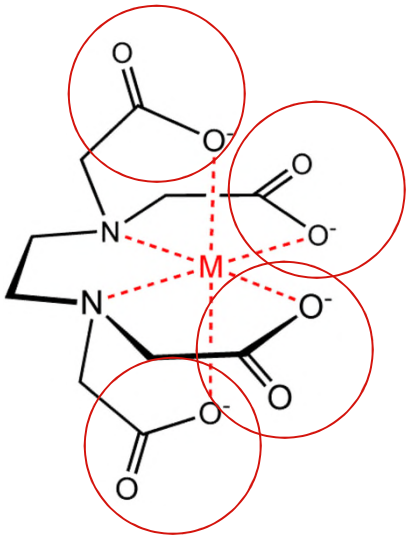
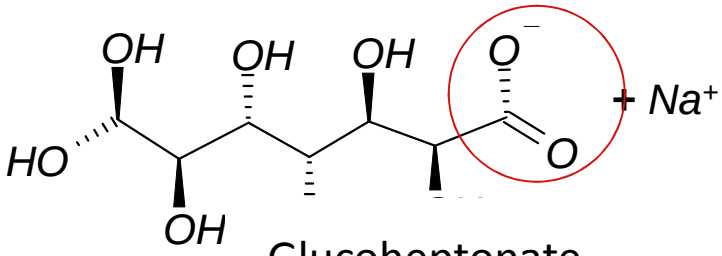
Fluid Compatibility Issues - Pesticides

Brian Haschemeyer
December, 2013

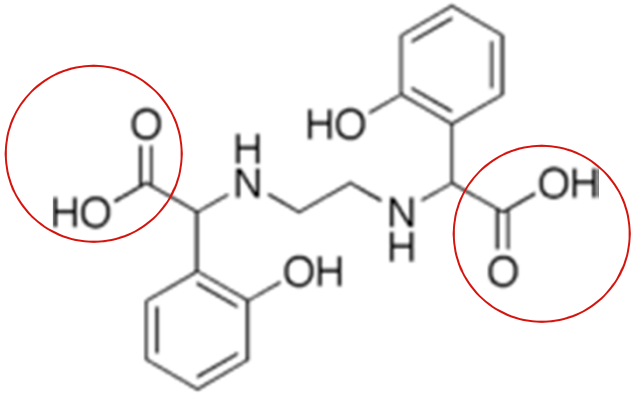
Name the Structure
What do they have in common?

EDTA
chelating
metal

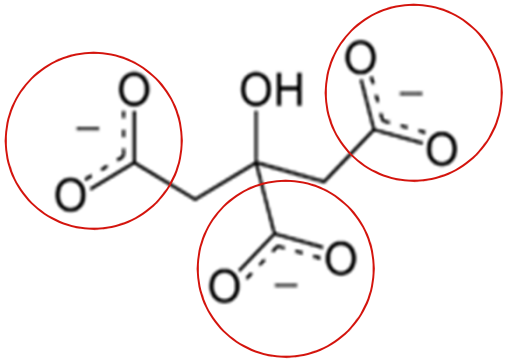




Glucoheptonate
complexing agent



EDDHA
chelating agent



Citric Acid
chelating agent

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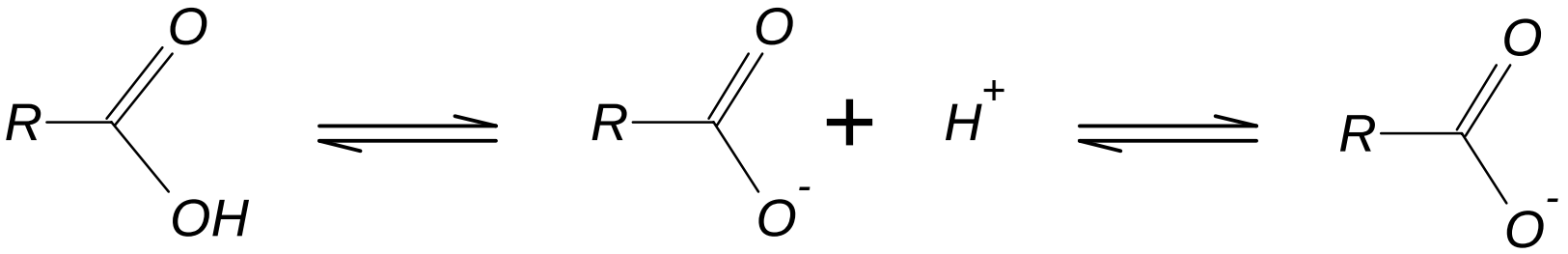
Carboxyl group – key function group of many Ag chemicals Chelates, Complexes and Herbicides

pKa - 1 | pKa | pKa + 1



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

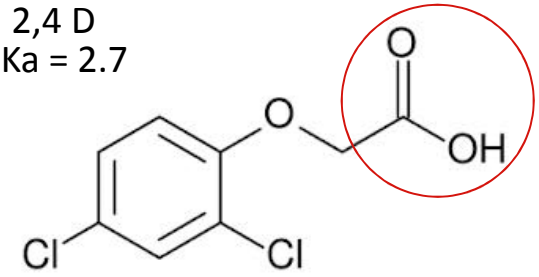
The pKa value is pH value where the functional groups if protonated 50% of the time

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

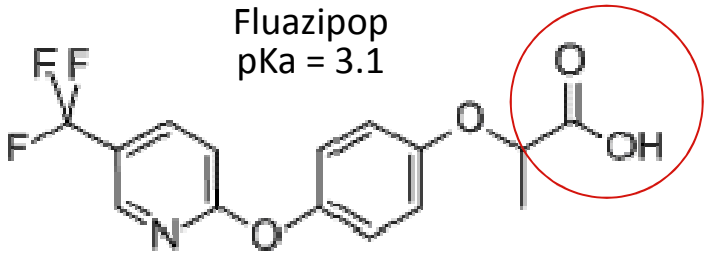
Phenoxy Herbicides

Do you recognize any functional groups? Carboxyl groups

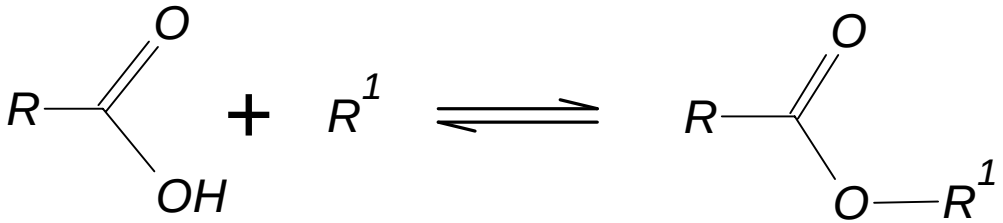
2,4 D
pKa = 2.7

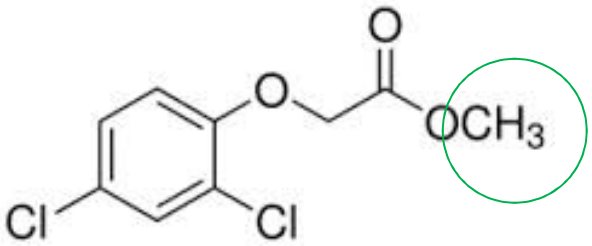


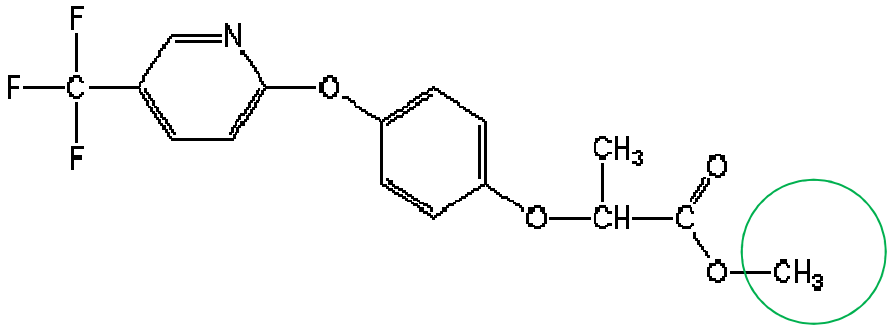
Fluazipop
pKa = 3.1



What about the ester formulation?







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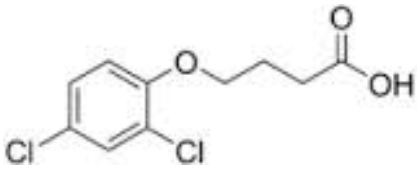
Phenoxy herbicides
Contain carboxyl groups

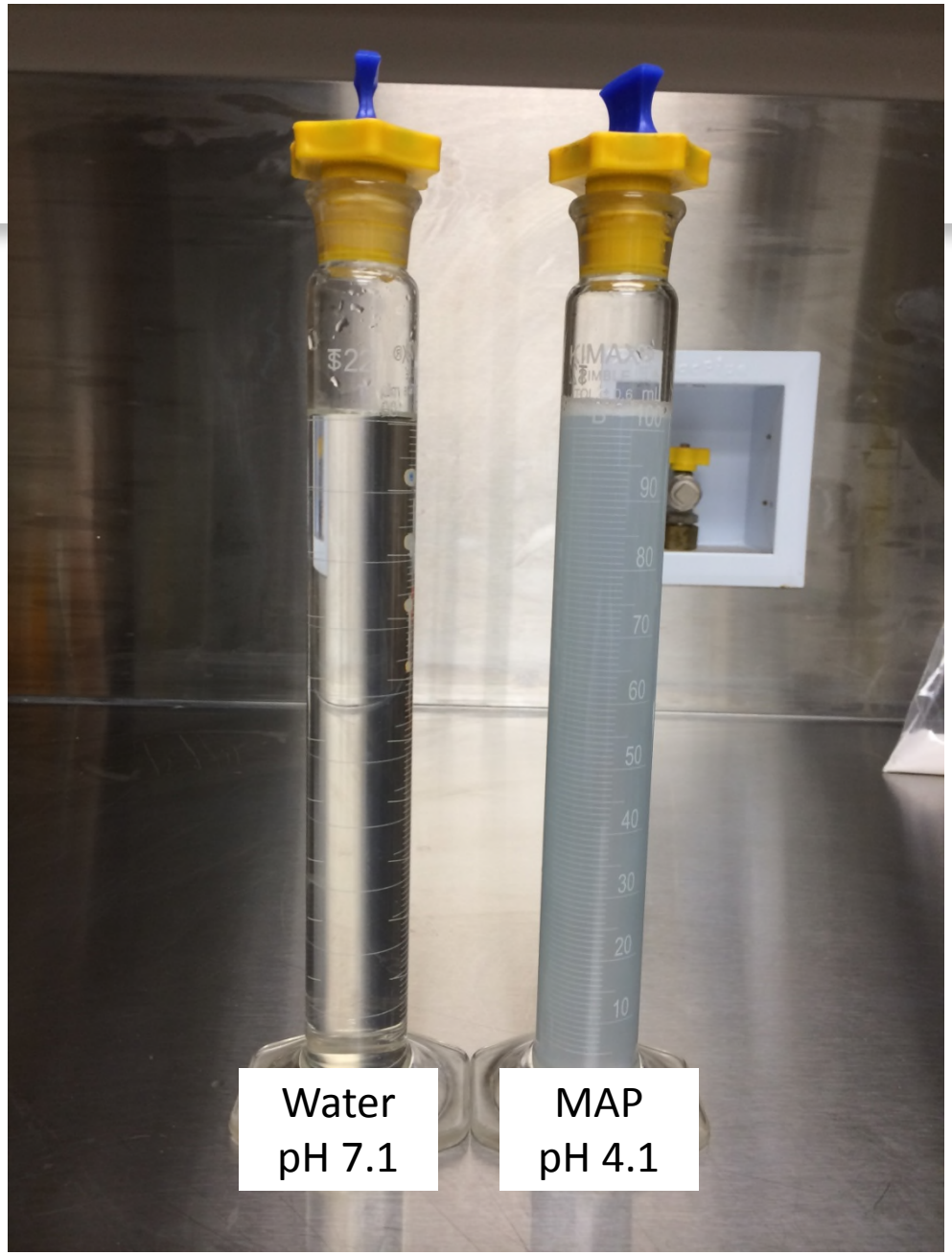
Active Salt / Ester	pKa	pka + 1	Formulation Type	Chemical Class	acid structure	Water Solubility Notes
2,4-D	2.7	3.7	SL	phenoxy acid	R_1-COOH	Acid and ester forms are sparingly soluble, the salts have high solubility. Formulated as both a water salt and oil soluble ester
2,4-DB	4.8	5.8	SL	phenoxy acid	R_1-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-COOH	Sparingly soluble - Products on market are Emulsifiable Concentrates
Fluazifop	3.1	4.1	EC	phenoxy acid	R_1-COOH	Sparingly soluble - Products on market are Emulsifiable Concentrates
Fluazifop-P-Butyl	2.9	3.9	EC	phenoxy acid	R_1-COOH	Sparingly soluble - Products on market are Emulsifiable Concentrates

pH precipitation soluble liquid herbicide

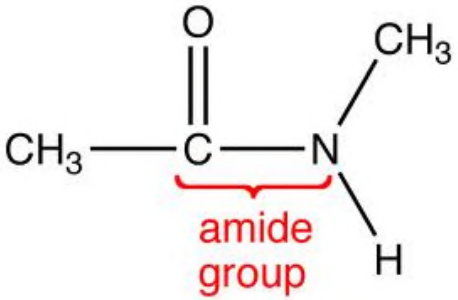
- Reflex Herbicide
- Active: 2,4-DB



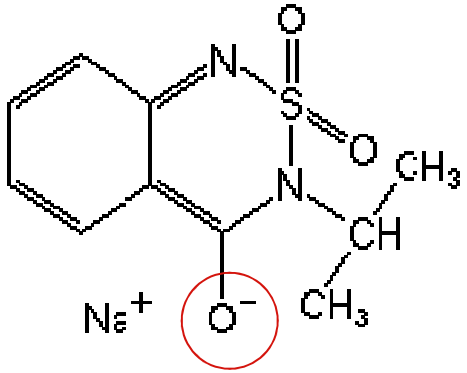
- SL Formulation
- pKa = 4.8
- Acid form is sparingly soluble, the salts have high solubility. Typically sold as a sodium salt



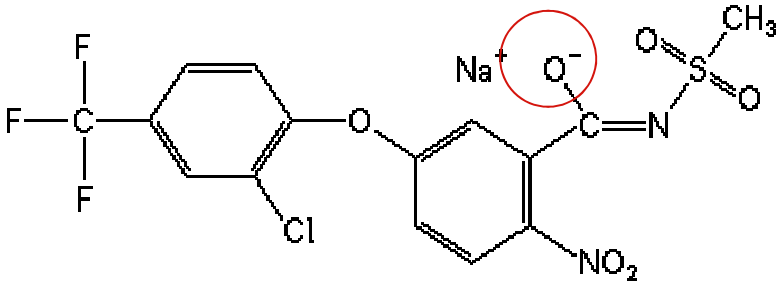
Herbicides – Amide groups



Sodium salt of Bentazon
pKa = 4.3

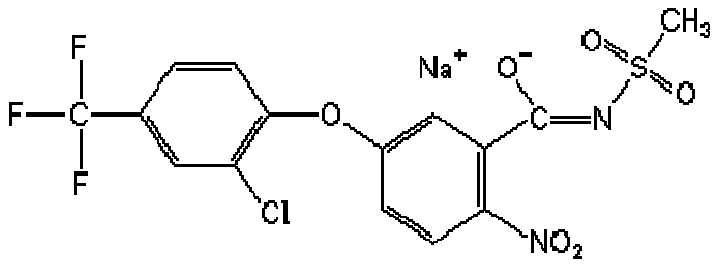


Sodium salt of Fomesafen
pKa = 3.8



pH precipitation soluble liquid herbicide

- Reflex Herbicide
- Active: Sodium Fomesafen



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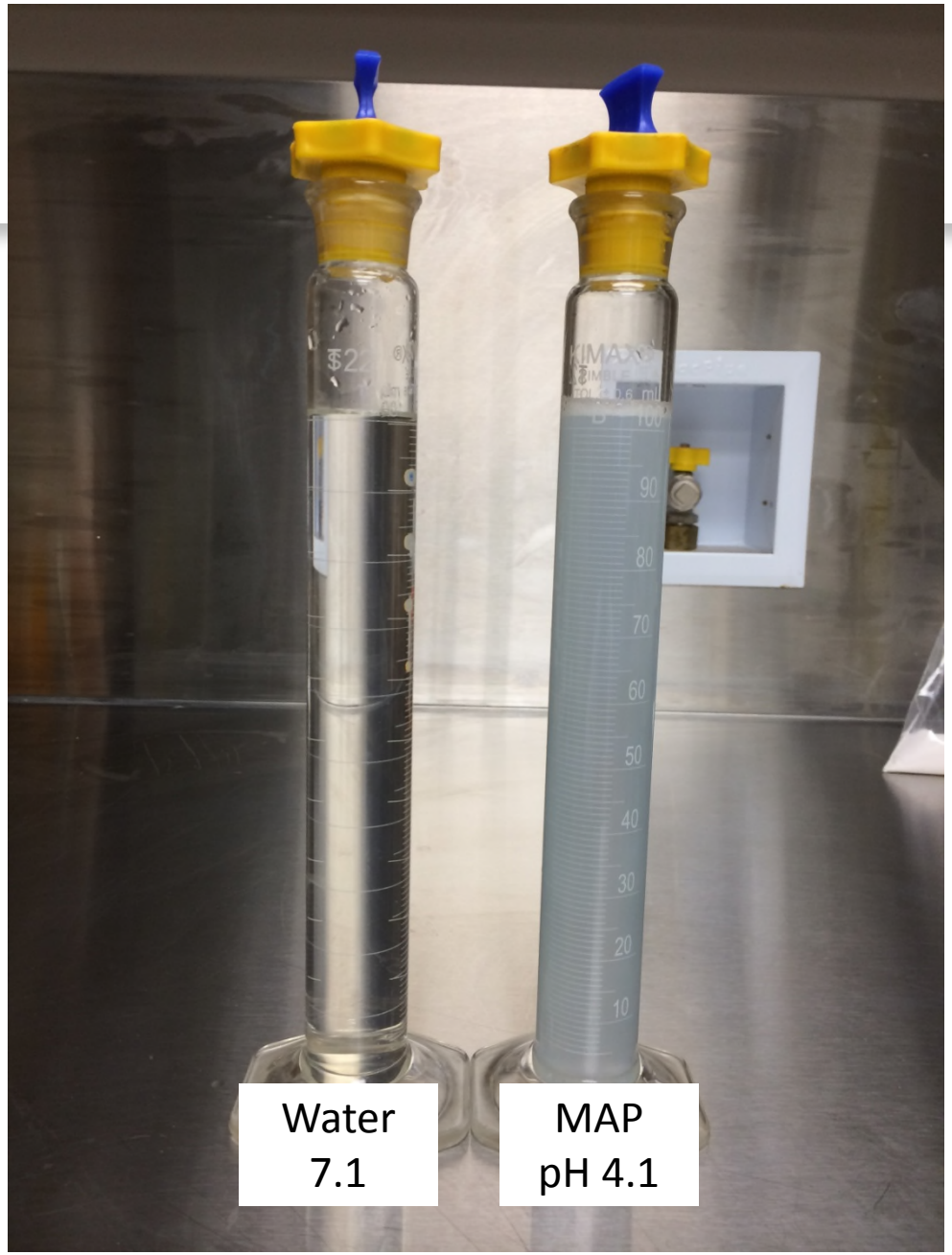
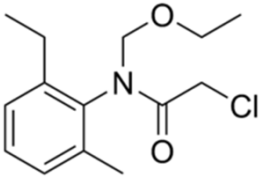
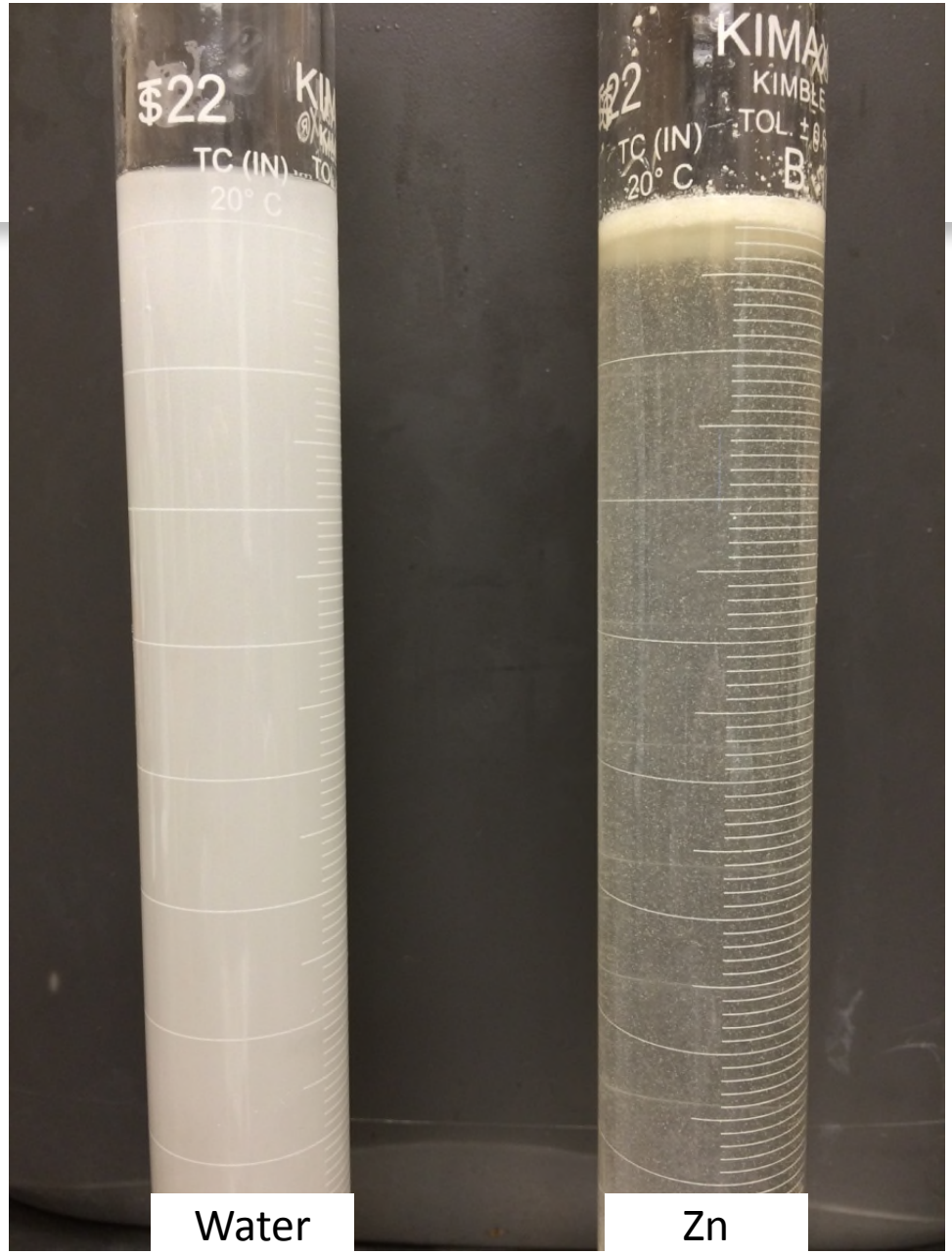


Suspension concentrate failure in presence of divalent cations

- Warrant Herbicide
- Active: Acetochlor

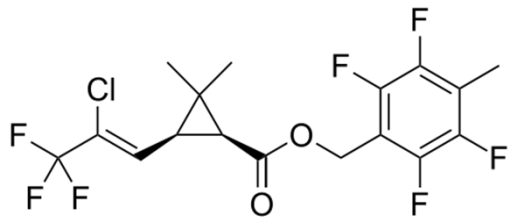


- SC Formulation
- Anionic dispersant fails do to binding divalent cations binding to the negative charged sites of the dispersant.

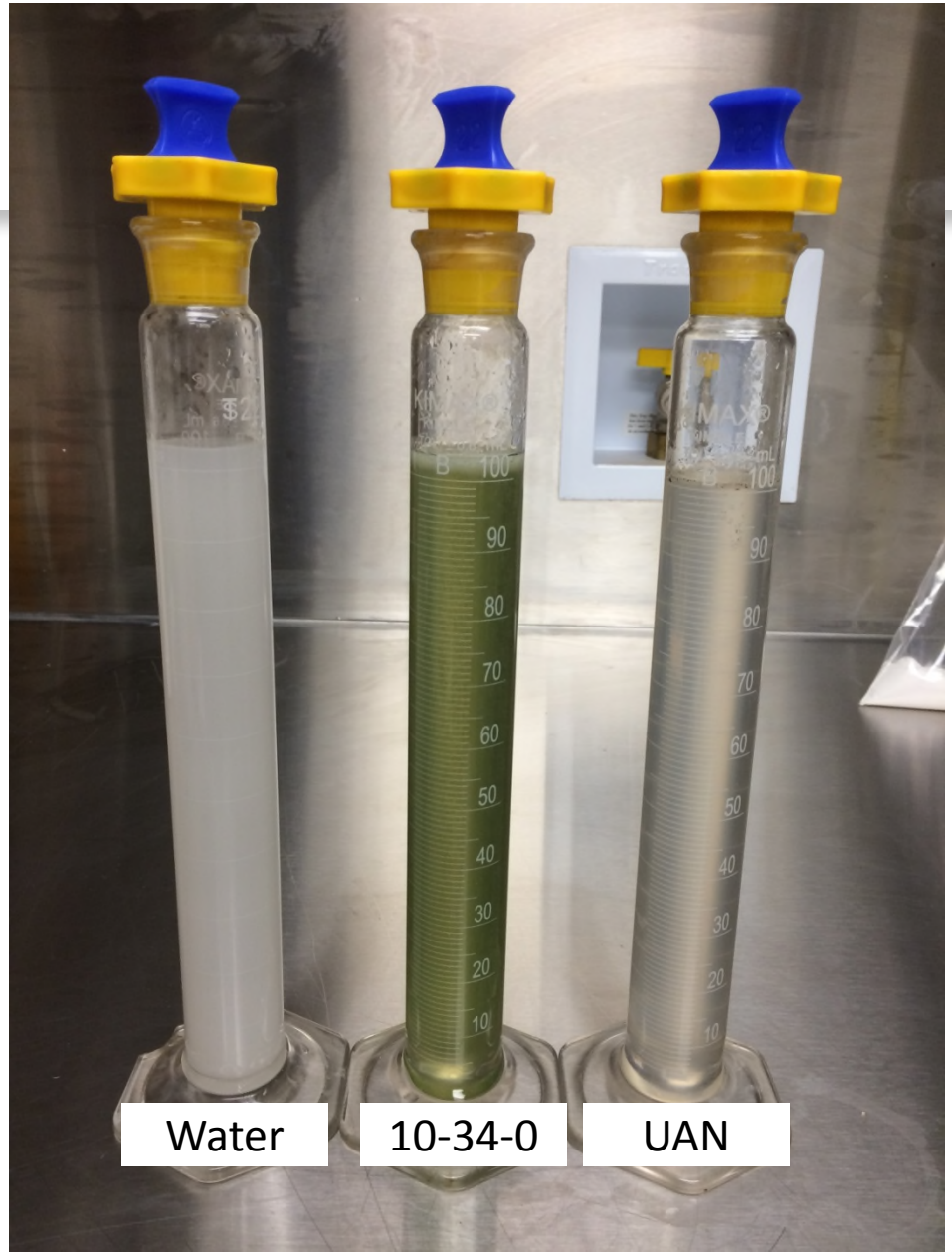


Suspension Concentrate failure in 10-34-0

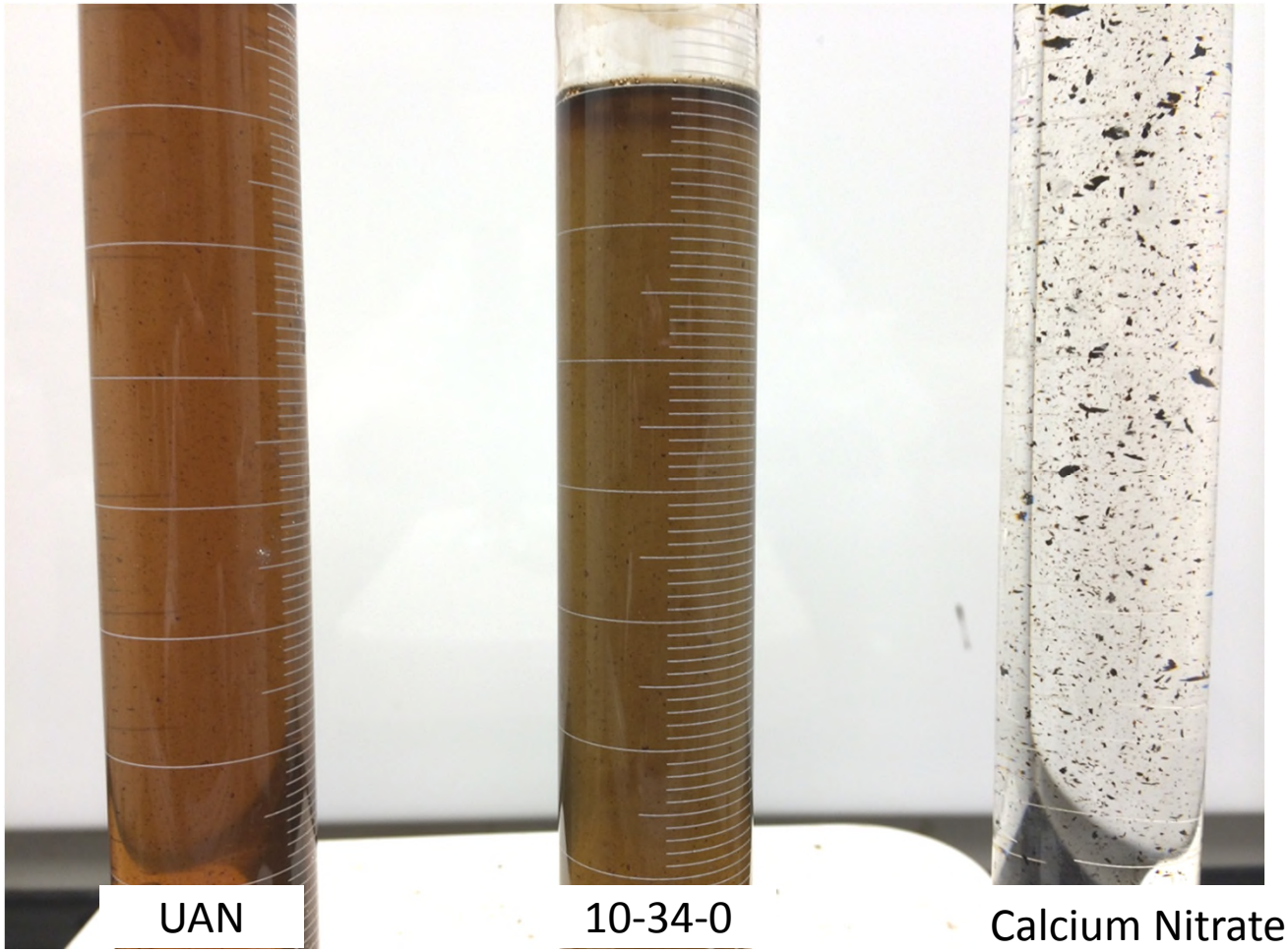
- Force Insecticide
- Active: Tefluthrin



- 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 in Liquid Fertilizer



UAN and ATS with Pre-emerge Herbicide

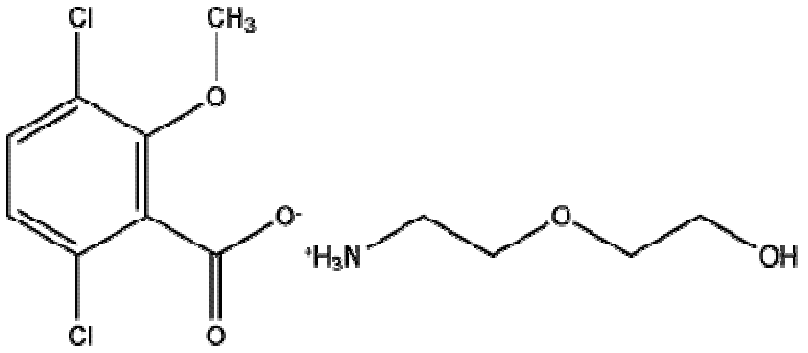
- Lexar EZ, Bicep II Magnum, etc.
- SC Formulation
- Sparingly soluble in water, liquid formulations are typically SC or EC
- Dispersant fails do to limited water to activate dispersing and emulsifying agents. Hi electrolyte solution, limited free water.

Counter Ion Affects Volatility of Dicamba
Ammonium can increase volatility

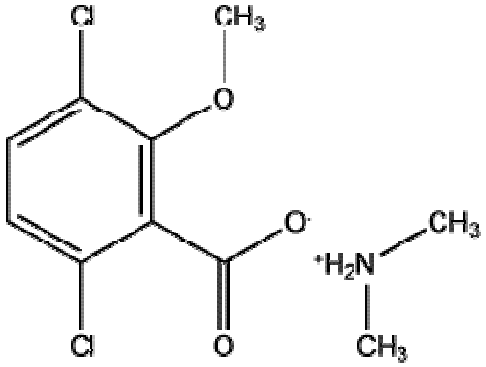
- Be caution of adding ammonium containing liquid fertilizers with Dicamba

$$NH_4^+$$

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

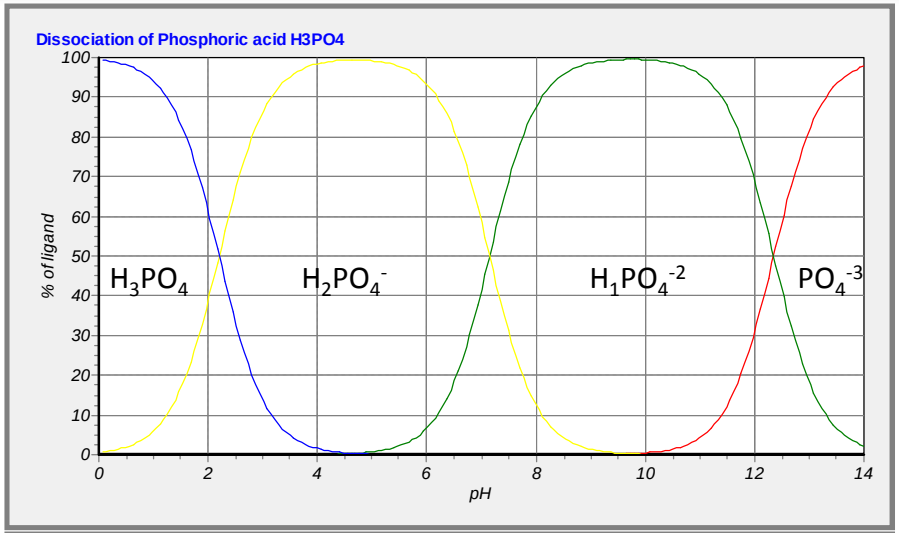


Dicamba, Diglycolomine salt



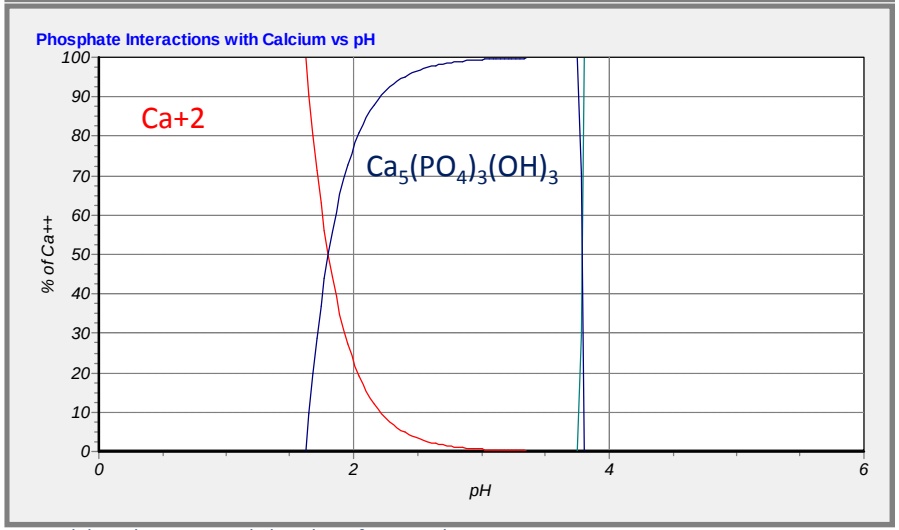
Dicamba, Dimethylamine salt

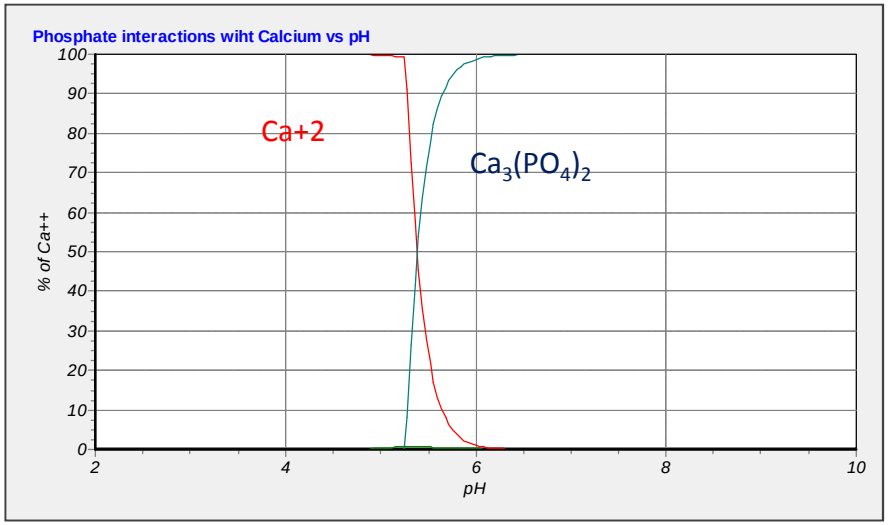
Phosphate Interactions
pH Dependence of Phosphate Binding



Acid	Mol. Form	pKa
H_3PO_4	$H_2PO_4^-$	2.2
	$H_1PO_4^{-2}$	7.2
	PO_4^{-3}	12.3

$[M]^{+n}$	Form	Ksp
Ca+2	$Ca_3(PO_4)_2$	$1x10^{-26}$
	$Ca_2(PO_4)_2(OH)_2$	$1x10^{-27}$
	$Ca_5(PO_4)_3(OH)_3$	$1x10^{-57}$





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

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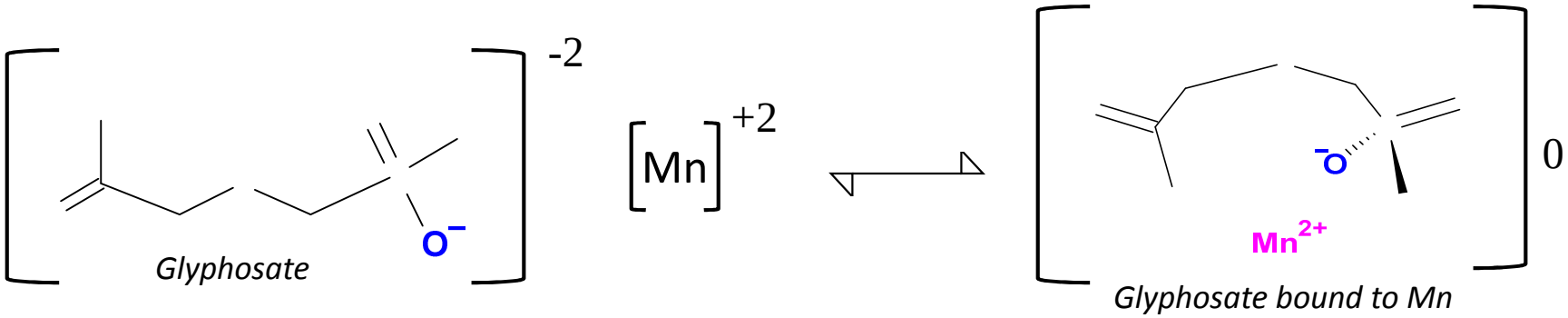
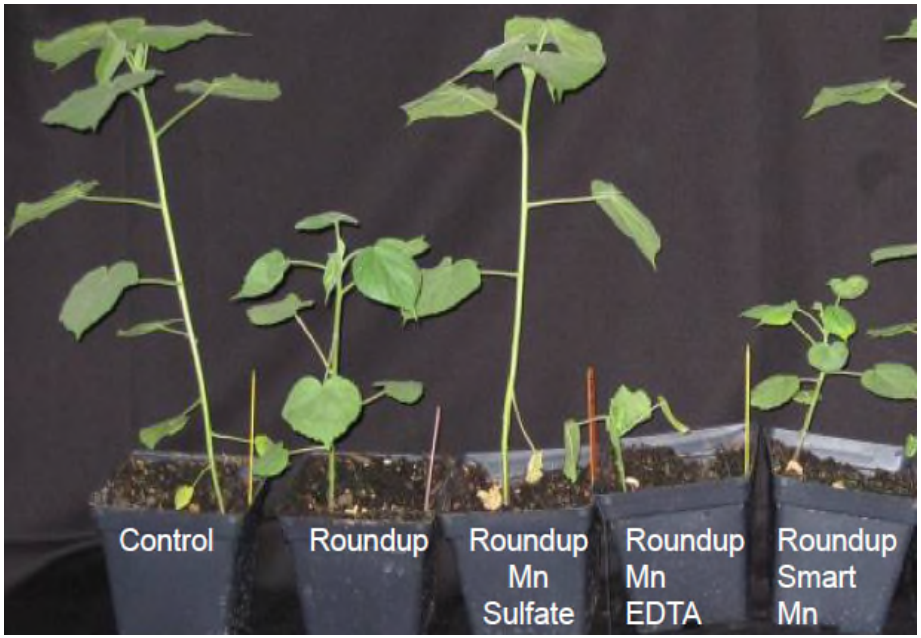
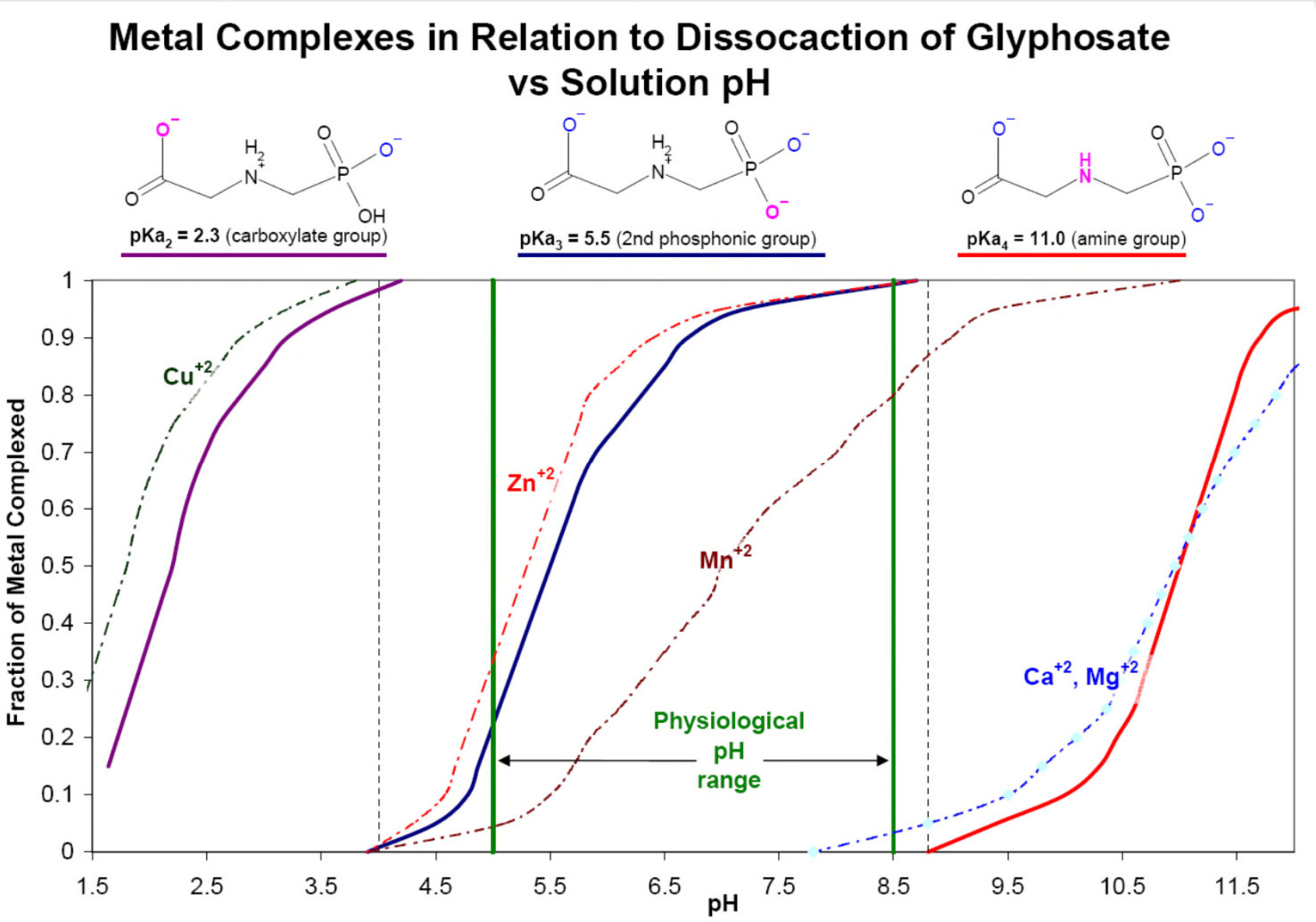
Glyphosate
Antagonized by Divalent Cations





Glyphosate – Solution Chemistry
Interactions between Cations and Glyphosate



Stability Constants

1:1 molar ratio
@ physiological pH

Cation	*($LogK_{m1}$)*
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***

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Foliar Micronutrients
Herbicide Safener – Stress Mitigation

Alfalfa - 2012
Pacific Northwest

- Butyrac / 2,4 DB
- Bromoxynil
- Nitrogen Based Surfactant
- 20 gal of water/acre

Safening affect observed with Brandt Smart Trio (Zinc and Manganese) @1 qt / acre

Foliar Micronutrients
Herbicide Safener – Stress Mitigation

Cotton - 2013
Virgina

Foliar Micronutrients
Herbicide Safener – Stress Mitigation

Sugarcane
Brazil

Gesapax (Ametrina) 3 litros/ Hectare
DMA (2-4D) 0,4 litros/ Hectare
Ancosar 720 (MSMA) 2,2 litros/ Hectare

Brandt Smart Trio® 2 liter/Ha
Gesapax (Ametrina) 3 litros/ Hectare
DMA (2-4D) 0,4 litros/ Hectare
Ancosar 720 (MSMA) 2,2 litros/ Hectare

Thank You

- Jar Test