Fertilisers providing micronutrients

Boron

Typical compounds used to provide boron include:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric acid</td>
<td>H$_3$BO$_3$</td>
<td>soluble in water - molecules, H$_3$BO$_3$(aq)</td>
</tr>
<tr>
<td>Borax</td>
<td>Na$_2$B$_4$O$_7$.10$H_2$O</td>
<td>soluble in water - anions, B$_4$O$_7^{2-}$(aq)</td>
</tr>
</tbody>
</table>

Figure 1 White crystals of boric acid consist of boric acid molecules held together in a lattice by hydrogen-bonds.

Metal ions

Simple salts such as sulfates are used commonly for copper, iron, manganese and zinc. These compounds are soluble, making the metal ions readily available to plants for rapid uptake.

These salts can be made in various ways such as the reaction of metal oxides, hydroxides or carbonates with sulfuric acid:

\[
\text{MO(s)} + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MSO}_4(\text{aq}) + \text{H}_2\text{O}(l)
\]

\[
\text{M(OH)}_2(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MSO}_4(\text{aq}) + 2\text{H}_2\text{O}(l)
\]

\[
\text{MCO}_3(\text{s}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MSO}_4(\text{aq}) + \text{H}_2\text{O}(l) + \text{CO}_2(\text{g})
\]

The metal sulfate solution is filtered to remove unreacted metal oxide, hydroxide or carbonate. The filtrate is evaporated and crystals of the salt form. These are filtered and dried.

When salts dissolve hydrated ions become free to move around in water.

\[
\text{MSO}_4.5\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{aq}) \rightarrow [\text{M(H}_2\text{O)}_6]^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]

For example:

\[
\text{CuSO}_4.5\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{aq}) \rightarrow [\text{Cu(H}_2\text{O)}_6]^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\]

However, there may be problems using these salts as fertilisers:

- Insoluble hydroxides and hydrated oxides may form in alkaline soils:
  \[
  [\text{M(H}_2\text{O)}_6]^{2+}(\text{aq}) + 2\text{OH}^- (\text{aq}) \rightarrow \text{M(OH)}_2(\text{s}) + 6\text{H}_2\text{O}(l)
  \]

- In calciferous soils insoluble carbonates may form,
  \[
  [\text{M(H}_2\text{O)}_6]^{2+}(\text{aq}) + \text{CO}_3^{2-} (\text{aq}) \rightarrow \text{MCO}_3(\text{s}) + 6\text{H}_2\text{O}(l)
  \]

Both of these types of reactions happening in soil reduce the availability of the metals to plants.

When used in liquid fertiliser formulations insoluble phosphates of the metals may form, also reducing their availability.
The other metal that is a micronutrient is molybdenum. It is provided in the form of ammonium molybdate, sodium molybdate or molybdenum trioxide.

Sodium molybdate can be synthesised by dissolving molybdenum trioxide in sodium hydroxide solution at about 60 °C. On cooling, the salt crystallises and can be obtained by filtration.

\[
\text{MoO}_3(\text{s}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Na}_2\text{MoO}_4(\text{aq}) + \text{H}_2\text{O}(\text{aq})
\]

The crystals have the formula \(\text{Na}_2\text{MoO}_4.2\text{H}_2\text{O}\).

**Metal complexes**

Organic molecules and molecular ions can form complexes with metal ions. They are called ligands and the complex that forms is called a chelate.

Amino acids are used to make chelated micronutrients. Glycine is the most commonly used amino acid. When dissolved in an alkaline solution, the carboxylic acid group ionises to give an ion with a single negative charge. It is called a glycinate ion.

In the molecular ion that forms, an oxygen atom in the carboxylate group and the nitrogen atom can bond to a metal ion. When a molecule or molecular ion has more than one atom bonded to a metal ion, a chelate forms.

Traditionally citric acid and oxalic acid have been used as ligands. Gluconic acid has also been used.

More recently chelates of ethylenediaminetetraacetic acid (EDTA) and a number of related compounds are also used to make micronutrient fertilisers.

![Figure 2 Glycine (systematic name: aminoethanoic acid).](image)

![EDTA](image)

![EDDS](image)

![DTPA](image)

![EDDHA](image)

*Figure 3 The structures of ethylenediaminetetraacetic acid (EDTA) and related compounds used to make micronutrient chelates.*
In these related molecules (EDTA, EDDS, DTPA and EDDHA), the carboxylic acid groups ionise in alkaline solution. In the molecular ions that form, an oxygen atom in each of the carboxylate groups and the two nitrogen atoms can bond to a metal ion. The molecular ion surrounds the metal ion and keeps it at the centre of a ‘cage’.

EDTA may be used for copper, iron, manganese and zinc. The others are only suitable for iron.

Examples of compounds used:

In liquid fertilizers
- EDTA-Cu(NH$_4$)$_2$
- EDTA-MnK$_2$
- EDTA-Zn(NH$_4$)$_2$

In solid fertilizers
- EDTA-CuNa$_2$
- EDTA-MnNa$_2$
- EDTA-ZnNa$_2$

**Benefits of chelated fertilisers**
The following benefits have been claimed for chelated fertilisers:
- availability of nutrients increased;
- insoluble precipitates not formed in alkaline soil;
- mobility of plant nutrients increased;
- leaching of nutrients prevented;
- toxicity to plants of some metal ions reduced;
- growth of some plant pathogens suppressed.

**Finding out**
How might the effectiveness of chelated and non-chelated forms of a metal nutrient be compared?