**ESM 202**

**Sulfur in the Environment**

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**Sulfur**

- **Relevance:**
  - Ubiquitous and large natural cycle
  - Major role sequestering metals
  - Important for many biological processes involving redox reactions
  - Major human disturbance to S cycle
    - Acid rain
    - Acid mine drainage

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**Sulfur Cycle**

- $\text{S} \rightarrow \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 \rightarrow \text{SO}_4^{2-}$
- $\text{SO}_4^{2-} \rightarrow \text{H}_2\text{S}, \text{HS}^-, \text{S}^2-$
- Organic compounds with sulfur
- Sulfide ion forms complexes with many metals (Fe$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Hg$^{2+}$)
  - Very low solubility
  - Form precipitates (FeS, PbS, CdS, HgS, Cu$_2$S)
- Sulfate can also form precipitates: FeSO$_4$, CuSO$_4$

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**Sulfur Compounds**

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**Sulfur Reservoirs**

<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Mass ($10^{18}$ g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmosphere</td>
<td>2.8 x 10$^{-6}$</td>
</tr>
<tr>
<td>Seawater</td>
<td>1280</td>
</tr>
<tr>
<td>Deep oceanic rocks</td>
<td>2400</td>
</tr>
<tr>
<td>Freshwater &amp; ice</td>
<td>9 x 10$^{-3}$</td>
</tr>
<tr>
<td>Sedimentary rocks</td>
<td></td>
</tr>
<tr>
<td>Shales</td>
<td>4970</td>
</tr>
<tr>
<td>Evaporites</td>
<td>2470</td>
</tr>
<tr>
<td>Organic reservoir</td>
<td></td>
</tr>
<tr>
<td>Terrestrial plants</td>
<td>0.6 x 10$^{-3}$</td>
</tr>
<tr>
<td>Marine plants</td>
<td>0.024 x 10$^{-3}$</td>
</tr>
<tr>
<td>Dead organic matter</td>
<td>5.0 x 10$^{-3}$</td>
</tr>
</tbody>
</table>
**Sulfur Cycle**

- **F1a**: Emissions to Atmosphere from Fossil Fuel Burning and Metal Smelting  
  - Tg S/yr: 95-115
- **F1b**: Effluents (to water) from chemical industry and mining  
  - Tg S/yr: 30
- **F1c**: Emissions to Soils that are transported to lakes and rivers  
  - Tg S/yr: 25-35
- **F1**: TOTAL Anthropogenic  
  - Tg S/yr: 150-180

Tg = teragram = $10^{12}$ g

**Sources of Sulfur**

- **Mining, processing & combustion of fossil fuels**
  - **Coal**
  - **Oil**
  - **Natural Gas**
- **Mining & processing of metals**
  - **Mining waste piles**
  - **Smelting**
- **Industrial processes**
**Sulfur Cycle**

- **Typical Emission Factors**
  - Coal combustion: 19 g/kg coal
  - Nat. gas combustion: 6.4 mg/m³ gas
  - Fuel oil: 20 g/L oil
  - Gasoline engine (older): 1.1 g/L gasol.
  - Diesel engine: 5 g/L diesel
  - Copper smelting: 625 g/kg ore
  - Lead smelting (prim.): 330 g/kg ore
  - Lead smelting (sec.): 75 g/kg metal
  - Zinc smelting: 265 g/kg ore
  - Cu₂S + O₂ → 2 Cu + SO₂

- Sulfuric acid production: 10-35 g/kg 100% acid
  - \( \text{S} \xrightarrow{O_2} \text{SO}_2 \xrightarrow{\text{water}} \text{H}_2\text{SO}_4 \)

- Pulp and paper mills
  - Use sulfate in “cooking liquor” to break down lignin and fibers
    - Kraft type: 1.2-6.7 g/kg dry pulp
    - Sulfite type: 20 g/kg dry pulp

**Sulfur in Atmosphere**

- Atmospheric reservoir small
- Lifetime in the atmosphere short
- Basic atmospheric chemistry of SO₂ emissions:
  \[ \text{OH} \cdot + \text{SO}_2 \xrightarrow{\text{light}} \text{HOSO}_2 \xrightarrow{\text{water}} \text{SO}_4^{2-} \]

- With typical OH• concentrations in urban air (~10⁷ molecules/cm³), the reaction occurs at a rate of about 0.5 - 5 percent/hr
Sulfur in Atmosphere

- All these gases react with OH•, eventually producing SO₂ or SO₄²⁻.
- Typical lifetimes in urban atmosphere:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Half-life (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂S</td>
<td>53</td>
</tr>
<tr>
<td>CS₂</td>
<td>1.8 x 10⁵</td>
</tr>
<tr>
<td>COS (also known as OCS)</td>
<td>0.3 x 10⁵</td>
</tr>
<tr>
<td>CH₃SH</td>
<td>3-13</td>
</tr>
<tr>
<td>DMS</td>
<td>31</td>
</tr>
<tr>
<td>DMDS</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Sulfur in Soils

- Sulfur in soils
- Agricultural 20 - 2000 mg/kg
- Volcanic ash ~3,000 mg/kg
- Desert soils > 10,000 mg/kg
- Typical C:N:S ratios in SOM are:
  - Average 130:10:1
  - Agricultural/grasslands 90:8:1
  - Forests 200:12:1

Hydrogen Sulfide System

- In anoxic conditions, sulfur or sulfate is reduced to hydrogen sulfide (H₂S).
- Several metal ores (e.g. FeS, CuS, CdS, ZnS, PbS) can be dissolved (weathered)
  - Low pH
  - Low concentration of metal ion (e.g. Fe²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Pb²⁺)
- Can also precipitate metals
  - High pH
  - High [Me²⁺] and/or [S²⁻]

Hydrogen Sulfide System

- Open system: H₂S(g)/H₂O/FeS

\[
H₂S(aq) = H₂S(g) \quad pK_H = -1
\]

\[
H₂S(aq) = H^+ + HS^- \quad pK_1 = 7
\]

\[
HS^- = H^+ + S^{2-} \quad pK_2 = 13
\]

\[
FeS = Fe^{2+} + S^{2-} \quad pK_{so} = 18.1
\]

\[
K_{so} = \frac{[Fe^{2+}][S^{2-}]}{[FeS]} = 10^{-18.1} \text{ M}^{-2}
\]
Hydrogen Sulfide System

- For other metal ions:
  - \( \text{pK}_{\text{so}} \)
  - FeS(s) 18.1
  - ZnS(s) 24.7
  - CdS(s) 27.0
  - PbS(s) 27.5
  - CuS(s) 36.1

Health Effects of Sulfur

- \( \text{SO}_2 \) and its oxidation products
  - acute broncho-constriction (airway narrowing)
  - increases in morbidity and mortality rates at high concentrations
- NAAQS are set at 80 \( \mu \text{g/m}^3 \) (annual) and 360 \( \mu \text{g/m}^3 \) (24 h max)
- Broncho-constriction can occur at ~300-400 \( \mu \text{g/m}^3 \) for sensitive pop.

Effects of Sulfur on Terrestrial Ecosystems

- Direct effect of \( \text{SO}_2 \) on agricultural crops
  - at concentration of 50-250 \( \mu \text{g/m}^3 \), the effect on crop yield loss is small (less than 10%)
  - typical rural \( \text{SO}_2 \) concentrations are around 5-50 \( \mu \text{g/m}^3 \)
- Acid deposition on agricultural soils
  - leaches out cations (\( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \))
  - requires application of lime (\( \text{CaCO}_3 \) or \( \text{Ca(HCO}_3)_2 \)) to balance acid and replenish \( \text{Ca} \)

Effects of Sulfur on Terrestrial Ecosystems

- Correlated with high levels of \( \text{SO}_2 \) and other pollutants. Effects over a 4 Mha area in Germany

Effects of Sulfur on Terrestrial Ecosystems

- Initial studies indicated that \( \text{SO}_4^{2-} \) (and \( \text{NO}_3^- \)) deposition led to
  - base-cation leaching
  - soil acidification
  - nutritional imbalance of forests
  - forest decline
- Latter studies in well-buffered (calcareous) soils also exhibiting forest decline has complicated the initial hypothesis
  - \( \text{O}_3 \)?
  - Excess N deposition?
  - Climate change?
Effects of Sulfur on Terrestrial Ecosystems

- Soil acidification releases metal ions, such as $\text{Al}^{3+}$, to potentially toxic concentrations
- $\text{Al}^{3+}$ at high concentrations causes
  - visible damage to root systems (disrupted cell walls)
  - deficient uptake of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ by trees due to inhibition by $\text{Al}^{3+}$
- Combined effect of
  - leaching of nutrients from foliage damaged by photooxidants
  - reduced uptake of nutrients from acidified soils
  - nutrient imbalance due to high nitrogen supply

Effects of Sulfur on Aquatic Ecosystems

- Major effect of acid deposition is
  - reduction in pH
  - elevated metal concentrations (e.g. $\text{Al}^{3+}$)
  - base cation depletion
- Actual effect on water catchments depends significantly on bedrock geology, soils and buffering capacity
- Most acid waters occur in areas with naturally acid soils

Impact of Acidic Deposition

<table>
<thead>
<tr>
<th>Buffering Capacity</th>
<th>Rock Type</th>
<th>Impact of acidic precipitation on surface waters</th>
<th>Impact of acidic precipitation on groundwater</th>
<th>Characteristics of first and second-order streams</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little to no capacity</td>
<td>Granite, gneiss, quartz</td>
<td>Whipped up impact, weathering, leaching of cations</td>
<td>Most areas susceptible to acidification, weathering and leaching of cations</td>
<td>Naturally acidic, poorly buffered</td>
</tr>
<tr>
<td>Low to medium</td>
<td>Sandstones, shales</td>
<td>Impact on first and second-order streams and small lakes</td>
<td>Many areas susceptible</td>
<td>Weekly acidic, poorly buffered</td>
</tr>
<tr>
<td>Medium to high</td>
<td>Slightly calcareous rocks, some volcanic rocks</td>
<td>Impact low except near surface drainage or in areas with acid soils</td>
<td>Low likelihood of acidification</td>
<td>Some alkalinity, well buffering</td>
</tr>
<tr>
<td>&quot;Infinite&quot;</td>
<td>Limestones, chalk, dolomite, highly fossiliferous sediments</td>
<td>No impact</td>
<td>No impact</td>
<td>Alkaline, highly buffered</td>
</tr>
</tbody>
</table>

Effects of Sulfur on Aquatic Ecosystems

- Lowering pH
  - not clearly shown a decrease in net primary productivity (NPP) of aquatic systems
  - small increase in NPP may occur due to reduced grazing pressure
  - reduced decomposition rates, possibly due to invertebrate scarcity and also reduced microbial activity
- Shift in phytoplankton and macrophyte diversity to more acid-tolerant species

Effects of Sulfur on Aquatic Ecosystems

- Fish are somewhat affected by lower pH, but are greatly affected by increased $\text{Al}^{3+}$ concentration
- Fish death rates increase significantly at pH 4.8-6 due to the type of $\text{Al}^{3+}$ hydroxides present, $\text{Al(OH)}_3^+$ and $\text{Al(OH)}_2^+$, which are quite toxic; hydroxides also deposit on the gill surfaces, causing respiratory stress
Effects of Sulfur on Aquatic Ecosystems

- Largest effect is during acidic episodes
- Transport of Al$^{3+}$ to the aquatic system is fast
- Not enough time
  - Physical or chemical processes to adsorb particles
  - Bind the Al$^{3+}$ in humic acids
- Young fry are most sensitive to high Al$^{3+}$

Coal and S
Emissions Control

SO$_2$ Emissions (lb/M BTU)

Coal Combustion Flow Diagram #1

Air (79% N$_2$, 21% O$_2$)

Raw Coal

Coal Combustion

Gases:
- Nitrogen (N$_2$)
- Water
- Carbon dioxide (CO$_2$)
- Sulfur dioxide (SO$_2$)
- Nitrogen oxides (NO$_x$)

particulates

Coal Combustion Flow Diagram #2

Raw Coal

Crushed Coal

Pulverized Coal

Washed Coal

Lime or limestone

Cleaned Gases

Scrubber

Flue Gases

ESP

Fine particulates

Solid waste

Waste water

Coal Combustion
**Scrubber**

Water Solution → Cleaned Gases → waste water

**Cost of Coal Desulfurization**

- Capital costs: $90,000/(ton/hr)
- Capital cost considers 30 year life and 5% real discount rate
- Operating costs: $4.30/ton
- For a 500 MW electric power plant
  - 1.3 Million tons of coal/year
  - $13,500,000 in capital costs
  - $5,600,000 in operating costs per year
  - 30-60% reduction in SO₂ emissions

**Treatment of Effects**

- Liming of lakes and watersheds
- Add powdered limestone or dolomite to neutralize acidity
- Must repeat addition frequently
- Mixing...?
- Localized effects...?
- Add “liming” agent to flue gas...?

**Alternatives for Reducing Emissions**

- Energy Conservation
- Increased Thermal Efficiency (buildings)
- Co-generation schemes
- Alternative Sources of Energy
  - Solar, geothermal, hydroelectric, nuclear, H₂
- Alternative Sources of Fuel
  - Gas (NG or LNG), biomass (EtOH, biodiesel)