Sulfur

- Introduction
  - S Forms, Distribution, Importance
- Basic processes of S Cycles
  - Examples of current research
  - Examples of applications
- Key points learned
Sulfur

Learning Objectives

- Identify the forms of S in wetlands
- Understand the importance of S in wetlands/global processes
- Define the major S processes/transformations
- Understand the importance of microbial activity in S transformations
- Understand the potential regulators of S processes
- See the application of S cycle principles to understanding natural and man-made ecosystems

Sources of Sulfur

- Sulfur is a ubiquitous element.
- Various sulfur compounds are present in:
  - The atmosphere
  - Minerals
  - Soils
  - Plant tissue
  - Animal tissue
  - Microbial biomass
  - Sediment
Reservoirs of Sulfur

- Atmosphere: $4.8 \times 10^9$ kg
- Lithosphere: $24.3 \times 10^{18}$ kg
- Hydrosphere:
  - Sea: $1.3 \times 10^{18}$ kg
  - Freshwater: $3.0 \times 10^{12}$ kg
- Pedosphere:
  - Soil: $2.6 \times 10^{14}$ kg
  - Soil Organic matter: $0.1 \times 10^{14}$ kg
- Biosphere: $8.0 \times 10^{12}$ kg

General Forms of Sulfur in the Environment

- **Organic S** in plant, animal, and microbial tissue (as essential components of amino acids and proteins)

  - Methionine: $\text{H}_2\text{S}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{S}-\text{R}_1\text{~R}_2$
  - Cysteine: $\text{H}_2\text{C-S-CH}_2-\text{CH}_2-\text{S}-\text{R}_1\text{~R}_2$
  - Thioester: $\text{R}_1\text{~C-S-R}_2$

- Organic sulfur primarily in soil and sediments as humic material (naturally occurring soil and sediment organic matter)
General Forms of Sulfur in the Environment

- **Gaseous S** compounds (SO$_2$, H$_2$S, DMSO, DMS)

- **Oxidized Inorganic S** (sulfate, SO$_4^{2-}$, is the primary compound).
  
  *Seawater contains about 2,700 mg/L (ppm) of sulfate*

- **Reduced Inorganic S** (elemental sulfur, S$_0$, and sulfide, S$_2^-$)

General Forms of Sulfur in the Environment

- **Minerals**
  
  Galena (PbS$_2$)  
  Gypsum (CaSO$_4$)  
  Jarosite(Fe$_2$S)  
  Barite (BaSO$_4$)  
  Pyrite (FeS$_2$)

- **Fossil Fuels**
  
  - Petroleum (0.1-10%)
  - Coal (1-20%)
Oxidation states of selected sulfur compounds

- Organic S (R-SH) -2
- Sulfide (S²⁻) -2
- Elemental S (S⁰) 0
- Sulfur dioxide (SO₂) +4
- Sulfite (SO₃²⁻) +4
- Sulfate (SO₄²⁻) +6

Global Sulfur Cycle
Sulfur Cycling Processes

1. Dissimilatory sulfate reduction
2. Assimilatory sulfate reduction
3. Desulfurylation
4. Sulfide oxidation
5. Sulfur oxidation
6. Dissimilatory S$^0$ reduction

Sulfur Cycle

[Diagram showing the sulfur cycle with aerobic and anaerobic processes, indicating pathways for dissimilatory and assimilatory sulfate reduction, desulfurylation, sulfide oxidation, and sulfur oxidation.]
Distribution of sulfur in soils

**Organic sulfur [93%]**
- Carbon-bonded sulfur (cysteine and methionine) 41%
- Non-carbon-bonded sulfur (ester sulfates) 52%

**Inorganic sulfur [7%]**
- Adsorbed + soluble sulfates 6%
- Inorganic compounds less oxidized than sulfates and reduced sulfur compounds (e.g. sulfides) 1%

---

**Organic Sulfur Forms**

![Bar graph showing sulfur forms](image)

- **Freshwater**
- **Brackish**
- **Salt**

**Sulfur, g/kg**
- Ester
- C-S
- Total

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*Organic Geochemistry* vol. 18, no. 4, pp. 489-500, 1992

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Inorganic Sulfur Forms

![Bar chart showing sulfur forms in different water types](chart)


Organic S Hydrolysis

\[
R - O-SO_3^{2-} + H_2O \rightarrow R-OH + SO_4^{2-} + H^+ \quad \text{Arylsulfatase}
\]

\[
R - S-H + H_2O \rightarrow R-OH + H_2S \quad \text{Sulfohydrolase}
\]

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Sulfur – Organism Groups

Assimilatory Sulfate Reduction
• Bacteria, fungi, algae, and plants

Dissimilatory Sulfate Reduction
• Heterotrophs
  Desulfovibrio, Desulfotomaculum, Desulfobacter, Desulfuromonas

Sulfide Oxidation
• Phototrophs: Chlorobium, Chromatium
• Chemolithoautotrophs: Thiothrix, Beggiatoa

Sulfate Reducing Bacteria: SRB (habitats)

Desulfovibrio - found in water-logged soils.
Desulfotomaculum - spoilage of canned foods.
Desulfomonas - found in intestines.
Archaeoglobus - a thermophilic Archea whose optimal growth temperature is 83°C.
Sulfate Reduction

Deposition SO$_4^{2-}$

Tidal Exchange

AEROBIC

Adsorbed SO$_4^{2-}$

Microbial Biomass-S

ANAEROBIC

Reduction

SO$_4^{2-}$

Reduction

S$^2_-$

S$^2_-$

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Glucose Oxidation

<table>
<thead>
<tr>
<th>Oxidation – Reduction Reaction</th>
<th>kJ/mol Glucose</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_6 + 6\text{O}_2 = 6\text{CO}_2 + 6\text{H}_2\text{O}$</td>
<td>2,880</td>
</tr>
<tr>
<td>$5\text{C}<em>6\text{H}</em>{12}\text{O}_6 + 24\text{NO}_3^- + 24\text{H}^+ = 30\text{CO}_2 + 12\text{N}_2 + 42\text{H}_2\text{O}$</td>
<td>2,712</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_6 + 12\text{MnO}_2 + 24\text{H}^+ = 6\text{CO}_2 + 12\text{Mn}^{2+} + 18\text{H}_2\text{O}$</td>
<td>1,920</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_6 + 24\text{Fe(OH)}_3 + 48\text{H}^+ = 6\text{CO}_2 + 24\text{Fe}^{2+} + 66\text{H}_2\text{O}$</td>
<td>432</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}\text{O}_6 + 3\text{SO}_4^{2-} = 6\text{CO}_2 + 3\text{S}^{2-} + 6\text{H}_2\text{O}$</td>
<td>381</td>
</tr>
</tbody>
</table>

Oxygen Equivalents - Energy Yield from Glucose

<table>
<thead>
<tr>
<th>Electron Acceptors</th>
<th>% of Aerobic Energy Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_2$</td>
<td>100%</td>
</tr>
<tr>
<td>$\text{NO}_3^-$</td>
<td>90%</td>
</tr>
<tr>
<td>$\text{MnO}_2$</td>
<td>60%</td>
</tr>
<tr>
<td>$\text{Fe(OH)}_3$</td>
<td>20%</td>
</tr>
<tr>
<td>$\text{SO}_4^{2-}$</td>
<td>10%</td>
</tr>
</tbody>
</table>
Oxidation-Reduction

\[ \text{Redox Potential, mV (at pH 7)} \]

Sequential Reduction of Electron Acceptors

\[ \text{Time After Flooding or Soil Depth} \]
Redox Zones With Depth

**WATER**

**SOIL**

Oxygen Reduction Zone
Eh = > 300 mV

Nitrate Reduction Zone
Mn⁴⁺ Reduction Zone
Eh = 100 to 300 mV

Fe³⁺ Reduction Zone
Eh = -100 to 100 mV

Sulfate Reduction Zone
Eh = -200 to -100 mV

Methanogenesis
Eh = < -200 mV

Redox Potential and pH

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### Microbial Activity

**[Site: Water Conservation 2A]**

- **Graph**
  - Equation: \( y = 0.33x + 1.3 \)
  - \( r^2 = 0.88; \ n = 24 \)

### Sulfate Respiration

- **Detrital Matter**
  - Complex Polymers: Cellulose, Hemicellulose, Proteins, Lipids, Waxes, Lignin
  - Monomers: Sugars, Amino Acids, Fatty Acids

- **Processes**:
  - Enzyme Hydrolysis
  - Oxidative phosphorylation
  - TCA Cycle
  - Substrate level phosphorylation
  - Uptake

- **Products**:
  - \( \text{CO}_2, \text{H}_2\text{O}, \text{S}^2-, \text{Nutrients} \)
  - Glucose, Pyruvate, Organic Acids

- **Species**:
  - [Sulfate Reducing Bacterial Cell]
  - [Fermenting Bacterial Cell]

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Electron donors used during sulfate reduction

- SRB lack enzymes necessary for complex carbon assimilation

\[
\text{CH}_3\text{COO}^- + \text{SO}_4^{2-} \rightarrow 2\text{HCO}_3^- + \text{HS}^- \\
2\text{H}_2 + \text{SO}_4^{2-} \rightarrow \text{S}^2^- + 2\text{H}_2\text{O} + 2\text{OH}^- 
\]
Electron Donors

<table>
<thead>
<tr>
<th>System</th>
<th>$H_2$</th>
<th>Acetate</th>
<th>Propionate</th>
<th>Butyrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Danish subtidal</td>
<td>5–10</td>
<td>40–50</td>
<td>10–20</td>
<td>10–20</td>
</tr>
<tr>
<td>Brittany mudflat</td>
<td>—</td>
<td>65</td>
<td>14</td>
<td>8</td>
</tr>
<tr>
<td>Colne Pt. salt marsh</td>
<td>—</td>
<td>~60</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Sulfate Reduction Rates**

<table>
<thead>
<tr>
<th>Activity</th>
<th>[nmol/g per day]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low carbon wetland</td>
<td>23</td>
</tr>
<tr>
<td>Peaty wetland</td>
<td>130</td>
</tr>
<tr>
<td>Oligotrophic lake</td>
<td>707</td>
</tr>
<tr>
<td>Eutrophic lake</td>
<td>1,224</td>
</tr>
<tr>
<td>Marine and salt-marsh</td>
<td>744-24,000</td>
</tr>
</tbody>
</table>

---

**Salt Marshes**

<table>
<thead>
<tr>
<th>Respiration [g C/m² year]</th>
<th>Sapelo Island [GA]</th>
<th>Sippewissett [MA]</th>
<th>Sapelo Island (1997)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic respiration</td>
<td>390</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>Denitrification</td>
<td>10</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Mn and Fe reduction</td>
<td>ND</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td><strong>Sulfate reduction</strong></td>
<td><strong>850</strong></td>
<td><strong>1,800</strong></td>
<td><strong>2,000</strong></td>
</tr>
<tr>
<td>Methanogenesis</td>
<td>40</td>
<td>1-8</td>
<td></td>
</tr>
</tbody>
</table>

S Respiration ~65% ~82% ~69-87%
Sulfate Respiration

<table>
<thead>
<tr>
<th>Site</th>
<th>Rate of carbon oxidation (mmol C m(^{-2}) d(^{-1}))</th>
<th>Respiratory mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O(_3) Resp</td>
<td>SO(_4) Resp</td>
</tr>
<tr>
<td>Marine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Linford</td>
<td>56</td>
<td>53</td>
</tr>
<tr>
<td>Slapwissert salt marsh</td>
<td>438</td>
<td>10</td>
</tr>
<tr>
<td>Sappo L. salt marsh</td>
<td>280</td>
<td>20</td>
</tr>
<tr>
<td>Slapwissert salt marsh</td>
<td>180</td>
<td>50</td>
</tr>
<tr>
<td>Sulfate-depleted marine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cape Lookout Shatt</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>Lagoon</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biscayne Tbar</td>
<td>42</td>
<td>2</td>
</tr>
<tr>
<td>Wintergreen Lake - A</td>
<td>3.1*</td>
<td>13†</td>
</tr>
<tr>
<td>Wintergreen Lake - B</td>
<td>14.4*</td>
<td>13†</td>
</tr>
<tr>
<td>Wintergreen Lake</td>
<td>108‡</td>
<td>30</td>
</tr>
<tr>
<td>Lake Vechter</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Lawrence Lake</td>
<td>3*</td>
<td>30-81†</td>
</tr>
<tr>
<td>Experimental Lakes Area</td>
<td>9.3-12</td>
<td>16-20†</td>
</tr>
</tbody>
</table>

* Assuming 2 cm active depth in sediments.
† Percentage of total inorganic carbon only.
‡ Area of 1 cm.

Seasonal Effects


Seasonal Effects
Spartina alterniflora marsh

Great Sippewissett Marsh

**Regulators of Sulfate Reduction**

- Presence of electron acceptor with higher reduction potentials
- Oxygen is toxic to sulfate reducers
- Sulfate concentration
  - Freshwater (< 0.1 mM)
  - Marine (20-30 mM)
- Substrate/ Electron Donor
- Temperature
- Microbial populations

Decreasing energy yield


Anaerobic Sludge Reactor (FISH)

Sulfidogenic aggregate

Sulfidogenic/Methanogenic aggregate

SRB Probe

Archeal Probe
Competition With Methanogens

<table>
<thead>
<tr>
<th>Electron donor</th>
<th>Methanogens</th>
<th>Sulfate repressors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyruvate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Lactate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Propionate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Butyrate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Valerate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Malate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Succinate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Benzoate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Propanol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Butanol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Alanine</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>$H_2$</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Acetate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Formate</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Dimethyl sulfide</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Monomethylamine</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Ethyldimethylamine</td>
<td>X</td>
<td>?</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>X</td>
<td>?</td>
</tr>
</tbody>
</table>

Sulfate Reducers vs Methanogens

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Methanogens $K_m$ ($\mu$M)</th>
<th>Sulfate repressors</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>$1.4$</td>
<td>$-$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$4.7$</td>
<td>$0.46$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$4.1$</td>
<td>$1.2$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$6$</td>
<td>$1$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$14$</td>
<td>$4$</td>
</tr>
<tr>
<td>Acetate</td>
<td>$3,000$</td>
<td>$200$</td>
</tr>
<tr>
<td>Acetate</td>
<td>$-$</td>
<td>$70$</td>
</tr>
</tbody>
</table>

$$V = [V_{\text{max}} S]K_m + S$$
Sulfate Reduction
Typical Lake Sediments


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Sulfate Reduction
Typical Lake Sediments

Freshwater Marine


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Sulfate Reduction
Cattail Marsh – Sunnyhill Farm Wetland

Sulfur Emissions

Gaseous S Emissions

Table 16b. Sulfur emission from a Spartina alterniflora Louisiana saltmarsh

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H2SO4</td>
<td>0.76</td>
<td>0.37</td>
<td>0.49</td>
<td>0.76</td>
<td>1.49</td>
<td>1.99</td>
<td>2.22</td>
<td>1.87</td>
<td>2.98</td>
<td>2.98</td>
<td>2.98</td>
</tr>
<tr>
<td>DMS</td>
<td>0.14</td>
<td>0.31</td>
<td>0.41</td>
<td>0.89</td>
<td>2.64</td>
<td>1.13</td>
<td>0.91</td>
<td>0.91</td>
<td>5.47</td>
<td>0.41</td>
<td>0.75</td>
</tr>
<tr>
<td>Methanal</td>
<td>0.27</td>
<td>0.51</td>
<td>1.81</td>
<td>0.58</td>
<td>0.44</td>
<td>0.22</td>
<td>0.03</td>
<td>0.37</td>
<td>1.34</td>
<td>0.37</td>
<td>1.34</td>
</tr>
<tr>
<td>Carboxyl sulfate</td>
<td>0.01</td>
<td>0.41</td>
<td>0.90</td>
<td>0.03</td>
<td>0.22</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>0.01</td>
<td>0.05</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Total reduced sulfur compound</td>
<td>0.01</td>
<td>0.41</td>
<td>0.90</td>
<td>0.03</td>
<td>0.22</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
</tbody>
</table>

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Gaseous Speciation
DeLaune et al. 2001

Figure 2. Summary data showing species and quantity evolved from freshwater, brackish and saltmarsh sites. ■ Hydrogen sulfide; □ Carbonyl sulfide; △ Methanethiol; ※ Dimethyl sulfide; ▲ Carbonyl disulfide; ◊ Total measured reduced gases sulfur.

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Sulfide Formation

AERobic

ANAeroBic

Mineralization

Reduction

SO_4^{2-}

H_2S

DMS

S^{2-}

Org-S

Mineralization

Reduction

H_2S

DMS

Org-S

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Problems With Hydrogen Sulfide

- Malodorous (rotten egg smell)
- Acidic (corrosion/fouling)
- Toxic (reactive with metalloenzyme systems)
Sulfide Toxicity

Tall vs. Short *Spartina alterniflora*
**Tall vs. Short Spartina alterniflora**

Sapelo Island Marsh

**Fe(II) (mM x 10), \( SO_4^{2-} \) and \( H_2S \) (mM)**

- **Creek**
- **Tall**
- **Short**

Kostka et al., 2002. *Biogeochemistry* 60:49-76.

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**Sulfide Toxicity**

Tall vs. Short Spartina alterniflora

**NH\(_4\)\(^+\) Uptake**

- Higher \( V_{max} \)
- Lower \( K_{m} \)
- Higher \( K_{m} \)

- Inc. \( NH_4^+ \), \( S_2^- \), and Salt Concentrations

- Inc. Flood Frequency, Pore Water Turnover

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Sulfide Precipitation

Iron and Sulfide Interactions

$2\text{FeOOH} + \text{H}_2\text{S} = \text{S}^\circ + 2\text{Fe}^{2+} + 4\text{OH}^-$

$\text{Fe}^{2+} + \text{H}_2\text{S} = \text{FeS} + 2\text{H}^+$

$\text{FeS} + \text{S}^\circ = \text{FeS}_2$

Acid Volatile S (AVS)

Chromium Reducible S (CRS)

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Pyrite Framboids

Pyrite Formation

Fe Oxides → Monosulfides (AVS) → FeS → ΣH₂S → Intermediate Redox S → FeS₂ (Pyrite (CRS))

Sulfate Reduction

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Metal Sulfide Solubility - Uptake by Rice Plant

% Uptake of added $^{35}$S

Solubility Product ($K_{sp}$)

Engler and Patrick, 1981

Sulfur Oxidation

Tidal Exchange

AEROBIC

Sulfide Oxidation

\[ 2\text{H}_2\text{S} + \text{O}_2 = 2\text{S}^0 + 2\text{H}_2\text{O} \]
-204 kJ/reaction

\[ 2\text{S}^0 + 3\text{O}_2 + 2\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 4\text{H}^+ \]
-583 kJ/reaction

\[ \text{H}_2\text{S} + 2\text{O}_2 = \text{SO}_4^{2-} + 2\text{H}^+ \]
-786 kJ/reaction

H\(_2\)S ↔ S\(^0\) ↔ SO\(_3\)\(^{2-}\) ↔ SO\(_4\)\(^{2-}\)
Sulfur Cycling
Cyanobacterial Mat Sediments

Surface
Aphanothece
Diatoms

Green Layer
Phormidium,
Lyngbya

Red Layer
Chromatium salexigens
Thiocapsa halophila.
Oxidation-Reduction
Soil-floodwater Interface

- Oxygen ($O_2$)
- Sulfate ($SO_4^{2-}$)
- Hydrogen sulfide ($H_2S$)

Aerobic soil
- $SO_4^{2-} \rightleftharpoons H_2S + O_2$

Anaerobic soil
- $SO_4^{2-} \rightarrow H_2S$

Sulfur Cycling
Salt Marsh Surface Sediments

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Oxidation-Reduction

Root- Soil Interface

Oxidation-Reduction

Infaunal Burrows

Uca spp.

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Oxidation-Reduction
Infaunal Burrows

ca. 12” Deep
Sulfur Cycle

\[ \text{Rates} = \text{mmol/m}^2 \text{ day} \]

Pyrite Oxidation

\[
\begin{align*}
\text{FeS}_2 + 3.5\text{O}_2 + \text{H}_2\text{O} & = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \\
\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ & = \text{Fe}^{3+} + 0.5\text{H}_2\text{O} \\
\text{FeS}_2 + 3.75\text{O}_2 + 0.5\text{H}_2\text{O} & = \text{Fe}^{3+} + 2\text{SO}_4^{2-} + \text{H}^+ \\
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} & = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+
\end{align*}
\]
Drainage Effects on Acid Sulfate Soils

Acid Sulfate Soils
Acid Mine Drainage

Sulfur Cycling in Wetlands

Plant Biomass-S

Litterfall

Mineralization

H₂S

DMS

Oxidation

Reduction

Tidal Exchange

Deposition

SO₄²⁻

AEROBIC

Adsorbed

SO₄²⁻

ANAEROBIC

Microbial Biomass-S

Me⁺-S

FeS₂

SO₄²⁻
Hg Methylation


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Hg Methylation

Desulfobacteriaceae

Hg Methylation

**Periphyton Delta $^{32}$S**

September 1996

**Methylmercury in Floating Periphyton**

All Cycles 1995-1996

Kendall et al., http://sofia.usgs.gov/publications/posters/

6/22/2008

P.W. Inglett
Importance of Sulfur in Wetlands

- Source of nutrient
- Source of energy
- Role in decomposition of organic matter
- Adverse effects of sulfide on plant growth
- Immobilization of toxic metals
- Contribution to acid development (oxidation)
- Role in methylation of Hg