Sulfur Chemistry

Air quality (health effects of particulate matter)

Ecosystems: Acid Rain

London Smog 1952

Climate

Visibility

Major Reservoirs and Burdens of Sulfur (TgS)

FIGURE 2.2 Major reservoirs and burdens of sulfur, in Tg(S) (Charlson et al., 1992). Reprinted by permission of Academic Press.
Global Sulfur Emission Estimates (TgS /yr)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Compound</th>
<th>Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oceans (without sea-salt)</td>
<td>DMS (CS₂, OCS)</td>
<td>15-25</td>
</tr>
<tr>
<td>Volcanoes</td>
<td>SO₂, SO₄²⁻ (H₂S, OCS)</td>
<td>9-12</td>
</tr>
<tr>
<td>Plants + Soils</td>
<td>SO₄²⁻, H₂S (DMS, CS₂)</td>
<td>0.2-1</td>
</tr>
<tr>
<td>Fossil Fuel Combustion (+industry)</td>
<td>SO₂ (SO₄²⁻, H₂S, CS₂)</td>
<td>70-80</td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>SO₂ (SO₄²⁻, OCS)</td>
<td>2-3</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>98-120</td>
</tr>
</tbody>
</table>

Sinks

<table>
<thead>
<tr>
<th></th>
<th>SO₂, SO₄²⁻</th>
<th>50-60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry Deposition</td>
<td></td>
<td></td>
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<tr>
<td>Wet Deposition</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CARBONYL SULFIDE (COS)

Tropospheric Oxidation, Stratospheric Photolysis

Sources ~ 1 Tg/yr
Lifetime ~ 7 years

COS
500 pptv

Oxidation

CS₂
DMS

PLANTS
SOILS
Biomass
Burning
ANTHROPOGENIC
OCEAN

Dimethyl Sulfide (DMS)

Air
Sea

Bacterial
oxidation
DMS

DMS formed from breakdown of DMSP (dimethyl sulfoniopropionate)

Mechanism for OH reaction of dimethyl sulfide (DMS)

Lifetime ~ 1 day

\[ \text{DMS} \rightarrow \text{DMSO} \]

\[ \text{MSA} = \text{methane sulfonic acid} \]
\[ \text{DMSO} = \text{dimethyl sulfoxide} \]

Also loss by reaction with NO3 (nighttime) → SO2


Trends in Anthropogenic Sulfur emissions (1850-2000)


Stern, Chemosphere 58 (2005)
Oxidation of SO$_2$

- **Gas-phase oxidation of SO$_2$ (~15% of total)**
  
  \[ \text{SO}_2 + \text{OH} + \text{M} \rightarrow \text{HSO}_3 + \text{M}, \]
  
  \[ \text{HSO}_3 + \text{O}_2 \rightarrow \text{SO}_3 + \text{HO}_2 \quad \text{(fast)}, \]
  
  \[ \text{SO}_3 + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4 + \text{M} \quad \text{(fast)}. \]

- **Aqueous phase oxidation of SO$_2$ (~85% of total oxidation)**

  \[ \text{SO}_2(g) \leftrightarrow \text{SO}_2 \cdot \text{H}_2\text{O}, \]
  
  \[ \text{SO}_2 \cdot \text{H}_2\text{O} \leftrightarrow \text{HSO}_3^- + \text{H}^+, \]
  
  \[ \text{H}_2\text{O}_2(g) \leftrightarrow \text{H}_2\text{O}_2(aq), \]
  
  \[ \text{HSO}_3^- + \text{H}_2\text{O}_2(aq) + \text{H}^+ \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O}. \]
Chin et al., JGR, 2000.

Surface

DMS

MIXING RATIO IN PPTV

JJA

DMS

MIXING RATIO IN PPTV

500 mbar

DMS

MIXING RATIO IN PPTV

JJA

DMS

MIXING RATIO IN PPTV

Chin et al., JGR, 2000.  Mixing ratios in pptv
Chin et al., JGR, 2000.

Surface SO₂ and SO₂ sulfate mixing ratios in pptv

Chin et al., JGR, 2000.

500 mbar SO₂ and SO₂ sulfate mixing ratios in pptv