SULFUR CHEMISTRY, SOIL TESTING FOR S, AND S SOURCES

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Sulfur
Sulfur

- Abundant element in earth’s crust – 0.06 to 0.10 %.
- Original source – metal sulfide minerals.
- When weathered, $S^{2-}$ oxidizes to $SO_4^{2-}$. 
**Sulfur**

- $\text{SO}_4^{2-}$ is:
  - Precipitated as soluble and insoluble $\text{SO}_4^{2-}$ salts in arid and semi-arid climates.
  - Utilized by living organisms.
  - Reduced by microorganisms to $\text{S}^{2-}$ or $\text{S}^0$ under anaerobic conditions.
  - North Dakota ground waters - ~100 to 500+ ppm $\text{SO}_4^{2-}$. 
Sulfur

- Soil S:
  - Organic and inorganic forms.
  - ≈ 90% of total S in noncalcareous soils exists as organic S.
  - Solution and adsorbed $\text{SO}_4^{2-}$ - readily plant available S.
  - S cycling similar to N cycling.
    - Gaseous component
    - Associated with OM.
Sulfur

- S conc. in plants range from 0.1 to 0.5 %.
- Absorbed by plant roots almost exclusively as $\text{SO}_4^{2-}$.
- $\text{SO}_4^{2-}$ is reduced in plant sap to -S-S and -SH forms.
- $\text{SO}_4^{2-}$ does occur in plant sap/tissues.
Plant S content:

- **Cruciferae** > **Leguminosae** > **Graminae**

Seed content:

- **Cruciferae** - ~ 1.1 to 1.7 %.
- **Leguminosae** - ~ 0.25 to 0.3 %.
- **Graminae** - ~ 0.18 to 0.19 %.
Sulfur

- Required for synthesis of S-containing amino acids:
  - Cystine.
  - Cysteine.
  - Methionine.
S in Soils

- **Solution $SO_4^{2-}$:**
  - Large seasonal and year-to-year fluctuations.
  - Organic S mineralization.
  - Movement of $SO_4^{2-}$ in soil water ($\uparrow$ or $\downarrow$).
  - $SO_4^{2-}$ uptake by plants.
  - S fertilization.
  - Deposition in precipitation and irrigation.
Solution $\text{SO}_4^{2-}$:
- $\text{SO}_4^{2-}$ readily leached through soil profile.
  - $\uparrow$ water $= \uparrow$ leaching.
  - Cations in solution.

Monovalent $>$ divalent
S in Soil

- **Adsorbed \( \text{SO}_4^{2-} \):**
  - Affected by:
    - Soil depth:
      - Subsoil > topsoil
    - Soil pH:
      - Adsorption potential ↓ with ↑ pH
      - Negligible at pH > 6.0.
Adsorbed $\text{SO}_4^{2-}$:
- Affected by:
  - Solution $\text{SO}_4^{2-}$
  - $\uparrow$ solution $\text{SO}_4^{2-}$, $\uparrow$ adsorbed $\text{SO}_4^{2-}$
- Competing ions
  $\text{OH}^- \succ \text{H}_2\text{PO}_4^{2-} \succ \text{SO}_4^{2-} \succ \text{NO}_3^- \succ \text{Cl}^-$
Reduced inorganic S ($S^{2-}$ and $S^0$):

- Do not accumulate/exist in well-drained soils.
- Under waterlogged, anaerobic conditions:
  - $H_2S$ accumulates.
  - OM decay.
  - $SO_4^{2-}$ inputs.
Reduced inorganic S ($S^2$ and $S^0$):
- $S^0$ not normally produced.
- Can be chemically oxidized in soil – very slow reaction.
- Most commonly biologically oxidized.
S in Soil

- S\(^0\) oxidation:
  - Soil Microbes:
  - Heterotrophic fungi and bacteria.
    - *Thiobacillus sp.* (bacteria).
    - *Fusarium sp.* (fungi).
    - *Streptomyces sp.* (actinomycetes).
  - Plant-growth promoting rhizobacteria (PGPR).
**S in Soil**

- **S\(^0\) oxidation:**
  - **Soil Microbes:**
    - *Thiobacillus sp.*
      - Autotrophic bacteria.
      - Obtain energy from S\(^0\) oxidation.
      - Obtain C from CO\(_2\).
    
    \[
    \text{CO}_2 + S^0 + 2^{1/2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \]
  
  \[
  \text{CO}_2 + S^0 + 2^{1/2}\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \]
S in Soil

- **$S^0$ oxidation:**
  - **Soil temperature:**
    - ↑ temperature, ↑ $S^0$ oxidation rate.
    - Optimum temperature - 25 to 40° C.
    - Above 55 to 60° C, microbial activity ↓.
S in Soil

- $S^0$ oxidation:
  - Soil moisture/aeration:
    - Aerobic conditions.
    - Reduction in activity when too wet or too dry.
    - Soil drying doesn’t affect oxidation ability but results in lag time on rewetting.
S in Soil

- $S^0$ oxidation:
  - Soil pH:
    - Can occur over wide range of pH.
    - *Thiobacillus thiooxidans* – pH 2.0 to 3.5.
    - Some species prefer neutral to slightly alkaline conditions.
Organic S:
- Close relationship between organic C, N, and S.
- C:N:S \(\sim 120:10:1.4\) in most well-drained, noncalcareous soils.
- N:S of 6:1 to 8:1 in most soils.
- Organic S governs plant-available S.
Mineralization/Immobilization:

- **Mineralization:**
  - Conversion of organic S to inorganic SO\(_4^{2-}\).
  - Similar to N mineralization.
  - Microbially mediated.
- Supplies ~ 2 to 15 lbs SO\(_4\)-S/a/yr.
Mineralization/Immobilization:
- Immobilization:
  - Reverse process of mineralization.
  - Similar to N immobilization.
Mineralization/Immobilization:

Factors:

- S content of OM (C:S ratio):
  - < 200:1 - mineralization
  - 200 – 400 - no change
  - > 400:1 - immobilization
  - Fresh residues ~ 50:1.
S in Soil

- Tendency for S deficiencies on low OM, coarse-textured soils.
- Losses due to leaching under high rainfall/irrigation conditions.
- Fertilizers containing both $\text{SO}_4^{2-}$ and $\text{S}^0$ may extend availability of S.
O. M. Mineralization

Figure 1. Sulfur mineralized from six soils varying in organic matter content over a 10 week period without addition of organic matter.
Figure 2. Sulfur mineralized from six soils varying in organic matter content over a 10 week period with addition of wheat
O. M. Mineralization

Figure 3. Sulfur mineralized from six soils varying in organic matter content over a 10 week period with addition of alfalfa.
Percent of soils testing less than 3 ppm S in 2010 (for states and provinces with at least 2,000 S tests).

North America
13%
2.5 million samples

% less than 3 ppm calcium phosphate extractable S or 6 ppm Mehlich 3 S

Courtesy IPNI. 2010
Currently, using NCR-13 MCP (500 ppm P) test.


Turbidimetric test.
Soil Testing

- Current calibration (in 2 ft profile):
  - Very low – 0-9 lbs S/A
  - Low – 10-19 lbs S/A
  - Medium – 20-29 lbs S/A
  - High – 30-39 lbs S/A
  - Very high – 40+ lbs S/A

- Recommendation:
  - If <16 lbs S/A – apply 20-30 lbs S/A
May work for acid to neutral pH soils in most cases.

Potential for many interferences:
- Contamination of lab equipment
- Contamination of lab reagents – most reagents have traces of S impurities.
- Interference with calcium in soil extracts/
- ??????
Table 4. A comparison of S values for nine soils using a Ca(H$_2$PO$_4$)$_2$ extractant.

<table>
<thead>
<tr>
<th>Soil</th>
<th>T (ug/g)</th>
<th>ICP (ug/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buse A</td>
<td>6.03±1.51</td>
<td>6.83±0.57</td>
</tr>
<tr>
<td>Buse B</td>
<td>5.67±1.54</td>
<td>1.50±0.74</td>
</tr>
<tr>
<td>Buse C</td>
<td>6.64±1.56</td>
<td>1.45±0.87</td>
</tr>
<tr>
<td>Barnes A</td>
<td>6.46±1.14</td>
<td>7.01±0.68</td>
</tr>
<tr>
<td>Barnes B</td>
<td>5.30±1.27</td>
<td>2.56±0.85</td>
</tr>
<tr>
<td>Barnes C</td>
<td>6.61±1.54</td>
<td>2.04±0.68</td>
</tr>
<tr>
<td>Svea A</td>
<td>7.21±0.90</td>
<td>12.08±0.73</td>
</tr>
<tr>
<td>Svea B</td>
<td>7.95±0.61</td>
<td>8.54±0.81</td>
</tr>
<tr>
<td>Svea C</td>
<td>5.53±0.65</td>
<td>4.34±0.62</td>
</tr>
</tbody>
</table>
Table 5. A comparison of S values for nine soils using a 0.25 M KCl extractant at room temperature.

<table>
<thead>
<tr>
<th>Soil</th>
<th>T</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buse A</td>
<td>0.45±0.30</td>
<td>23.09±0.69</td>
</tr>
<tr>
<td>Buse B</td>
<td>0.16±0.15</td>
<td>7.30±0.16</td>
</tr>
<tr>
<td>Buse C</td>
<td>0.44±0.23</td>
<td>7.11±0.18</td>
</tr>
<tr>
<td>BarnesA</td>
<td>1.34±0.56</td>
<td>26.18±0.18</td>
</tr>
<tr>
<td>Barnes B</td>
<td>0.60±0.97</td>
<td>16.35±0.20</td>
</tr>
<tr>
<td>Barnes C</td>
<td>0.74±0.19</td>
<td>10.25±0.34</td>
</tr>
<tr>
<td>Svea A</td>
<td>2.78±0.54</td>
<td>31.43±0.39</td>
</tr>
<tr>
<td>Svea B</td>
<td>3.24±0.48</td>
<td>28.15±0.42</td>
</tr>
<tr>
<td>Svea C</td>
<td>2.01±0.46</td>
<td>17.57±0.39</td>
</tr>
</tbody>
</table>
0.25 M KCl may be more sensitive to differences in soil SO₄-S.

However, it requires more complex, expensive ICP instrumentation (higher cost).

Soil test recommendations may need extensive recalibration.
S Sources

Atmospheric sources
Organic S:
- Sufficient quantities usually found in solid wastes and manures.
- Organic waste S content – 0.2 to 1.5 % (5 to 25 lbs/t dry wt.).
S Sources

- **Inorganic S:**
  - Fertilizer materials.
  - Surface applied and incorporated or moved into the soil with rainfall or irrigation.
  - Usually immediately available unless immobilized by microbes in high residue situation.
  - Most materials equally effective.
S Sources

- **Ammonium sulfate** \((\text{NH}_4)_2\text{SO}_4\) or AS:
  - Contains 24 % S and 21% N.
  - Used where both N and S are required.
  - Manufactured in ND (DakSul).
  - Used for canola production.
Potassium sulfate ($\text{K}_2\text{SO}_4$)/potassium magnesium sulfate ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4$):

- Potassium sulfate – K fertilizer
- K-Mag, Sul-Po-Mag.
- Contain 17 % and 22 % S, respectively.
- Highly soluble, low salt index.
S Sources

- Ammonium thiosulfate ((NH₄)₂S₂O₃ or ATS):
  - Clear liquid containing 12 % N and 26 % S.
  - Compatible with N and N-P-K solutions that are near neutral or slightly acidic in pH.
  - Popular liquid S source.
Ammonium thiosulfate \((\text{NH}_4)_2\text{S}_2\text{O}_3\) or ATS:

- Can be applied:
  - Directly to soil
  - In fertilizer mixtures.
  - Through irrigation systems.
- **Ammonium thiosulfate** ((NH$_4$)$_2$S$_2$O$_3$ or ATS):
  - Forms colloidal S and (NH$_4$)$_2$SO$_4$ when applied to soil.
    - SO$_4^{2-}$ immediately available.
    - S$^0$ must be oxidized to SO$_4^{2-}$.
    - Extended availability.
  - Some urease inhibition effect.
Elemental S ($S^0$)
- Conversion to $SO_4$-S previously discussed.
- Needs to be applied prior to desired growing season.
- May not be as effective as other sources due to environmental conditions required and leaching potential.
S Sources

- **Gypsum?**
  - Results equivalent to AS.
  - Better than elemental S°.
S chemistry is complex.
S analysis is difficult.
Current S soil tests do not appear to be fully effective in the Northern Plains.
Need for a new (or different) test?
AS, K sulfate, K-Mg sulfate and gypsum most effective fertilizer sources.
Questions?