References:

• Handbook of Plant Nutrition:
  Chapter 7. Sulfur. Pp. 183-238

Plant nutrition: Introduction

Plants are ~70 to >90% water by weight

93% of plant dry mass is composed of C, O and H

42% Carbon
44% Oxygen
7% Hydrogen

CO₂, photosynthesis

H₂O water

7% Other, from soil

These elements are obtained mainly from soil, are often referred to as mineral nutrients, and are the subject of the topic Plant Nutrition
Plants assimilate mineral nutrients mainly as cations or anions

<table>
<thead>
<tr>
<th>MACRONUTRIENTS</th>
<th>MICRONUTRIENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>μmol / g (dry wt)</strong></td>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>-----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>250</td>
<td>Potassium (K)</td>
</tr>
<tr>
<td>1000</td>
<td>Nitrogen (N)</td>
</tr>
<tr>
<td>60</td>
<td>Phosphorus (P)</td>
</tr>
<tr>
<td>30</td>
<td>Sulfur (S)</td>
</tr>
<tr>
<td>80</td>
<td>Magnesium (Mg)</td>
</tr>
<tr>
<td>125</td>
<td>Calcium (Ca)</td>
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WHAT is sulfur?

Atomic number: 16.
Symbol: S
Native form: is a yellow crystalline (crystal like) solid.

In nature: it can be found as the pure element, and as sulfide and sulfate minerals. It is critical in the environment, climate and the health of ecosystems.

Random facts: it can also be referred to as brimstone. It’s the tenth most abundant element in the universe.
Sulfur: Clean air can lead to deficient plants

Until recently, sulfur dioxide emission from fossil fuel combustion led to acid rain and extensive damage to vulnerable plants.

Eliminating S from air pollution uncovered crop plant deficiencies, particularly in oilseed rape and wheat.

Sulfur can be found in many inorganic forms

<table>
<thead>
<tr>
<th>Species</th>
<th>Name</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^2-$, $H_2S$, $R$-SH</td>
<td>Sulfide</td>
<td>-2</td>
</tr>
<tr>
<td>$S^0$, $S_8$</td>
<td>Sulfur</td>
<td>0</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>Sulfur dioxide (toxic gas)</td>
<td>+4</td>
</tr>
<tr>
<td>$SO_3^-$</td>
<td>Sulfite</td>
<td>+4</td>
</tr>
<tr>
<td>$SO_4^{2-}$</td>
<td>Sulfate</td>
<td>+6</td>
</tr>
</tbody>
</table>

Plants take up sulfur from soil as $SO_4^{2-}$ and to a lesser extent from the atmosphere as $SO_2$ or $H_2S$
Sources of Sulfur

• Soil organic matter
  – 95% of most soil S content present in soil organic matter

• Soil minerals
  – Weathering of minerals into soil make some S available in sulfate form

• The atmosphere
  – Burning of fuels, industry, S escapes as sulfur dioxide \( \text{SO}_2 \)
  – \( \text{SO}_2 \) in the atmosphere is highest in industrial zone

• Irrigation water
  – Sulfur is present in irrigation water in sulfate form and important for S uptake

• Fertilizer
Plants are an important part of the global sulfur cycle

Atmospheric pool of sulfur – mostly SO$_2$ (sulfur dioxide)

Volcanic activity

Combustion of fossil fuels

H$_2$S → SO$_2$ → SO$_4^{2-}$

O$_2$ → H$_2$O

Acid rain*

SO$_4^{2-}$

*Since the 1980s, SO$_2$ emissions and SO$_4^{2-}$ precipitation have been declining

Prokaryotic oxidation

Prokaryotic reduction

R-SH → S → SO$_4^{2-}$

Assimilation by plants

manure

decomposition

Nutrients in the soil

SO$_4^-$

Leaching

What creates charges on soil colloids?

SO$_4^-$ is not attracted to negatively charged soil colloids
Plants take up sulfur primarily as sulfate ($\text{SO}_4^{2-}$), but can also absorb sulfur dioxide ($\text{SO}_2$) gas through their leaves.
Sulfur is an essential macronutrient in amino acids & other compounds

- **Cysteine (Cys)**
  \[ \text{HS-CH}_2\text{-CH-COOH} \]

- **Methionine (Met)**
  \[ \text{CH}_2\text{-COOH} \]

- **Amino acids**
  - Cysteine (Cys)
  - Methionine (Met)

- **Flavor or odor**
  - Allicin (garlic flavor)
  - Allyl-isothiocyante (horseradish flavor)

- **Oxidation / reduction, metal transport and detox**
  - Glutathione
  - Glutathione is an amino acid derivative involved in Redox reactions

- **Defense**
  - Camalexin is a defense compound induced by pathogens

- **Glucosinolates are anti-herbivores**

Sulfur

- Essential plant food for production of protein.
- Promotes activity and development of enzymes and vitamins.
- Helps in chlorophyll formation.
- Improves root growth and seed production.
- Helps with vigorous plant growth and resistance to cold.
Uptake, Transport, and assimilation of Sulfate

- S moves to root by mass flow

- Actively absorbed against a concentration gradient as sulfate

- Transport across the plasma membrane occurs with protons at a ratio of $1 \text{SO}_4^{2-} : 3 \text{H}^+$ (**symport**)

- The driving force for this active transport is $\text{H}^+$ gradient created by $\text{H}^+$ ATPase
Transport of Sulfate

Two types of Sulfate transport are found in plants

- **Low affinity** — mostly expressed in leaves… also in roots
- **High affinity** — mostly expressed in roots in response to sulfur starvation
Sulfate uptake occurs primarily through SULTR transporters

In *Arabidopsis*, 12 genes encode SULTR transporters that fall into four groups.

Most are 12-membrane spanning $\text{SO}_4^{2-} / \text{H}^+$ co-transporters.

Primary assimilation in roots occurs mainly through SULTR1;1 and SULTR1;2.

In higher plants, SULTR transporters effect inter-organelle movement


Primary sulfur metabolism (overview)

- **Sulfate**
  - Adenosine 5'-phosphosulfate
  - 5'-Phosphoadenosine 3'-phosphosulfate

- **PAPS**
  - Sulfated compounds
  - Sulfoquinosovyl diacylglycerides

- **Sulfite**
  - Serine

- **Sulfide**
  - O-acetylserine

- **Cysteine**
  - Cystathionine
  - γ-EC
  - Lipoic acid
  - Thiamine
  - MoCo
  - Biotin
  - Fe/S
  - CoA

- **Glutathione**: S-adenosylmethionine

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Sulfate is assimilated by ATP sulfurylase into APS

\[
\text{Sulfate} + \text{ATP} \xrightarrow{\text{ATP sulfurylase}} \text{Adenosine 5'-phosphosulfate (APS)} + \text{Pyrophosphate (PP}_4\text{)}
\]

This reaction occurs in the cytosol and plastid

APS can enter two pathways for primary or secondary reactions

Adenosine 5'-phosphosulfate (APS)

Sulfide is assimilated into cysteine by the cysteine synthase complex

Foliar uptake and metabolism of Sulfurous Gas

• Volcanic eruptions, breakdown of organic matter in swamps and tidal flats, and the evaporation of water, especially seawater, release sulfur directly into the atmosphere

• Sulfur eventually settles to earth or comes down with rainfall

• S in atmosphere can be absorb by stomata of leaves

• \( \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}^+ \text{HSO}_3^- \rightarrow 2\text{H}^+ \text{SO}_3^{2-} \)
Plants deficient in S show a pale green coloring of younger leaves.
Figure 8. Sulfur-deficient plants (left) and normal plants (right).
Addressing S deficiency in plants

With stricter laws on S emissions, less S enters soils and plants are more prone to S deficiency.

Soil can be augmented with elemental sulfur, ammonium sulfate or other fertilizers.

Documented sulfur deficiencies are increasing because of:

- Increased crop yields
- Use of high analysis fertilizers containing little incidental S
- Less use of high S fuels
Diesel fuel with lower content of S
• Reduction of acid rain.
  – 2005: 12-14 kg/ha
• Fewer S - containing pesticides
• Slower organic matter breakdown with conservation tillage
Use of S to reduce soil pH
How does sulfur reduce pH?

- S is oxidized by soil bacteria which generates sulfuric acid $\text{H}_2\text{SO}_4$:

  $$2 \text{S} + 3 \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-}$$

- Each 10 lbs of elemental S produces enough acidity to neutralize approx. 30 lbs of lime

- Transformation is temperature dependant (takes 3 to 4 weeks at 75F)
Range of S Application (ton/acre) to Lower Soil pH to 6.5

<table>
<thead>
<tr>
<th>Original pH</th>
<th>Sandy soil</th>
<th>Clay soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.5</td>
<td>0.7-1.0</td>
<td>1.0-1.3</td>
</tr>
<tr>
<td>8.0</td>
<td>0.5-0.7</td>
<td>0.7-1.1</td>
</tr>
<tr>
<td>7.5</td>
<td>0.2-0.3</td>
<td>0.4-0.5</td>
</tr>
</tbody>
</table>
Summary: Sulfur uptake and metabolism

- Found in many redox forms and can be assimilated from atmosphere
- Deficiency more common with cleaner air
- SULTR transporter family primarily involved in uptake and transport
- Uptake and assimilation into organic forms subject to positive and negative regulation