



# Fluid Compatibility Issues - Pesticides

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# Having fun yet?





# Jar Test

## ASTM E1518 - 05(2012)

### Standard Practice for Evaluation of Physical Compatibility of Pesticides in Aqueous Tank Mixtures by the Dynamic Shaker Method

#### 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.

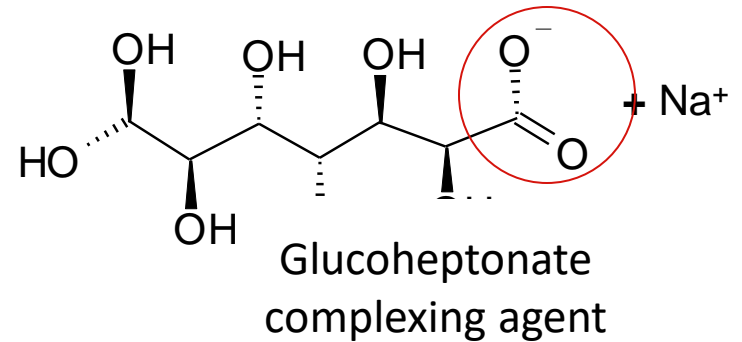
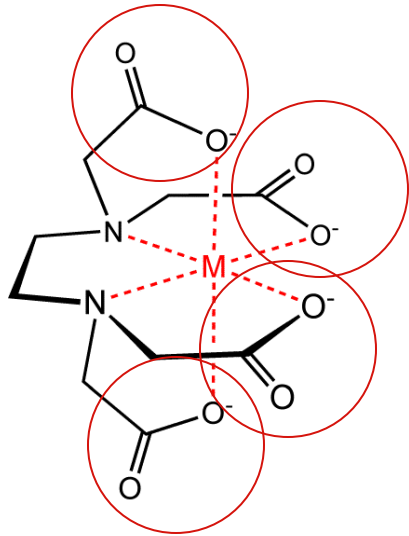
1.3 Compatibility is complex and can be affected by other variables such as order of addition, pH of the dilution water, pumping shear, etc. Under the parameters of this practice, the results will define whether the pesticide mixture is or is not compatible in the laboratory. Compatibility or incompatibility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



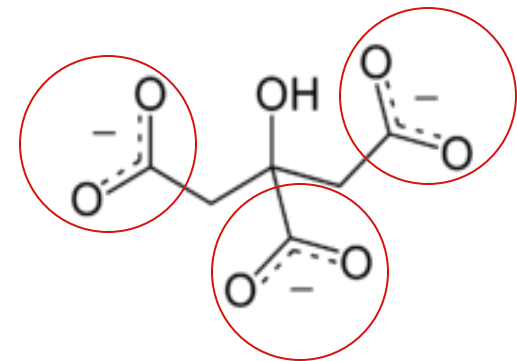
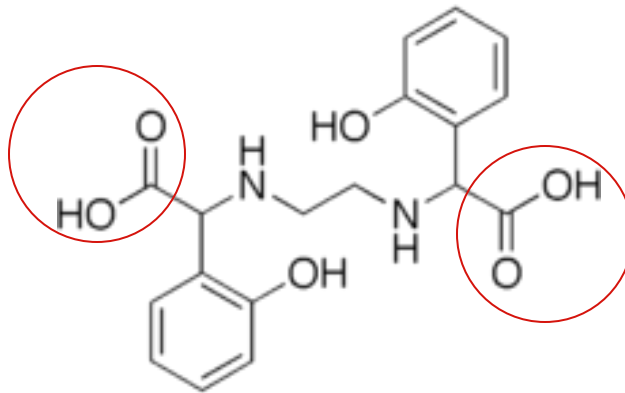
# Name the Structure

What do they have in common?

EDTA  
chelating  
metal



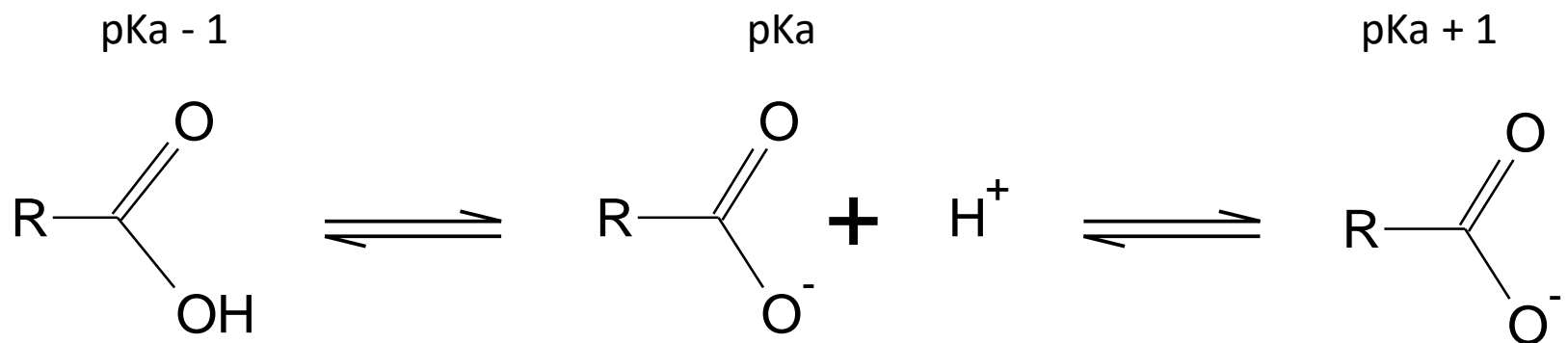
EDDHA  
chelating agent



Citric Acid  
chelating agent

# Carboxyl group – key function group of many Ag chemicals

## Chelates, Complexes and Herbicides



pKa - 1 is the pH value where the carboxyl groups exhibits no charge 100% of the time

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

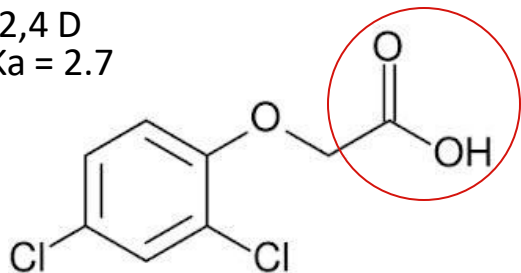
pKa + 1 is the pH value where the carboxyl groups has a negative charge 100% of the time

# Phenoxy Herbicides

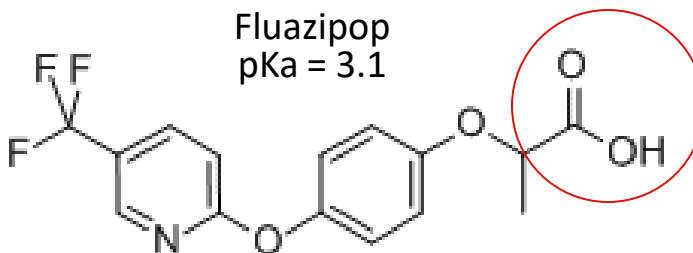
Do you recognize any functional groups?

**Carboxyl groups**

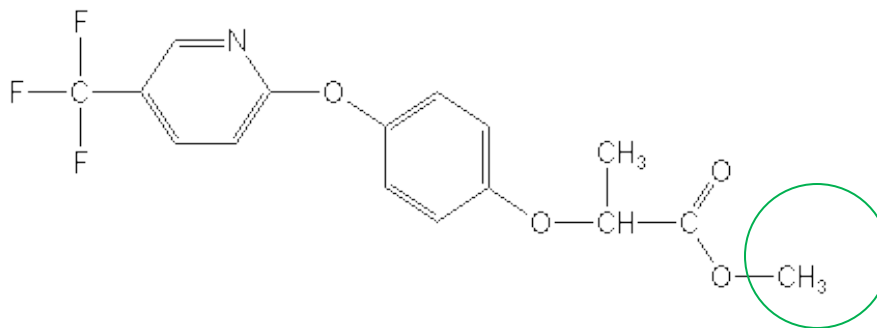
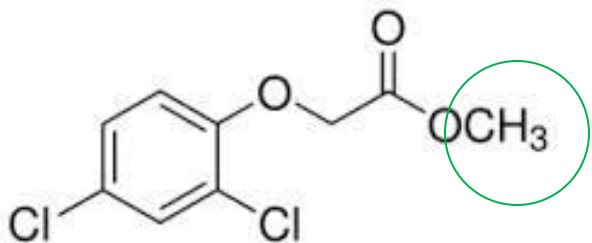
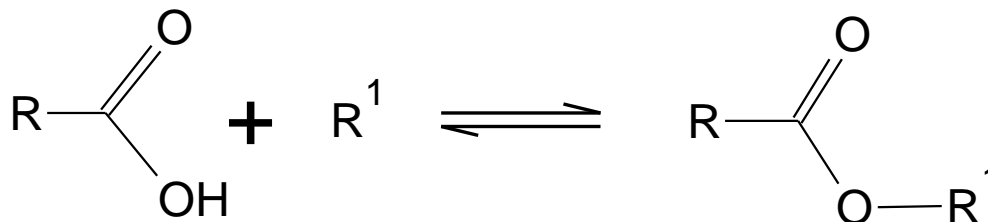
2,4 D  
pKa = 2.7



Fluazipop  
pKa = 3.1



**What about the ester formulation?**



# Phenoxy herbicides

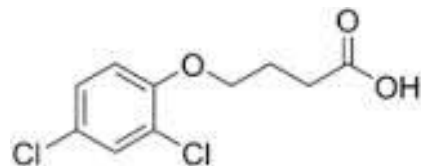
## Contain carboxyl groups

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

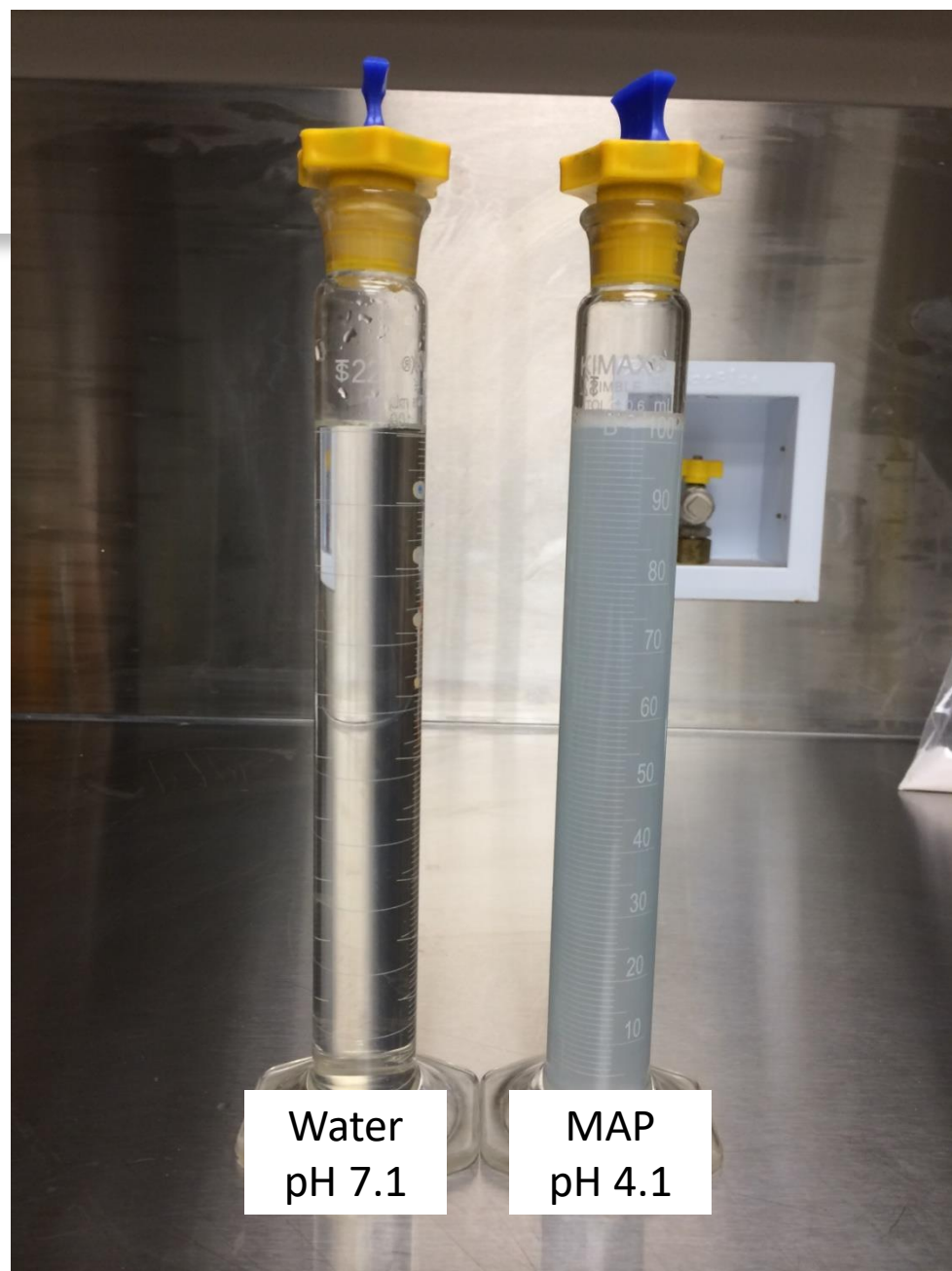


# pH precipitation soluble liquid herbicide

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

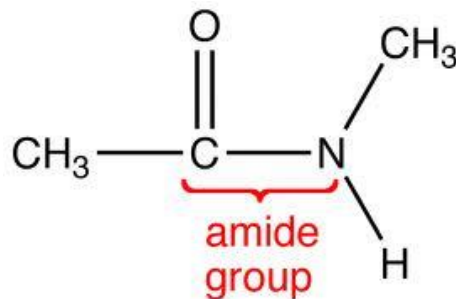
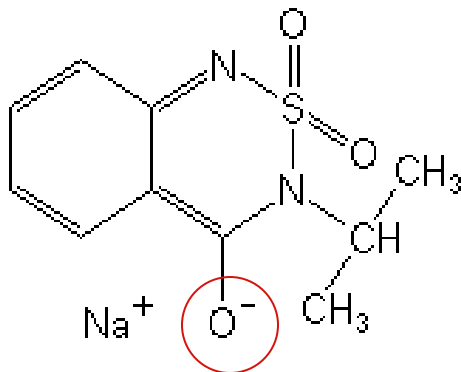


- SL Formulation
- $pK_a = 4.8$
- Acid form is sparingly soluble, the salts have high solubility.  
Typically sold as a sodium salt

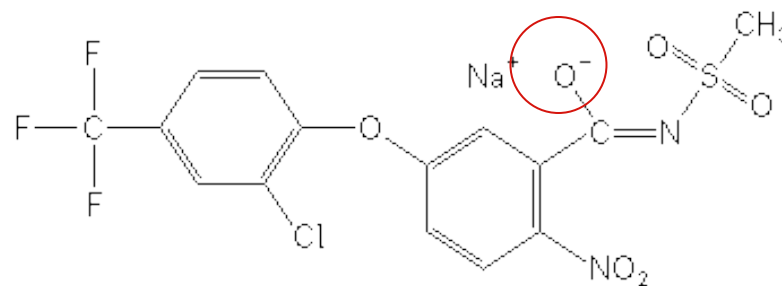


# Herbicides – Amide groups

Sodium salt of Bentazon  
pKa = 4.3

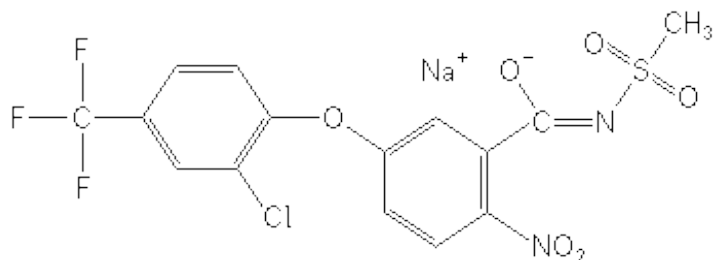


Sodium salt of Fomesafen  
pKa = 3.8



# pH precipitation soluble liquid herbicide

- Reflex Herbicide
- Active: Sodium Fomesafen

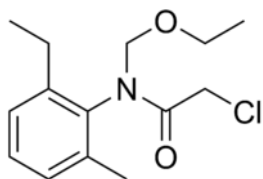


- SL Formulation
- pKa = 3.8
- Acid form is sparingly soluble, the salts have high solubility.  
Typically sold as a sodium salt



## Suspension concentrate failure in presence of divalent cations

- Warrant Herbicide
- Active: Acetochlor

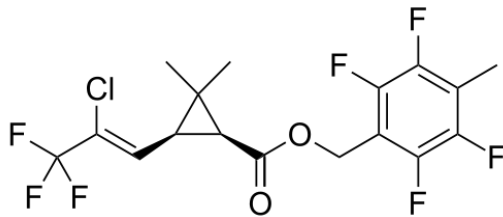


- SC Formulation
- Anionic dispersant fails do to binding divalent cations binding to the negative charged sites of the dispersant.

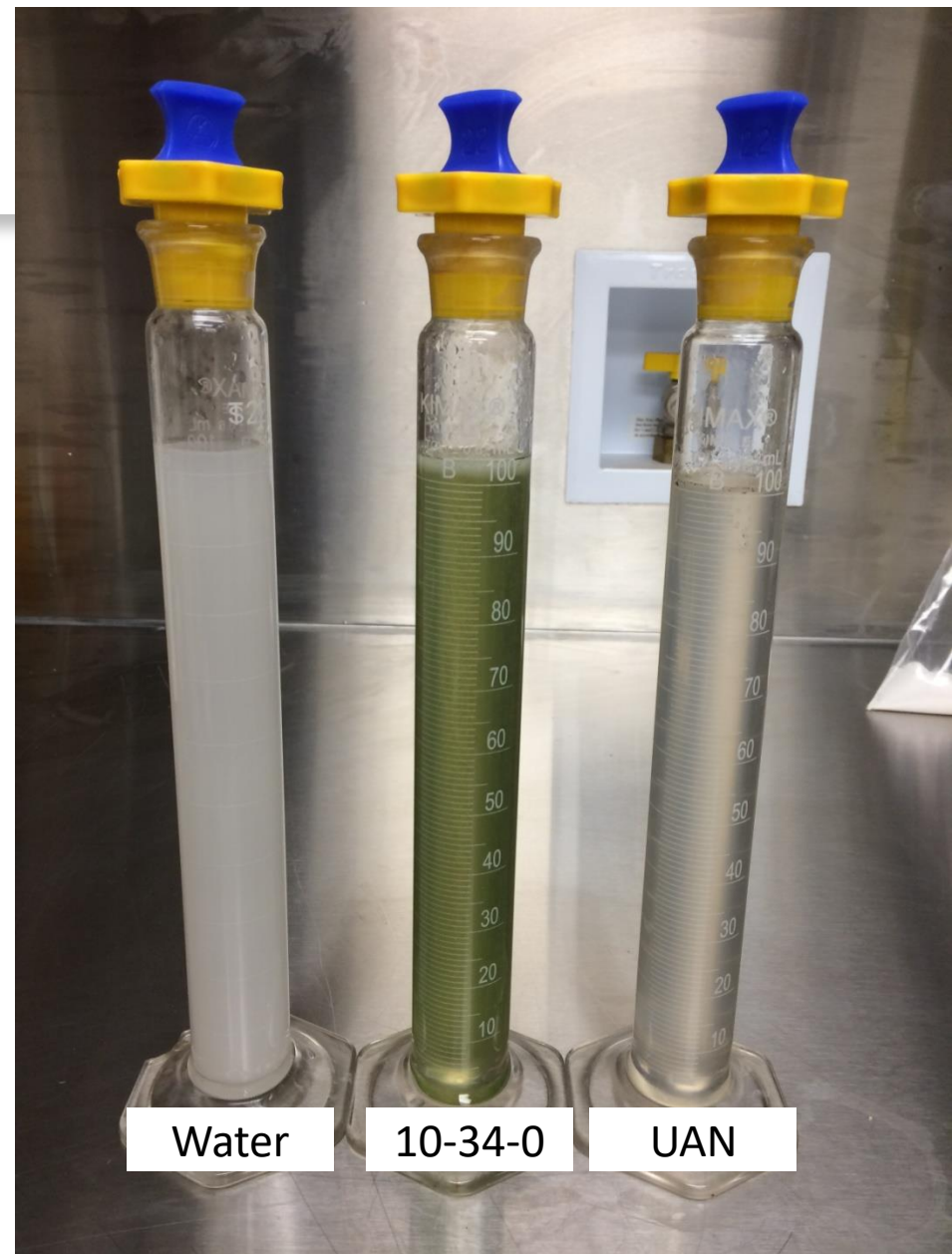


# Suspension Concentrate failure in 10-34-0

- Force Insecticide
- Active: Tefluthrin



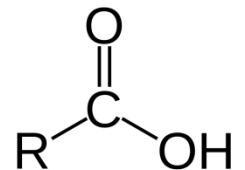
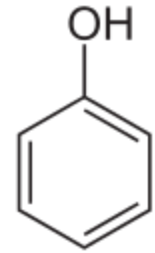
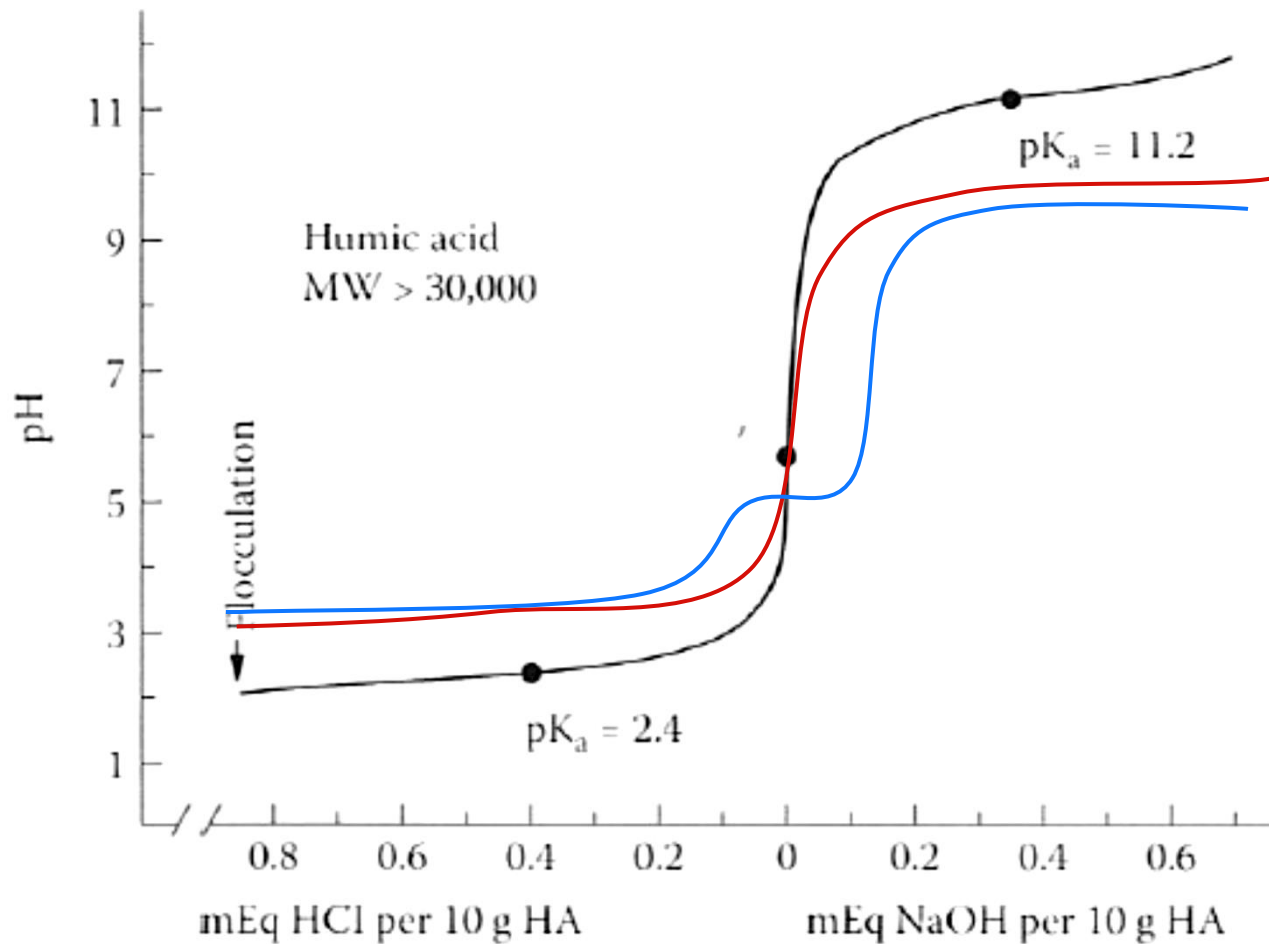
- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails due to limited water to activate dispersing and emulsifying agents.





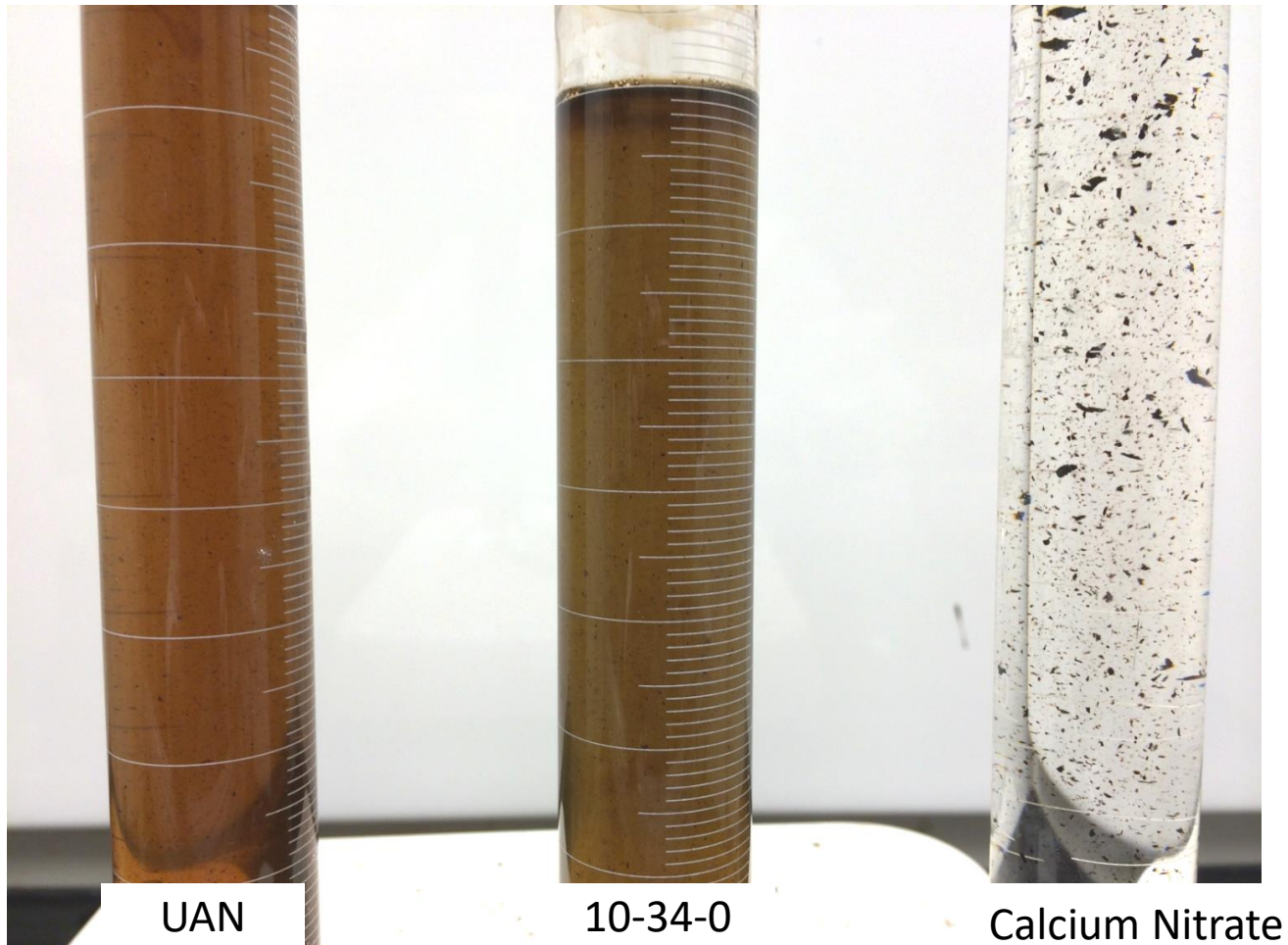
# Humic Acid

pKa values, solubility in alkaline solutions





# Humic Acid in Liquid Fertilizer



## UAN and ATS with Pre-emerge Herbicide

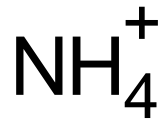
- Lexar EZ, Bicep II Magnum, etc.
- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails do to limited water to activate dispersing and emulsifying agents. Hi electrolyte solution, limited free water.



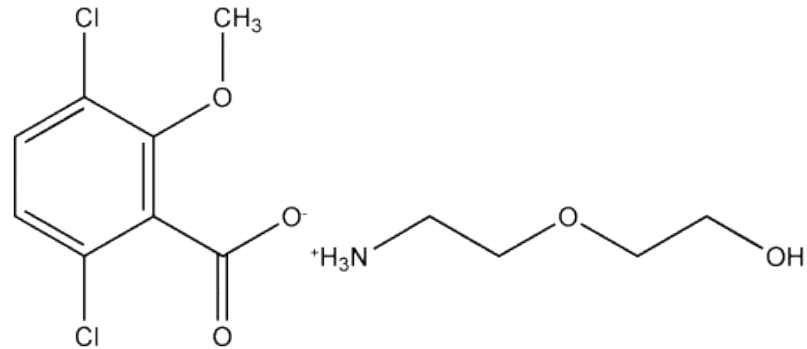
# Counter Ion Affects Volatility of Dicamba

## Ammonium can increase volatility

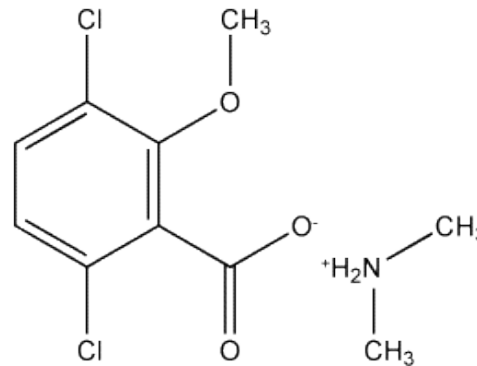
- Be caution of adding ammonium containing liquid fertilizers with Dicamba



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



Dicamba, Diglycolomine salt

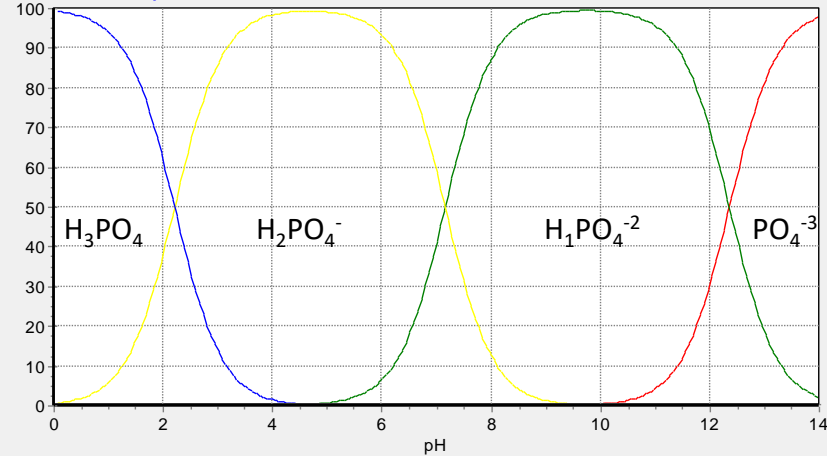


Dicamba, Dimethylamine salt

# Phosphate Interactions

## pH Dependence of Phosphate Binding

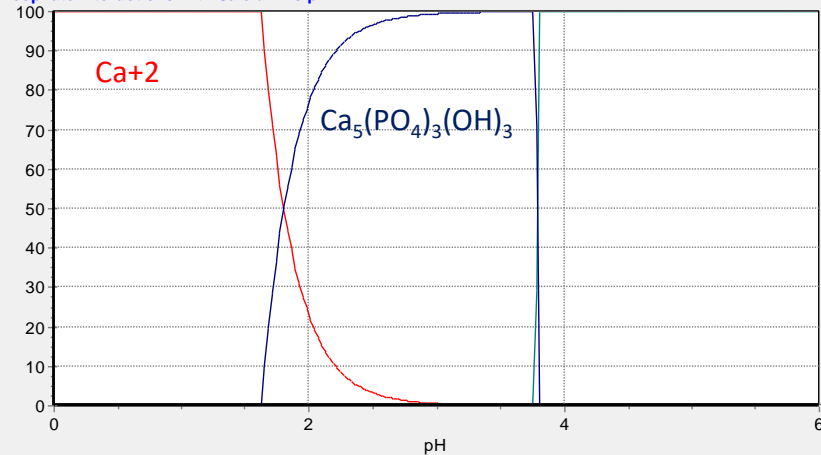
Dissociation of Phosphoric acid H<sub>3</sub>PO<sub>4</sub>



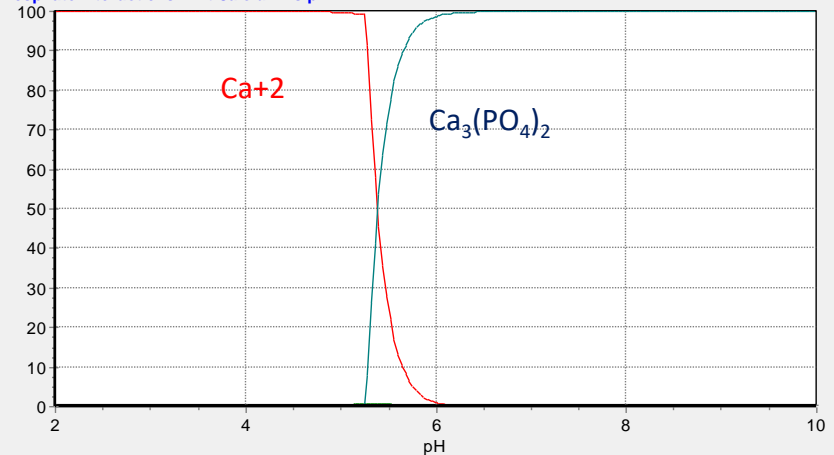
Acid	Mol. Form	pKa
H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2.2
	H <sub>1</sub> PO <sub>4</sub> <sup>-2</sup>	7.2
	PO <sub>4</sub> <sup>-3</sup>	12.3

[M] <sup>+n</sup>	Form	Ksp
Ca+2	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	1x10 <sup>-26</sup>
	Ca <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>2</sub>	1x10 <sup>-27</sup>
	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH) <sub>3</sub>	1x10 <sup>-57</sup>

Phosphate Interactions with Calcium vs pH



Phosphate interactions with Calcium vs pH

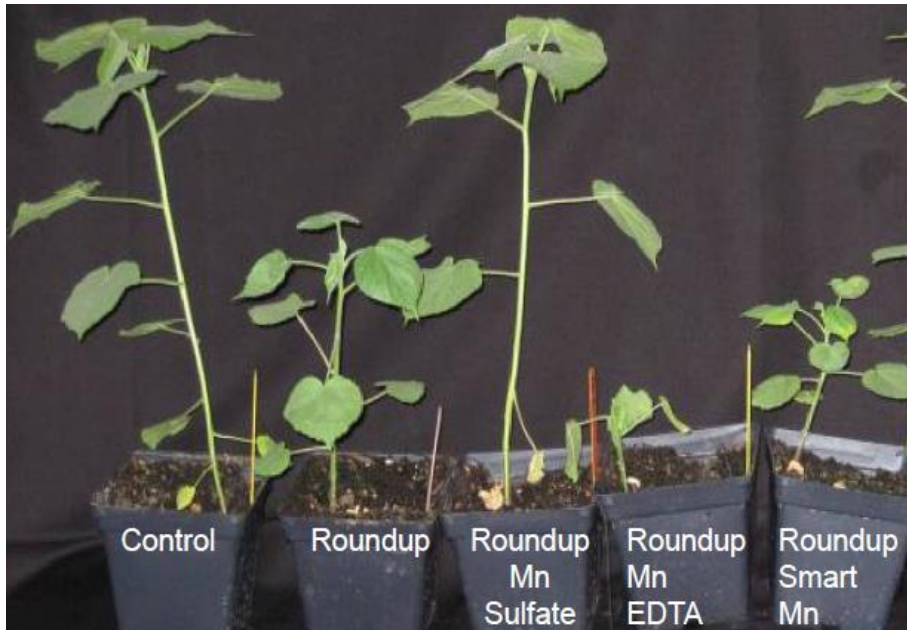
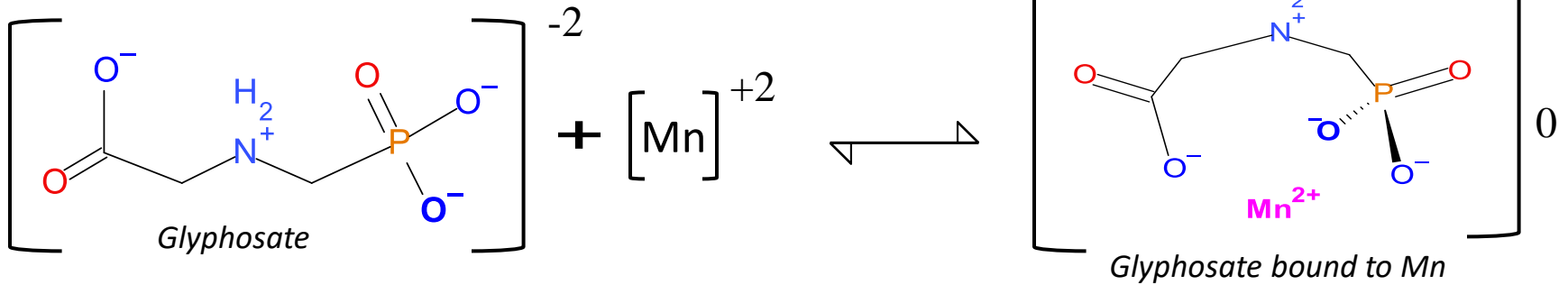


Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations.

**BRANDT**

# Glyphosate

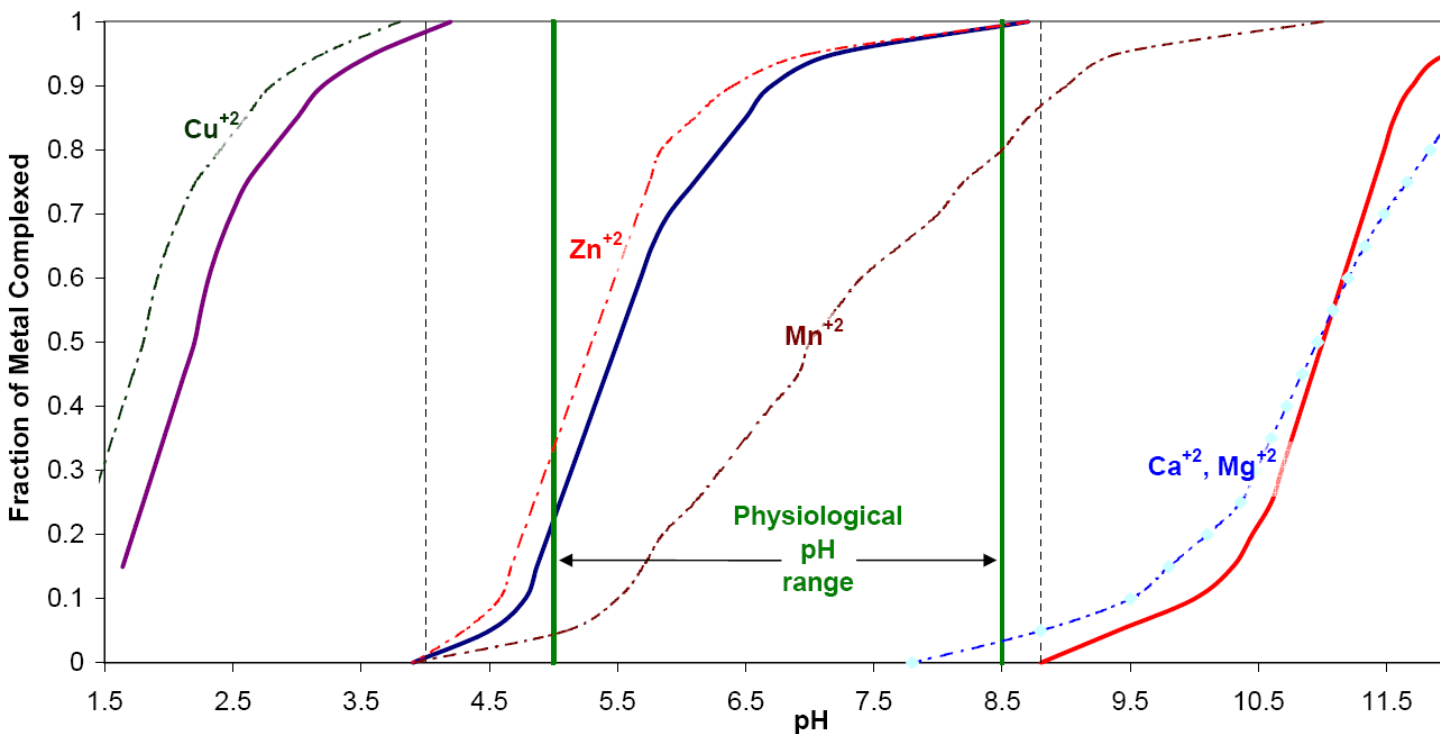
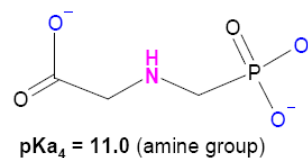
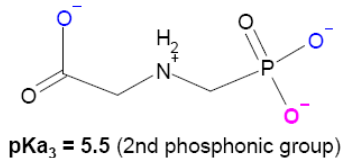
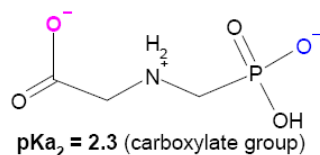
## Antagonized by Divalent Cations



# Glyphosate – Solution Chemistry

## Interactions between Cations and Glyphosate

### Metal Complexes in Relation to Dissociation of Glyphosate vs Solution pH



### Stability Constants

1:1 molar ratio

@ physiological pH

Cation	(LogK <sub>m1</sub> )
<b>Ca<sup>+2</sup></b>	<b>3.3</b>
<b>Mg<sup>+2</sup></b>	<b>3.3</b>
<b>Cu<sup>+2</sup></b>	<b>11.2</b>
Fe <sup>+2</sup>	6.9
Fe <sup>+3</sup>	16.1
<b>Mn<sup>+2</sup></b>	<b>5.5</b>
<b>Zn<sup>+2</sup></b>	<b>8.4</b>



Thank You

- Jar Test

