Having fun yet?
1. Scope
1.1 This practice describes the method for the evaluation of the physical compatibility and stability of pesticide tank mixtures diluted for aqueous application. This practice may also be adapted to use with liquid fertilizers in replacement of the water diluent.

1.2 Tank mix compatibility can be affected by many variables. Care should be taken to duplicate test conditions. This practice addresses the standard variables such as time, temperature, water hardness, method of agitation, and degree of agitation.

1.3 Compatibility is complex and can be affected by other variables such as order of addition, pH of the dilution water, pumping shear, etc. Under the parameters of this practice, the results will define whether the pesticide mixture is or is not compatible in the laboratory. Compatibility or incompatibility should be confirmed under field spray conditions.
Name the Structure
What do they have in common?

EDTA chelating agent

EDDHA chelating agent

Glucoheptonate complexing agent

Citric Acid chelating agent
Carboxyl group – key function group of many Ag chemicals
Chelates, Complexes and Herbicides

\[
\begin{align*}
\text{pKa} - 1 & \quad \text{pKa} & \quad \text{pKa} + 1 \\
\begin{array}{c}
\text{pKa} - 1 \text{ is the pH value where the carboxyl groups exhibits no charge 100\% of the time} \\
\end{array}
\end{align*}
\]

The pKa value is pH value where the functional groups if protonated 50\% of the time.

\[
\begin{align*}
\begin{array}{c}
pKa + 1 \text{ is the pH value where the carboxyl groups has a negative charge 100\% of the time}
\end{array}
\end{align*}
\]
Phenoxy Herbicides
Do you recognize any functional groups?  

**Carboxyl groups**

2,4 D  
\[ \text{pKa} = 2.7 \]

\[ \begin{array}{c}
\text{Cl} \\
\text{O}
\end{array} \]
\[ \begin{array}{c}
\text{Cl} \\
\text{O}
\end{array} \]
\[ \text{O} \]
\[ \text{OH} \]
\[ \text{R} \]
\[ + \]
\[ \text{R}^1 \]

**Fluazipop**  
\[ \text{pKa} = 3.1 \]

\[ \text{F} \]
\[ \text{F} \]
\[ \text{F} \]
\[ \text{N} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{R}^1 \]

**What about the ester formulation?**

\[ \text{R} \text{C} = \text{O} \]
\[ \text{OH} \]
\[ + \]
\[ \text{R}^1 \]
\[ \leftrightarrow \]
\[ \text{R} \text{C} = \text{O} \]
\[ \text{O} \]
\[ \text{R}^1 \]

\[ \text{Cl} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{Cl} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{R} \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{H} \]
\[ \text{CH}_3 \]
\[ \text{O} \]
\[ \text{O} \]
\[ \text{C} \]
\[ \text{H} \]
\[ \text{CH}_3 \]
Phenoxy herbicides  
Contain carboxyl groups

<table>
<thead>
<tr>
<th>Active Salt / Ester</th>
<th>pKa</th>
<th>pka + 1</th>
<th>Formulation Type</th>
<th>Chemical Class</th>
<th>acid structure</th>
<th>Water Solubility Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>2.7</td>
<td>3.7</td>
<td>SL</td>
<td>phenoxy acid</td>
<td>R₁-COOH</td>
<td>Acid and ester forms are sparingly soluble, the salts have high solubility. Formulated as both a water salt and oil soluble ester</td>
</tr>
<tr>
<td>2,4-DB</td>
<td>4.8</td>
<td>5.8</td>
<td>SL</td>
<td>phenoxy acid</td>
<td>R₁-COOH</td>
<td>Acid and ester forms are sparingly soluble, the salts have high solubility. Formulated as both a water salt and oil soluble ester</td>
</tr>
<tr>
<td>Fenoxaprop-P</td>
<td>3.2</td>
<td>4.2</td>
<td>EC</td>
<td>phenoxy acid</td>
<td>R₁-COOH</td>
<td>Sparsingly soluble - Products on market are Emulsifiable Concentrates</td>
</tr>
<tr>
<td>Fluazifop</td>
<td>3.1</td>
<td>4.1</td>
<td>EC</td>
<td>phenoxy acid</td>
<td>R₁-COOH</td>
<td>Sparsingly soluble - Products on market are Emulsifiable Concentrates</td>
</tr>
<tr>
<td>Fluazifop-P-Butyl</td>
<td>2.9</td>
<td>3.9</td>
<td>EC</td>
<td>phenoxy acid</td>
<td>R₁-COOH</td>
<td>Sparsingly soluble - Products on market are Emulsifiable Concentrates</td>
</tr>
</tbody>
</table>
pH precipitation soluble liquid herbicide

- 2,4-DB
- Active: 2,4-DB

- SL Formulation
- pKa = 4.8
- Acid form is sparingly soluble, the salts have high solubility. Typically sold as a sodium salt
Herbicides – Amide groups

Sodium salt of Bentazon
pKa = 4.3

Sodium salt of Fomesafen
pKa = 3.8
pH precipitation soluble liquid herbicide

- Reflex Herbicide
- Active: Sodium Fomesafen

- SL Formulation
- pKa = 3.8
- Acid form is sparingly soluble, the salts have high solubility. Typically sold as a sodium salt

![Chemical structure of Sodium Fomesafen](image)

Water pH 7.1
MAP pH 4.1
Suspension concentrate failure in presence of divalent cations

- Warrant Herbicide
- Active: Acetochlor

SC Formulation

Anionic dispersant fails do to binding divalent cations binding to the negative charged sites of the dispersant.
Suspension Concentrate failure in 10-34-0

- Force Insecticide
- Active: Tefluthrin

SC Formulation
Sparingly soluble in water, liquid formulations are typically SC or EC
Dispersant fails due to limited water to activate dispersing and emulsifying agents.
Humic Acid

pKa values, solubility is alkaline solutions

Humic acid
MW > 30,000

pKa = 11.2

pKa = 2.4

mEq HCl per 10 g HA

mEq NaOH per 10 g HA

OH

R

COOH
Humic Acid in Liquid Fertilizer

- UAN
- 10-34-0
- Calcium Nitrate
UAN and ATS with Pre-emerge Herbicide

- Lexar EZ, Bicep II Magnum, etc.
- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails do to limited water to activate dispersing and emulsifying agents. Hi electrolyte solution, limited free water.
Counter Ion Affects Volatility of Dicamba
Ammonium can increase volatility

- Be caution of adding ammonium containing liquid fertilizers with Dicamba

\[ \text{NH}_4^+ \]

- AMS Solutions
- ATS Solutions
- UAN Solutions
- MAP Solutions

Dicamba, Diglycolomine salt

Dicamba, Dimethylamine salt
Phosphate Interactions
pH Dependence of Phosphate Binding

Dissociation of Phosphoric acid H₃PO₄

<table>
<thead>
<tr>
<th>Acid</th>
<th>Mol. Form</th>
<th>pKa</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PO₄</td>
<td>H₂PO₄⁻</td>
<td>2.2</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>HPO₄⁻²</td>
<td>7.2</td>
</tr>
<tr>
<td>PO₄⁻³</td>
<td></td>
<td>12.3</td>
</tr>
</tbody>
</table>

[M]ⁿ | Form                          | Ksp    |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca+2</td>
<td>Ca₃(PO₄)₂</td>
<td>1x10⁻²⁶</td>
</tr>
<tr>
<td></td>
<td>Ca₂(PO₄)₂(OH)₂</td>
<td>1x10⁻²⁷</td>
</tr>
<tr>
<td></td>
<td>Ca₅(PO₄)₃(OH)₃</td>
<td>1x10⁻⁵⁷</td>
</tr>
</tbody>
</table>

Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations.
Glyphosate
Antagonized by Divalent Cations

\[
\text{Glyphosate} \quad -2 \quad + \quad [\text{Mn}]^{+2} \quad \rightarrow \quad \text{Glyphosate bound to Mn}
\]

Control  Roundup  Roundup Mn Sulfate  Roundup Mn EDTA  Roundup Smart Mn
Stability Constants

1:1 molar ratio
@ physiological pH

<table>
<thead>
<tr>
<th>Cation</th>
<th>(LogK\textsubscript{m1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca\textsuperscript{+2}</td>
<td>3.3</td>
</tr>
<tr>
<td>Mg\textsuperscript{+2}</td>
<td>3.3</td>
</tr>
<tr>
<td>Cu\textsuperscript{+2}</td>
<td>11.2</td>
</tr>
<tr>
<td>Fe\textsuperscript{+2}</td>
<td>6.9</td>
</tr>
<tr>
<td>Fe\textsuperscript{+3}</td>
<td>16.1</td>
</tr>
<tr>
<td>Mn\textsuperscript{+2}</td>
<td>5.5</td>
</tr>
<tr>
<td>Zn\textsuperscript{+2}</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Thank You

- Jar Test