



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

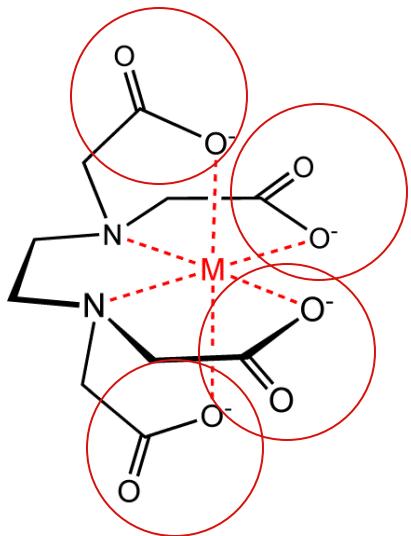
1.1 This practice describes the method for the evaluation of the physical compatibility and stability of pesticide tank mixtures diluted for aqueous application. This practice may also be adapted to use with liquid fertilizers in replacement of the water diluent.

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.

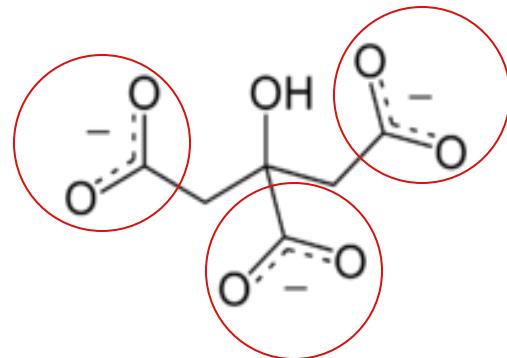
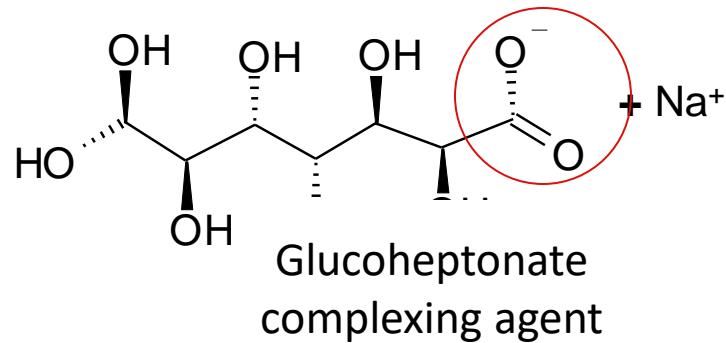
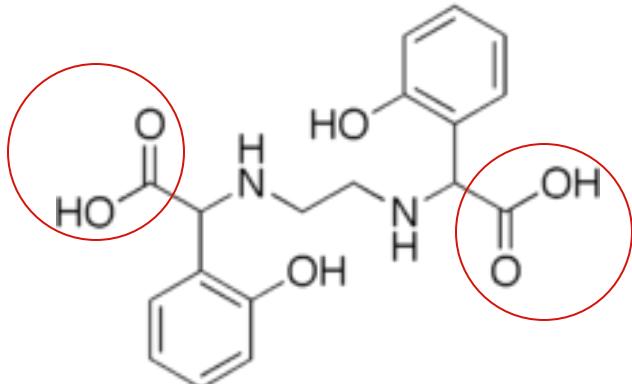
1.3 Compatibility is complex and can be affected by other variables such as order of addition, pH of the dilution water, pumping shear, etc. Under the parameters of this practice, the results will define whether the pesticide mixture is or is not compatible in the laboratory. Compatibility or incompatibility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

Name the Structure What do they have in common?

EDTA
chelating
metal



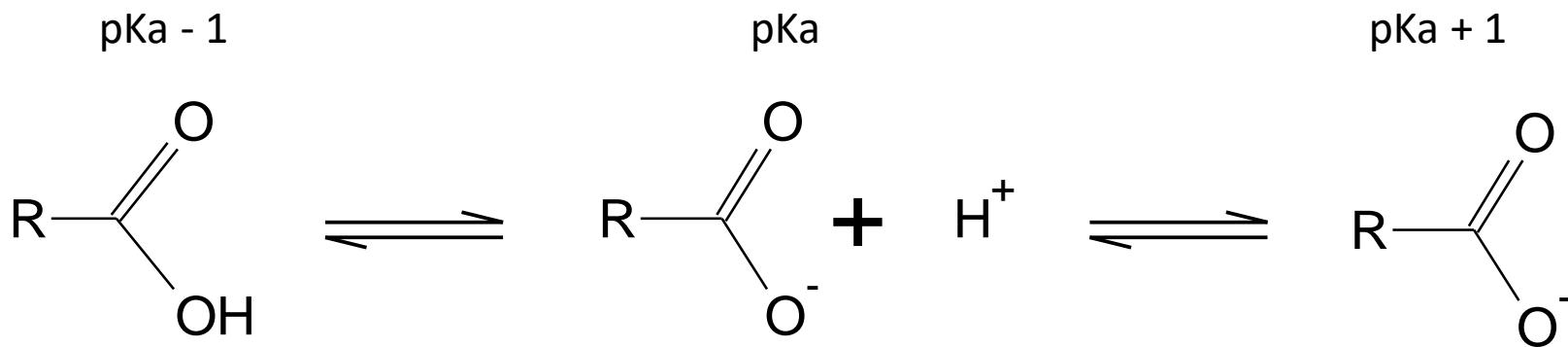
EDDHA
chelating agent



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

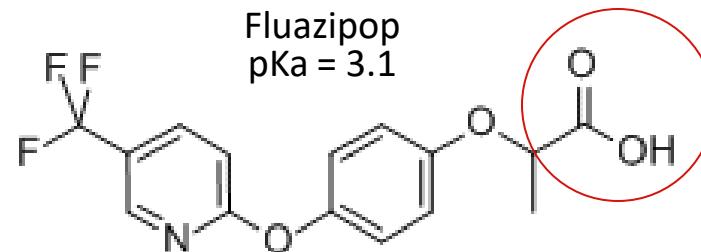
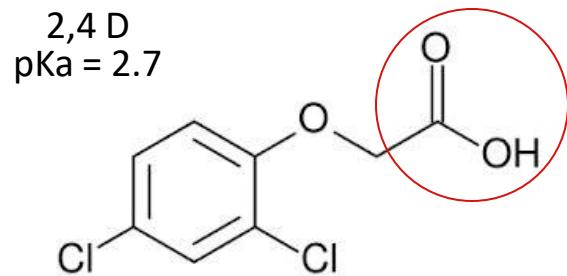
The pKa value is pH value where the functional groups if protonated 50% of the time

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

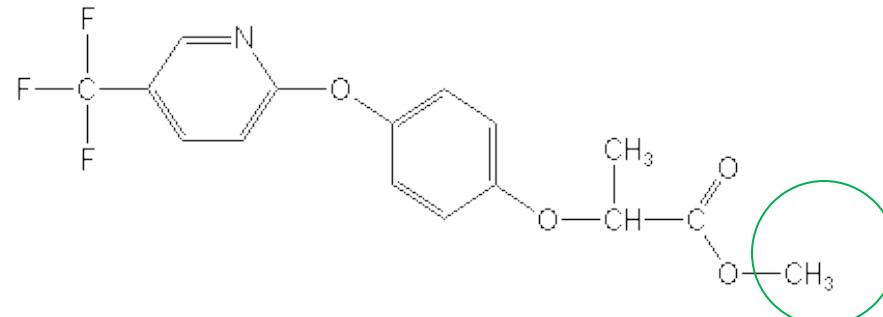
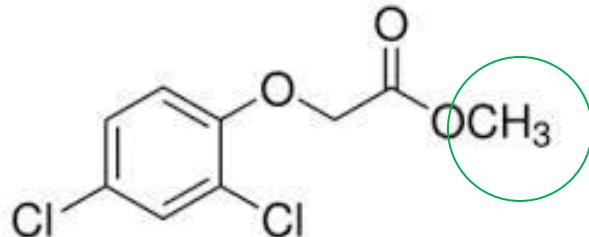
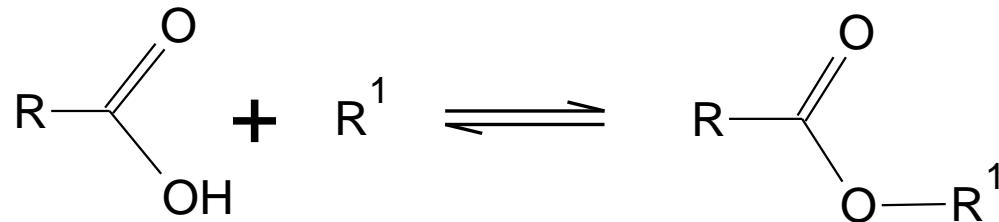
Phenoxy Herbicides

Do you recognize any functional groups?

Carboxyl groups



What about the ester formulation?



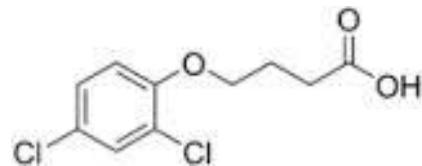
Phenoxy herbicides

Contain carboxyl groups

Active Salt / Ester	pKa	pka + 1	Formul ation	Chemical Class	acid structure	Water Solubility	Notes
2,4-D	2.7	3.7	SL	phenoxy acid	$R_1\text{-COOH}$	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	$R_1\text{-COOH}$	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	$R_1\text{-COOH}$	Sparingly soluble - Products on market are Emulsifiable Concentrates	
Fluazifop	3.1	4.1	EC	phenoxy acid	$R_1\text{-COOH}$	Sparingly soluble - Products on market are Emulsifiable Concentrates	
Fluazifop-P-Butyl	2.9	3.9	EC	phenoxy acid	$R_1\text{-COOH}$	Sparingly soluble - Products on market are Emulsifiable Concentrates	

pH precipitation soluble liquid herbicide

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



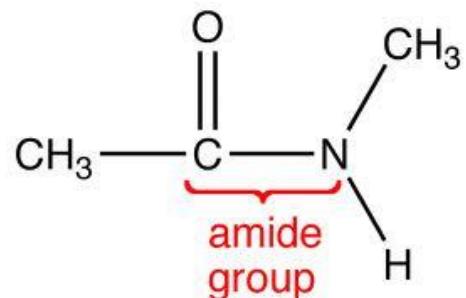
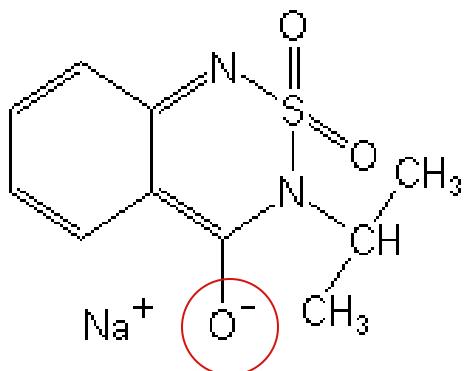
- SL Formulation
- $pK_a = 4.8$
- Acid form is sparingly soluble, the salts have high solubility.

Typically sold as a sodium salt

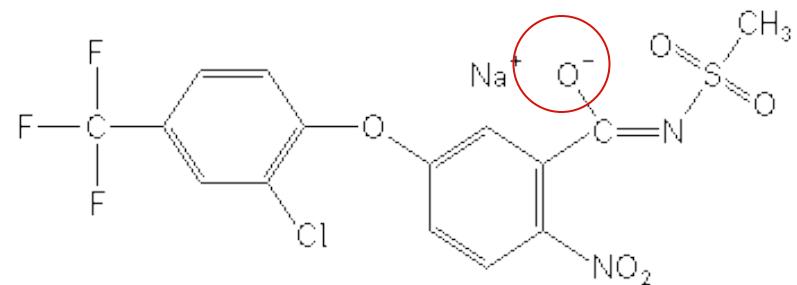


Herbicides – Amide groups

Sodium salt of Bentazon
pKa = 4.3

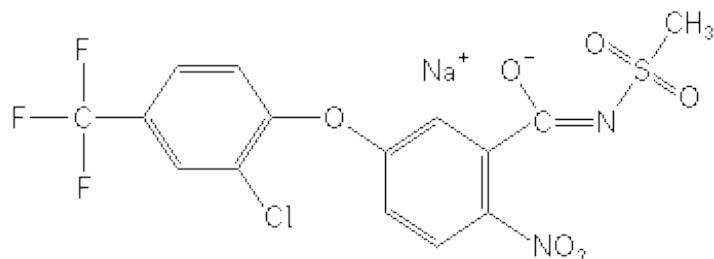


Sodium salt of Fomesafen
pKa = 3.8



pH precipitation soluble liquid herbicide

- Reflex Herbicide
- Active: Sodium Fomesafen

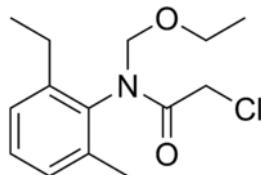


- SL Formulation
- $\text{pK}_a = 3.8$
- Acid form is sparingly soluble, the salts have high solubility.
Typically sold as a sodium salt



Suspension concentrate failure in presence of divalent cations

- Warrant Herbicide
- Active: Acetochlor

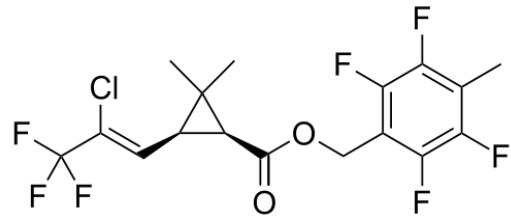


- SC Formulation
- Anionic dispersant fails do to binding divalent cations binding to the negative charged sites of the dispersant.

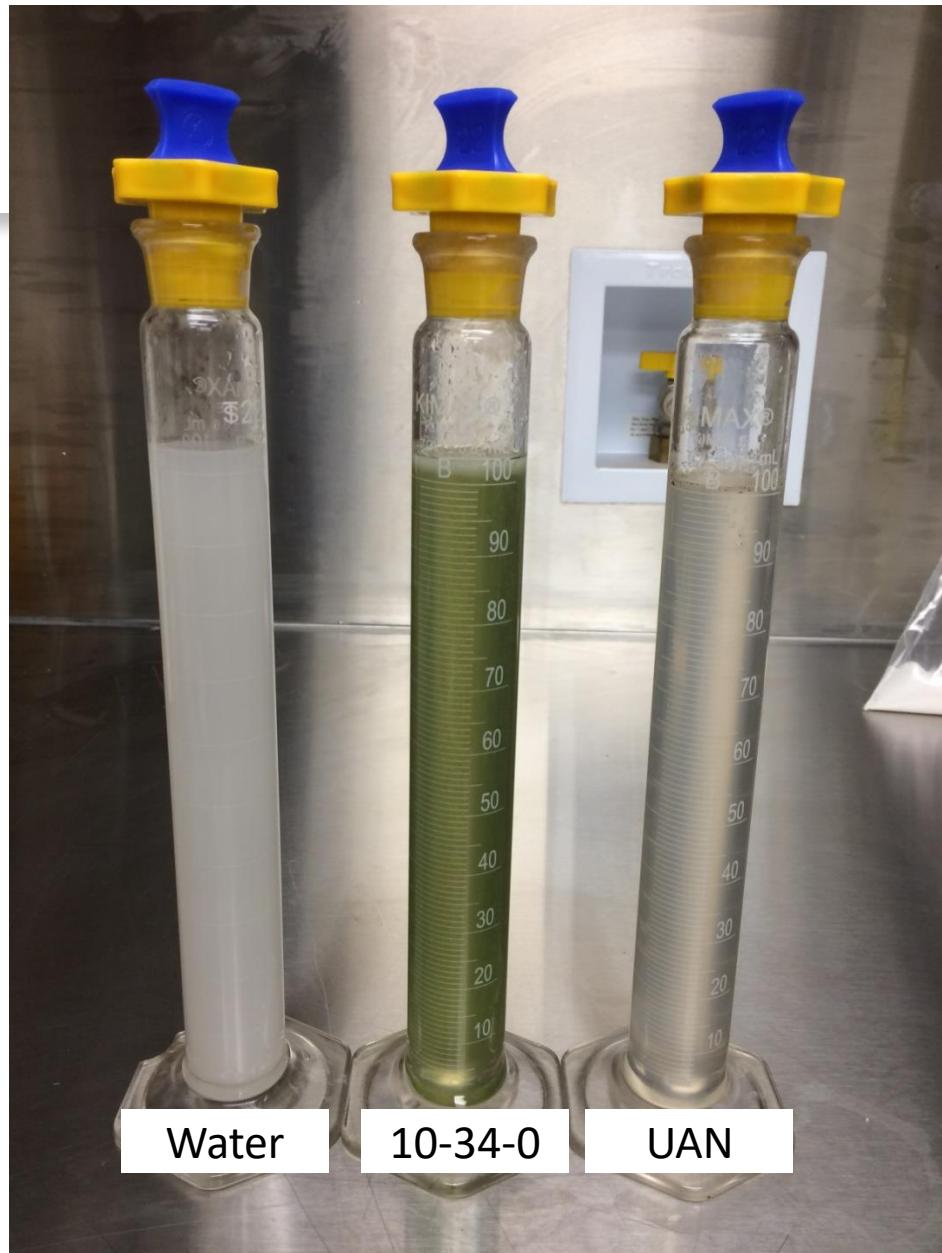


Suspension Concentrate failure in 10-34-0

- Force Insecticide
- Active: Tefluthrin

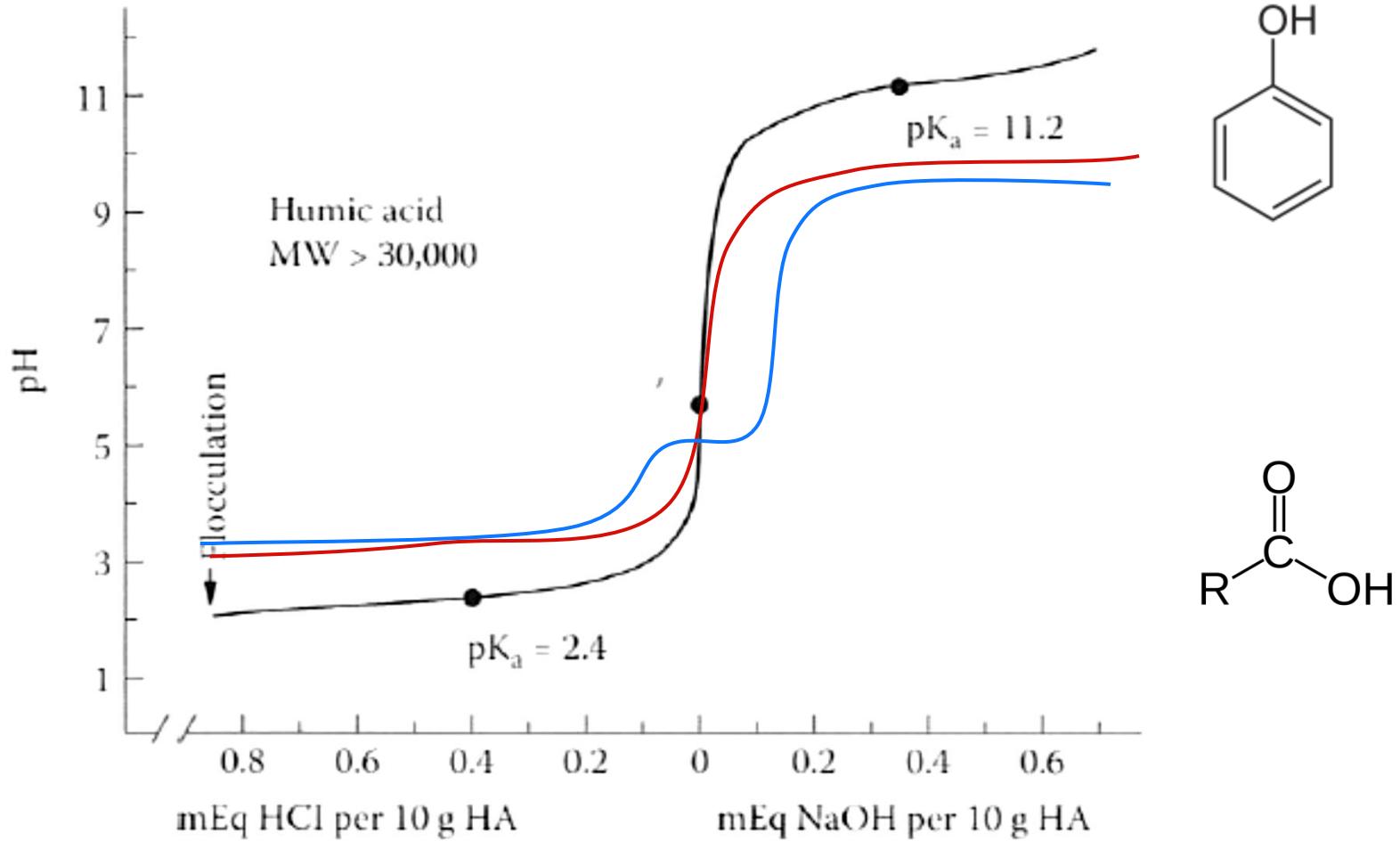


- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails do to limited water to activate dispersing and emulsifying agents.



Humic Acid

pKa values, solubility is alkaline solutions



Humic Acid in Liquid Fertilizer



UAN



10-34-0



Calcium Nitrate

UAN and ATS with Pre-emerge Herbicide

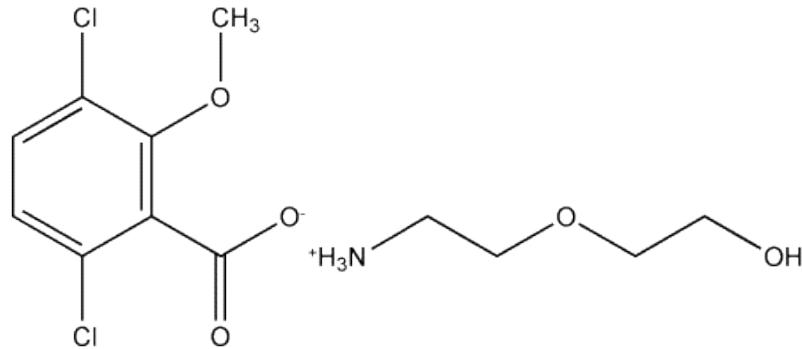
- Lexar EZ, Bicep II Magnum, etc.
- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails do to limited water to activate dispersing and emulsifying agents. Hi electrolyte solution, limited free water.



Counter Ion Affects Volatility of Dicamba

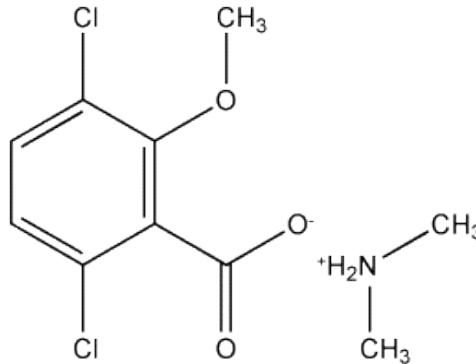
Ammonium can increase volatility

- Be caution of adding ammonium containing liquid fertilizers with Dicamba



Dicamba, Diglycolamine salt

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

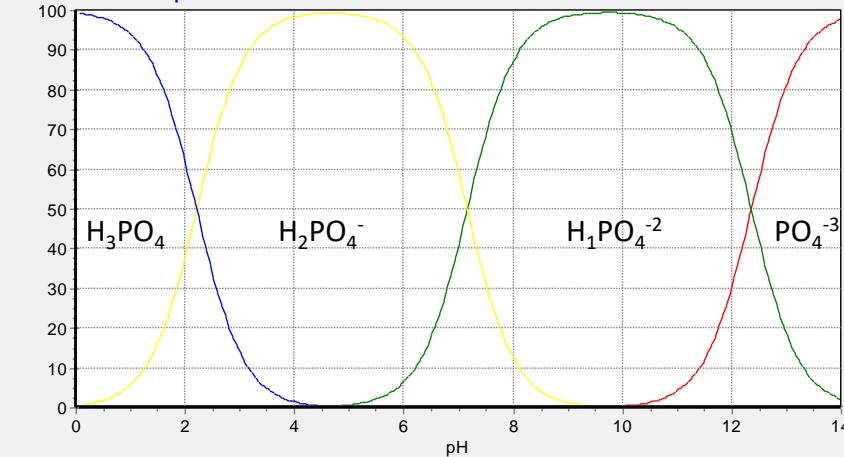


Dicamba, Dimethylamine salt

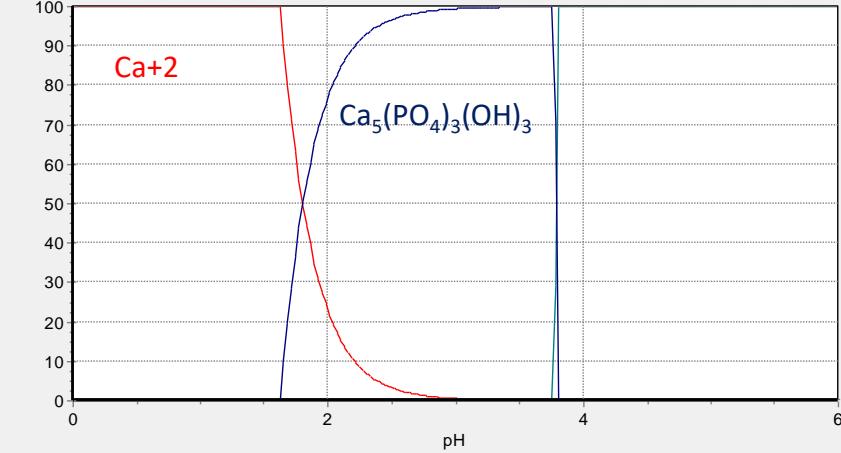
Phosphate Interactions

pH Dependence of Phosphate Binding

Dissociation of Phosphoric acid H_3PO_4



Phosphate Interactions with Calcium vs pH



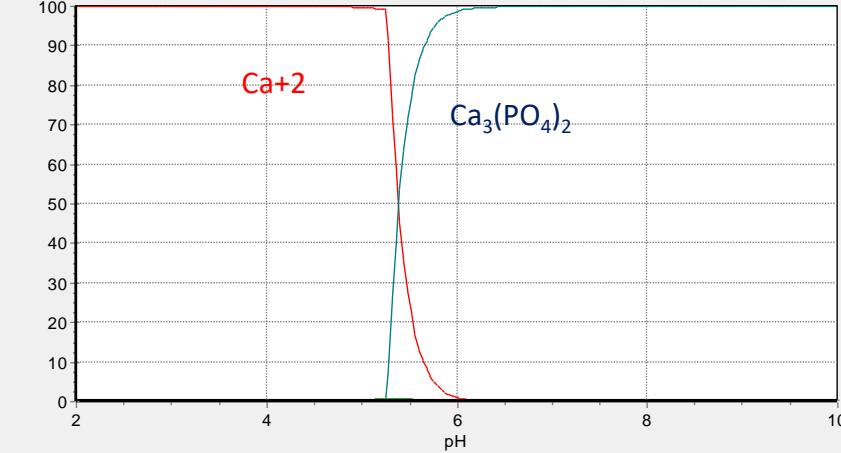
Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations

BRANDT

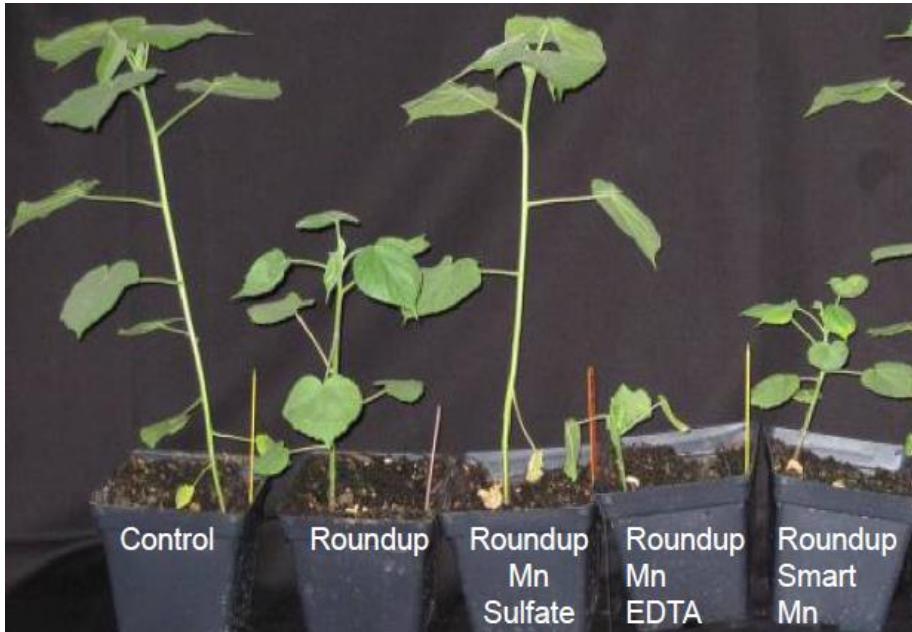
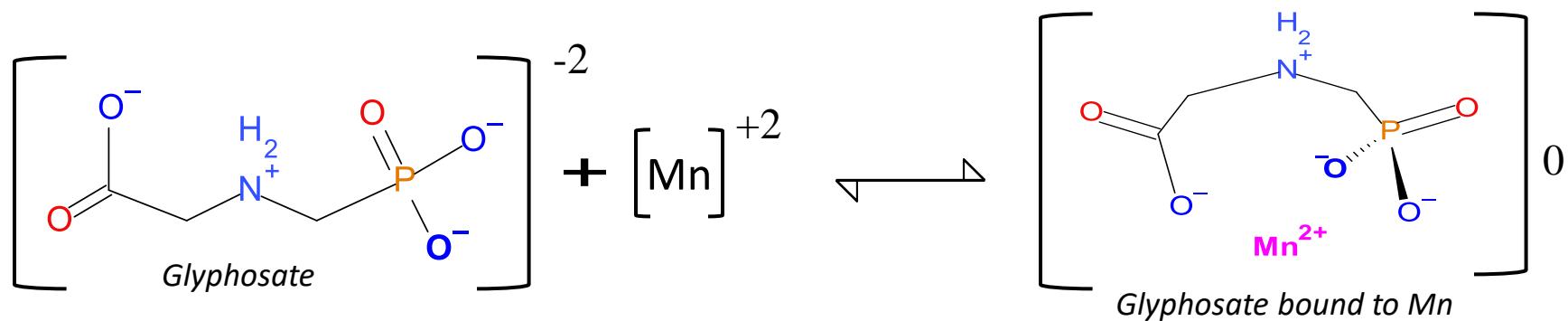
Acid	Mol. Form	pKa
H_3PO_4	H_2PO_4^-	2.2
	$\text{H}_1\text{PO}_4^{-2}$	7.2
	PO_4^{-3}	12.3

$[\text{M}]^{+n}$	Form	Ksp
Ca+2	$\text{Ca}_3(\text{PO}_4)_2$	1×10^{-26}
	$\text{Ca}_2(\text{PO}_4)_2(\text{OH})_2$	1×10^{-27}
	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})_3$	1×10^{-57}

Phosphate interactions with Calcium vs pH



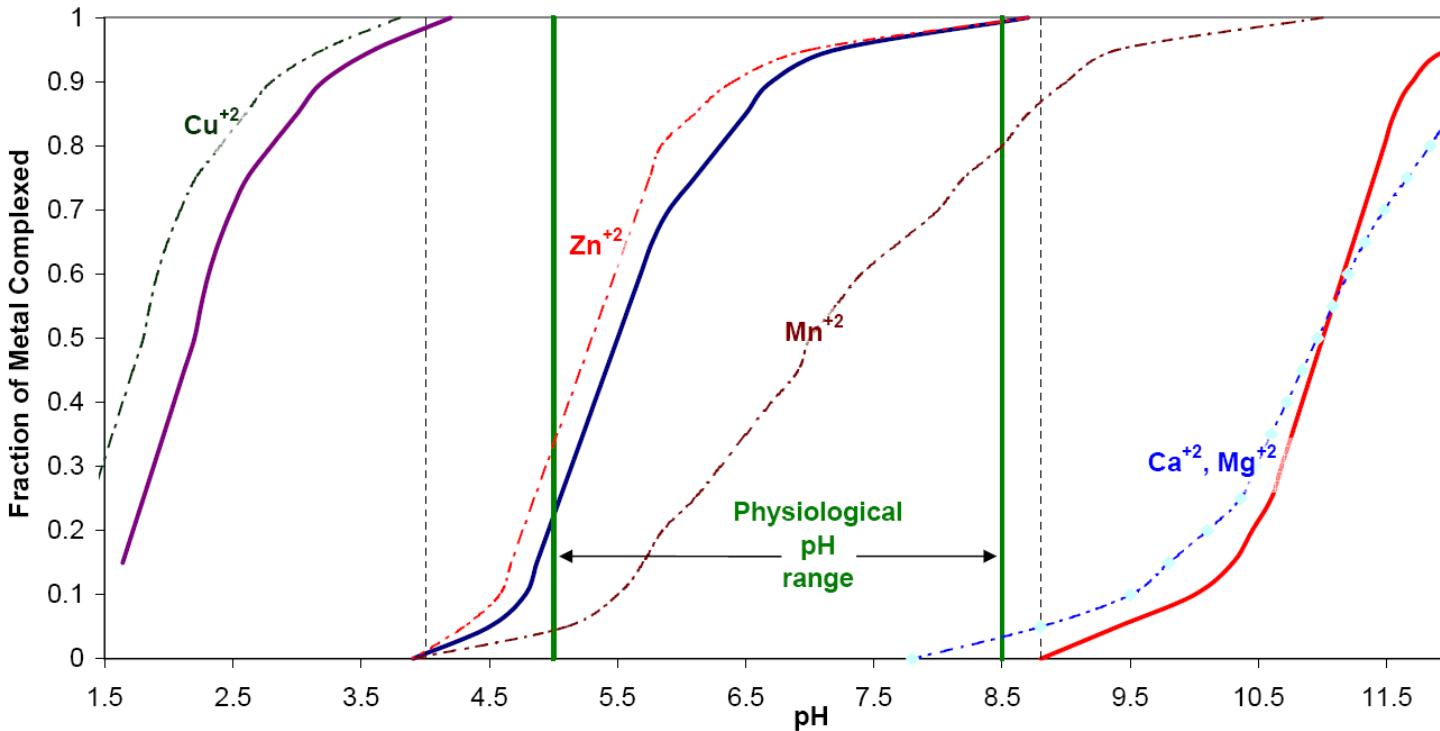
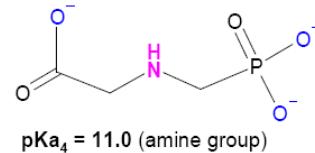
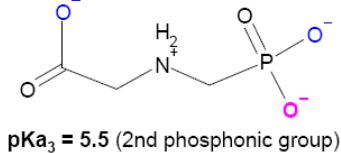
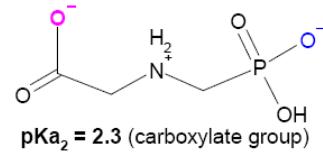
Glyphosate Antagonized by Divalent Cations



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	$(\text{Log}K_{m1})$
Ca^{+2}	3.3
Mg^{+2}	3.3
Cu^{+2}	11.2
Fe^{+2}	6.9
Fe^{+3}	16.1
Mn^{+2}	5.5
Zn^{+2}	8.4

Thank You

- Jar Test

