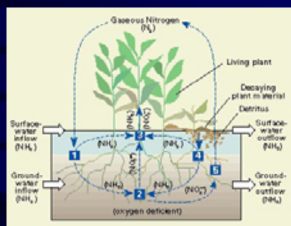
Chemical Transformations in Wetlands



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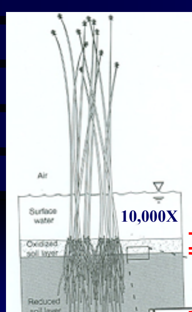
Oxygen Depletion

Oxidized to Reduced State



Oxidation: Molecule loses an e^- (greater + valence)

Reduction: Molecule gains an e^- (greater − valence)

Redox Potential: Tendency of e^- to flow between molecules (mV)

400−700 unflooded; −400 to 400 flooded

Oxygen is a common e^- acceptor

When anaerobic, other compounds must be e^- acceptors for biochemical reactions

- Aerobic (<2 cm)
- Anaerobic (2 hrs to 2 days)

Thickness of Aerobic Layer

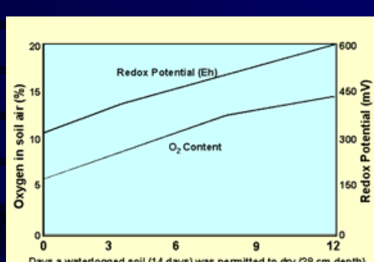
- •Rate of O_2 Transfer
- •Microbe Abundance
- •Algal O_2 Production
- •Wind Action

Root respiration & Decomposition

Oxygen Depletion

Change in Redox Potential

Electron acceptor required in biochemical processes associated with breakdown of organic C and nitrogenous waste and for respiration!



NOTE: Microbial populations mediate nearly all chemical transformations in wetlands to accomplish activities to left!

Redox potential decreases with soil flooding.

Thus, the potential for e^- transfer decreases with flooding.

Why?

Anaerobic (reduced) State

Order of Chemical Transformations

$O_2 + 4e^- + 4H^+$ → $2H_2O$

Until all dissolved oxygen is depleted, O_2 is the terminal e^- acceptor (400−600 mV)

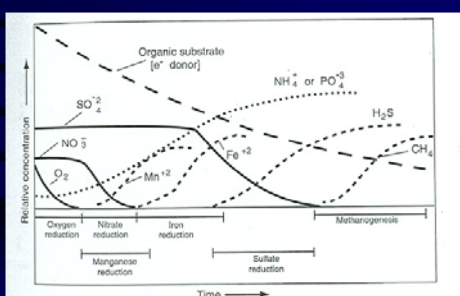
"Microbial preference" →

Element	Oxidized Form	Reduced Form	Approximate Redox Potential for Transformation (mV)
Nitrogen	NO_3^- (nitrate)	N_2O, N_2, NH_4^+	250
Manganese	Mn^{4+} (manganic)	Mn^{2+} (manganous)	225
Iron	Fe^{3+} (ferric)	Fe^{2+} (ferrous)	+100−−100
Sulfur	$SO_4^=$ (sulfate)	$S^=$ (sulfide)	−100−−200
Carbon	CO_2 (carbon dioxide)	CH_4 (methane)	Below −200

1) $2NO_3^- + 10e^- + 12H^+ \longrightarrow N_2 + 6H_2O$
2) $MnO_2 + 2e^- + 4H^+ \longrightarrow Mn^{2+} + H_2O$
3) $Fe(OH)_3 + e^- + 3H^+ \longrightarrow Fe^{2+} + 3H_2O$
4) $SO_4^= + 8e^- + 9H^+ \longrightarrow HS^- + 4H_2O$
5) $CO_2 + 8e^- + 8H^+ \longrightarrow CH_4 + 2H_2O$

Anaerobic (reduced) State

Order of Chemical Transformations

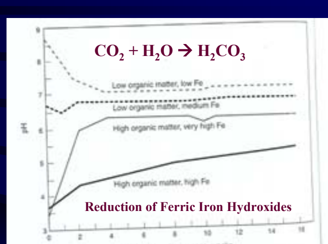


Notice Sequence & Concentration of Reduced Forms

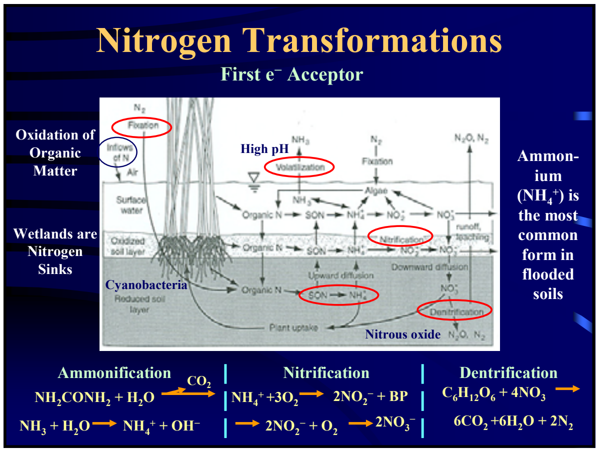
Changes in Acidity

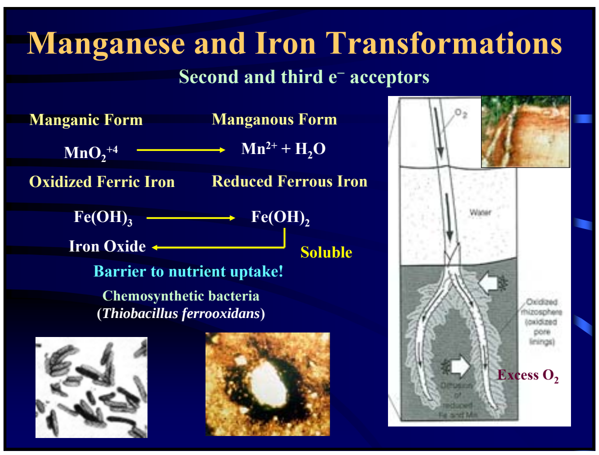
Organic Carbon & Time Dependent

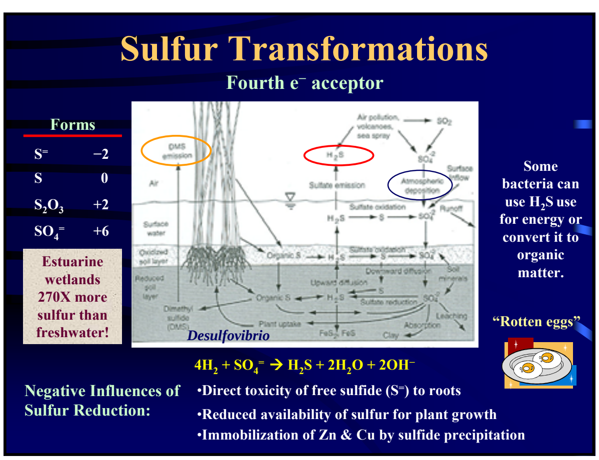
In general, mineral hydric soils are higher in pH than organic soils and they become more acidic with flooding.



In contrast, organic hydric soils are lower in pH than mineral soils and they become more basic with flooding.


Nitrogen Transformations
First e⁻ Acceptor
Oxidation of Organic Matter
Wetlands are Nitrogen Sinks
High pH
Cyanobacteria
Nitrous oxide
Fixation
Volatilization
Nitrification
Denitrification
Plant uptake
Upward diffusion
Downward diffusion
Ammon-ium (NH_4^+) is the most common form in flooded soils
Ammonification
$NH_2CONH_2 + H_2O \rightarrow CO_2$
$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
Nitrification
$NH_4^+ + 3O_2 \rightarrow 2NO_2^- + BP$
$\rightarrow 2NO_2^- + O_2 \rightarrow 2NO_3^-$
Dentrification
$C_6H_{12}O_6 + 4NO_3 \rightarrow$
$6CO_2 + 6H_2O + 2N_2$


Manganese and Iron Transformations
Second and third e⁻ acceptors
Manganic Form
Manganous Form
$MnO_2^{+4} \rightarrow Mn^{2+} + H_2O$
Oxidized Ferric Iron
Reduced Ferrous Iron
$Fe(OH)_3 \rightarrow Fe(OH)_2$
Iron Oxide
Soluble
Barrier to nutrient uptake!
Chemosynthetic bacteria
(*Thiobacillus ferrooxidans*)
Water
Oxidized rhizosphere (oxidized pore linings)
Excess O_2


Sulfur Transformations
Fourth e⁻ acceptor
Forms
$S^=$ −2
S 0
S_2O_3 +2
$SO_4^=$ +6
Estuarine wetlands 270X more sulfur than freshwater!
DMS emission
H_2S
Atmospheric deposition
Sulfate emission
Sulfate oxidation
Sulfate reduction
Desulfovibrio
Some bacteria can use H_2S use for energy or convert it to organic matter.
"Rotten eggs"
$4H_2 + SO_4^= \rightarrow H_2S + 2H_2O + 2OH^-$
Negative Influences of Sulfur Reduction:
•Direct toxicity of free sulfide ($S^=$) to roots
•Reduced availability of sulfur for plant growth
•Immobilization of Zn & Cu by sulfide precipitation

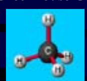
Carbon Transformations

Fifth e⁻ acceptor

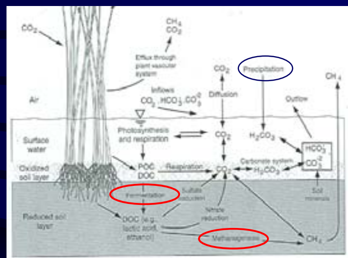
Methane

"Swamp gas"

Natural Greenhouse Gas



Heat 23X CO_2



CH_4 Release (mg C/m² d)

- **Bogs** (150)
- **Marshes** (90)
- **Forested Swamps** (53)
- **Riparian Wetlands** (23)

Fermentation: Use of **organic matter** as an electron acceptor during anaerobic respiration by microbes with **ethanol** and **CO_2** as byproducts.

Methanogenesis: Use of **CO_2** as an electron acceptor by prokaryotic Archaea microbes with **methane** (CH_4) as a byproduct.

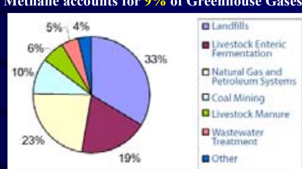
Atmospheric Methane Sources

http://www.epa.gov/methane/sources.html

Anthropogenic:

60% of Total Atmospheric Methane

Methane accounts for 9% of Greenhouse Gases



Natural Sources:

40% of Total Atmospheric Methane

30% Natural Wetlands!