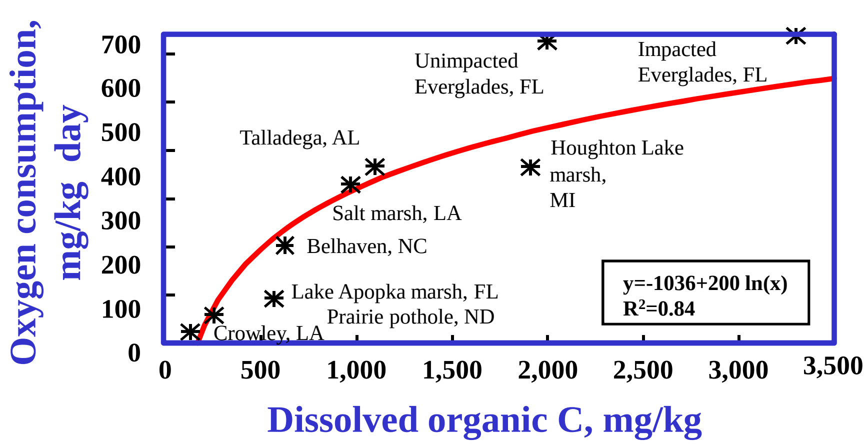
Aerobic Respiration



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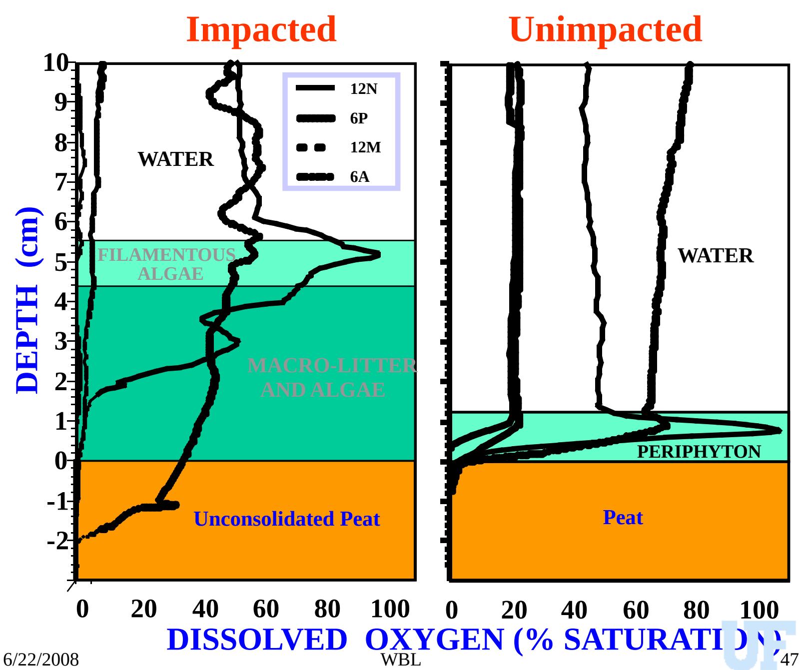

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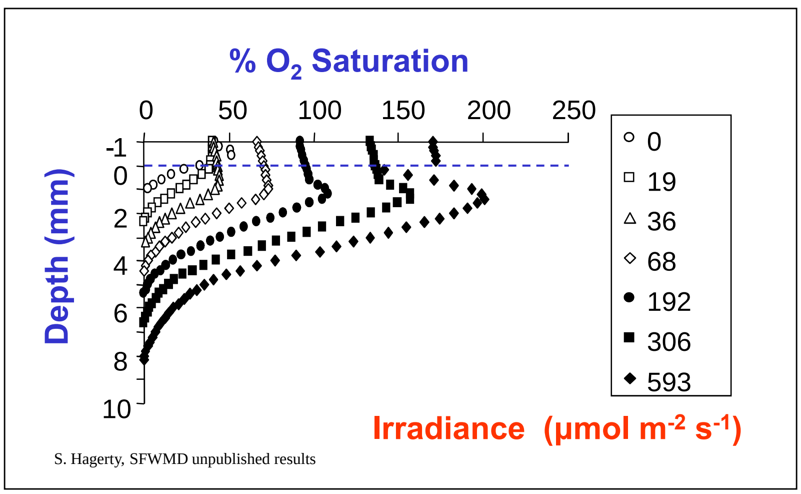
Oxygen - Periphyton



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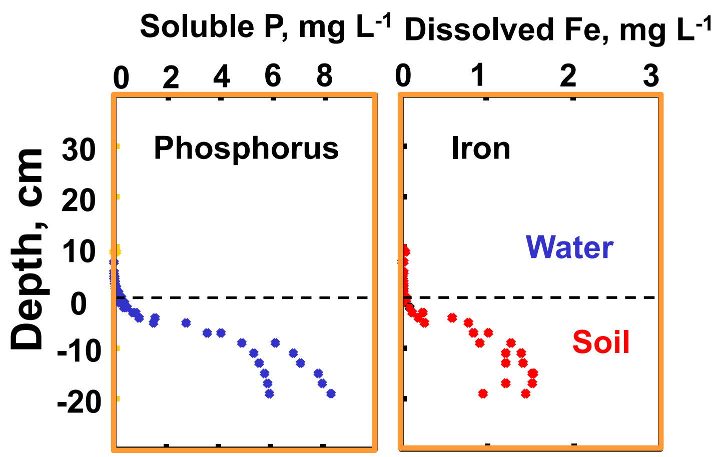
Lake Apopka Marsh



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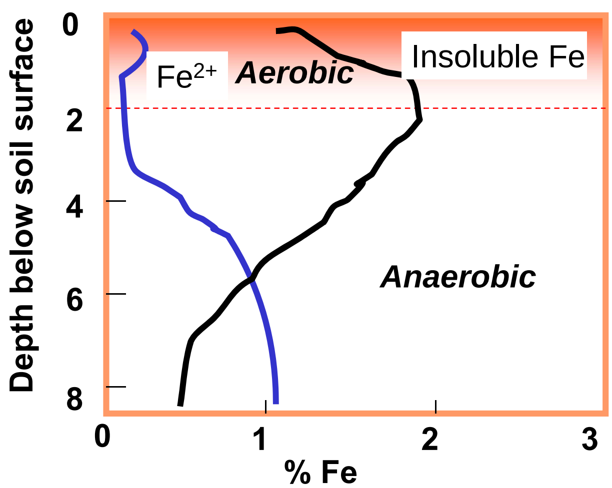
Mobile and Immobile Iron



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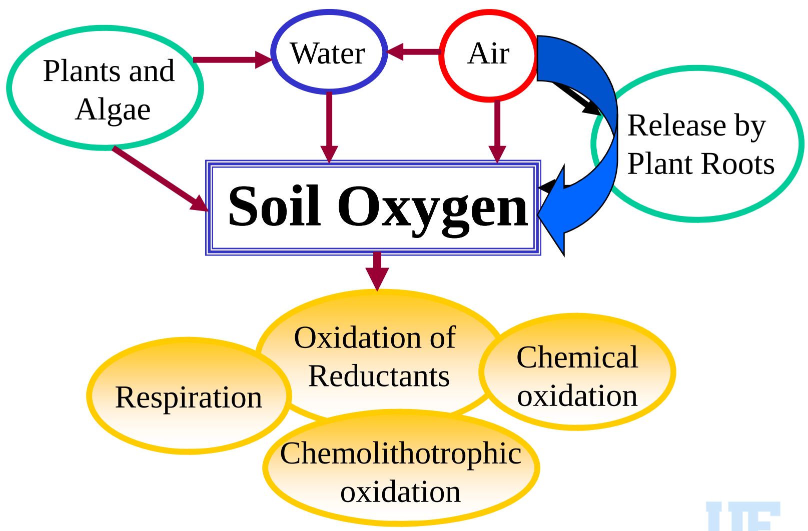
OXYGEN: Sources and Sinks



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

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