Micronutrient Compatibility with Pesticides and NPK Fertilizers

Brian Haschemeyer
Director of Discovery and Innovation

BRANDT 60 YEARS

When you have a tank mix question or issue what do you do?

Google it

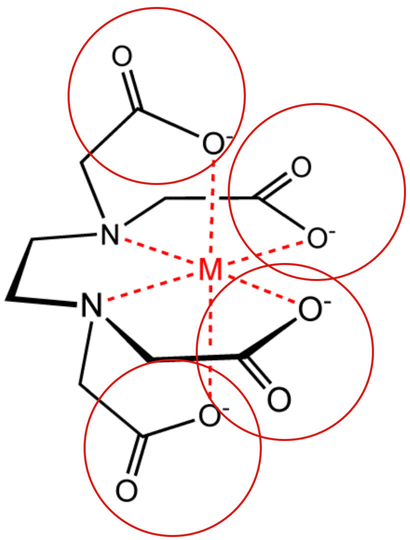
If its on the internet it must be fact

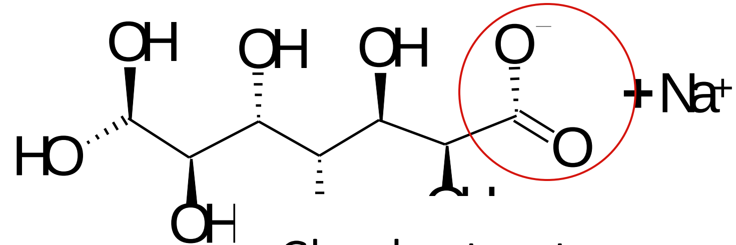
Call Trusted Advisor

I like to know Why and How
Who else likes to know why and how?

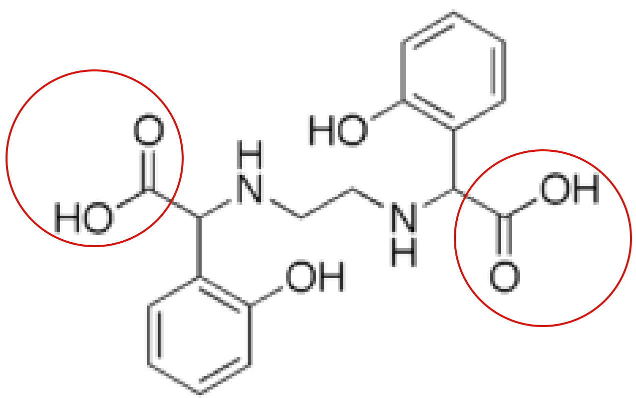
Name the Structure - Chelates
What do they have in common?

EDTA
chelating
metal

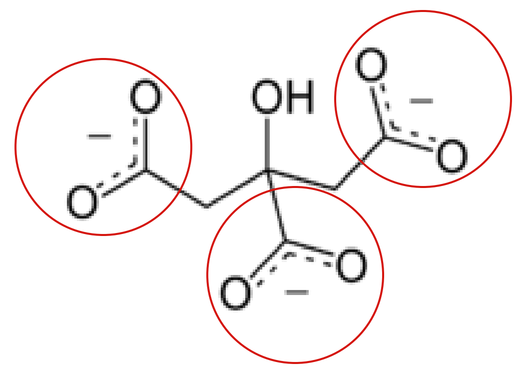




Glucoheptonate
complexing agent



EDDHA
chelating agent



Citric Acid
chelating agent

It Helps if Understand Ammonia Chemistry Basics

Yes – I as your presenter already know that most of you don't like chemistry and you didn't come here to sit through a chemistry class.

$$NH_4^{+} \rightleftharpoons :NH_3^{\delta-}$$

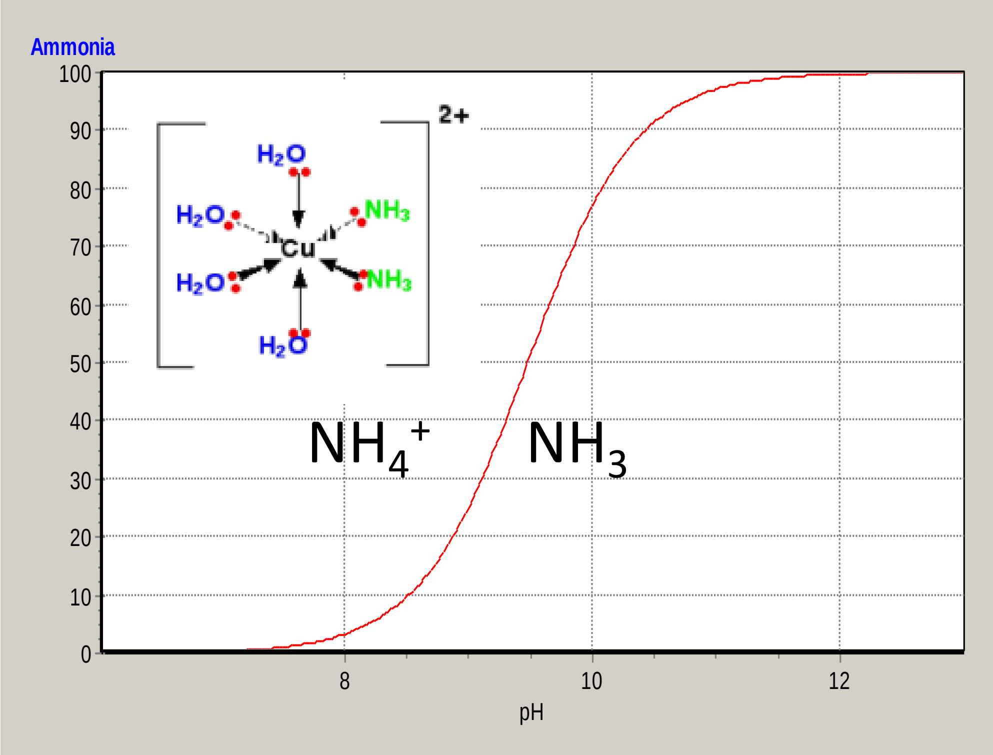
$$\downarrow$$

pH 9

Equilibrium point

Ammonia ($NH_3 \Leftrightarrow NH_4^+$)
pH and concentration dependent

Ammonium (NH4+) is deprotinated to ammonia (NH3) in alkaline conditions so solutions need to be sufficiently alkaline (pH's >9) to allow ammonia to complex metal. Common for use in polyphosphate solutions. Ammonium is often used to complex metals in conjunction with other organic acids such as citric acid.



Stepwise Formation Constants

ion	K_n	log K_n
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	4.25
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	3.61
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	2.98
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_4	2.24
$[Cu(NH_3)_4(H_2O)_2]^{2+}$	K_f	13.08

Equilibrium Reaction	Log K_f
$Cu^{2+} + 4NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$	13.0
$Zn^{2+} + 4NH_3 \leftrightarrow [Zn(NH_3)_4]^{2+}$	8.6

Take Away: Ammonia with Metals

Take away concepts:

1. At alkaline pHs above 9 ammonia has a partial negative charge and is volatile.

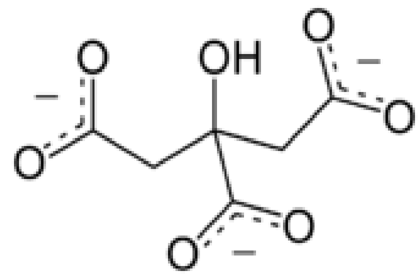
2. The negatively charged ammonia can coordinate with metals such as Zinc, Copper, etc.

3. It takes a high concentration of ammonia to metal to provide any significant amount protection to the metal

Citrates

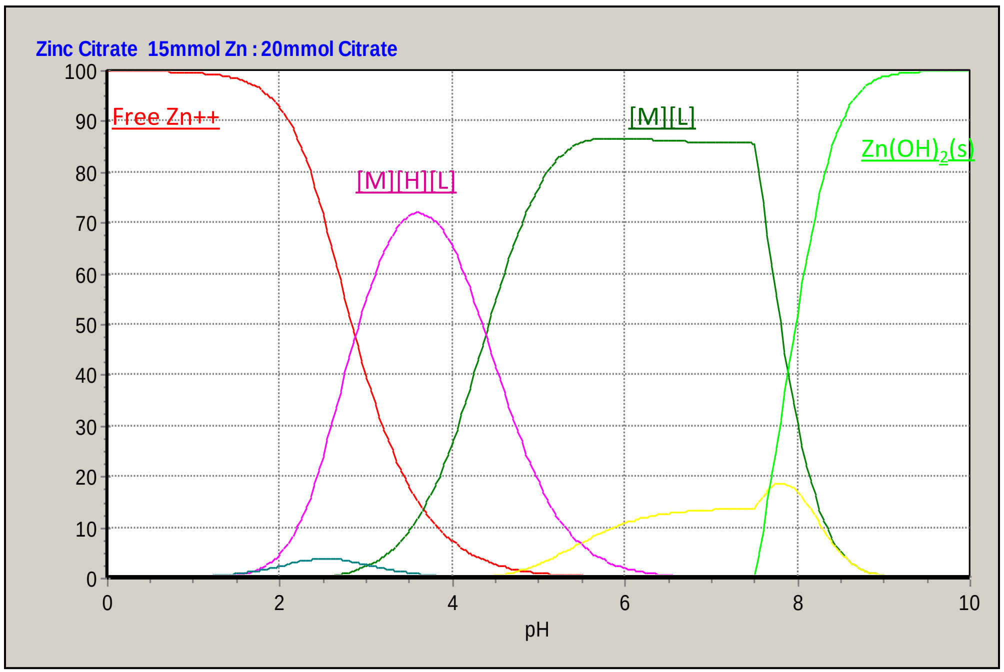
Ammoniated Citrates are Common for use with 10-34-0

Citric acid is natural biodegradable chelate. Because of its carboxyl groups, citric acid chelates / complexes metals in the acidic environment. Often used for formulation stability and foliar applications



Citrate

	pKa	Log Kf
pK_3	6.1	6.1
pK_2	4.6	10.7
pK_1	3.1	13.8



Stability Constants (Log K Values)[1]

CITRATE

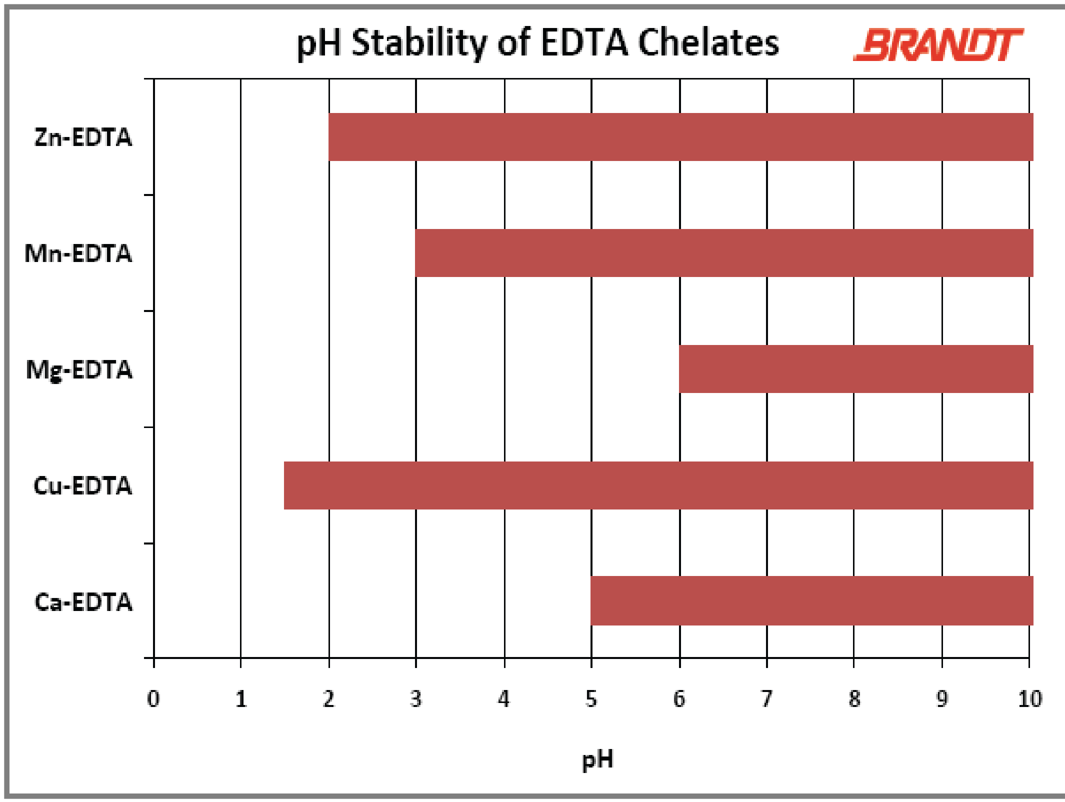
	[MHL]/[M][H][L]	[ML]/[M][L]
Al +3	11.8	8.1
Ca +2	7.6	3.4
Cu +2	9.5	6.7
Fe +2	8.7	4.5
Fe +3	12.4	11.2
Mg +2	7.2	3.2
Mn +2	7.1	3.7
Zn +2	8.7	5.0

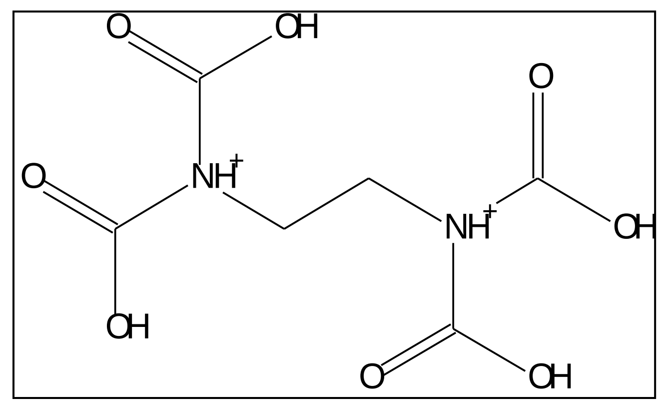
[1] R.M Smith; A.E. Martell, Crtical Stability Constants, Plenum Press, New York and London, 3rd Edition.

EDTA

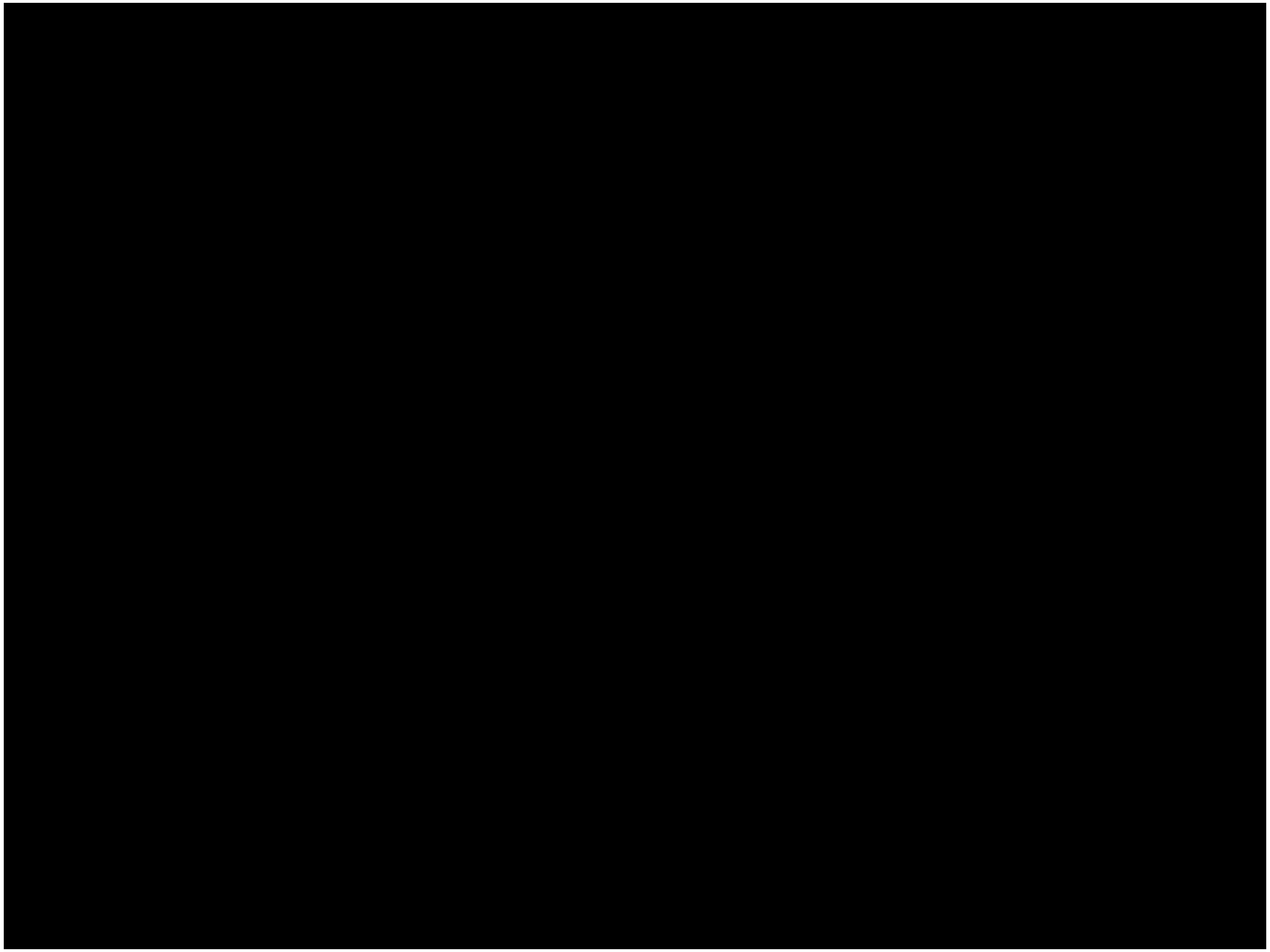
	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6
	0.0	1.5	2.0	2.66	6.16	10.24
	Log Kf = 24.06	Log Kf = 22.56	Log Kf = 21.06	Log Kf = 19.06	Log Kf = 16.4	Log Kf = 10.24

Ion	[M][H][L]	[M][L]
Al +3	20.7	18.0
Ca +2	15.0	11.6
Cu +2	22.9	19.7
Fe +2	18.2	15.3
Fe +3	28.0	26.5
Mg +2	19.9	9.8
Mn +2	18.2	14.8
Zn +2	10.7	17.5

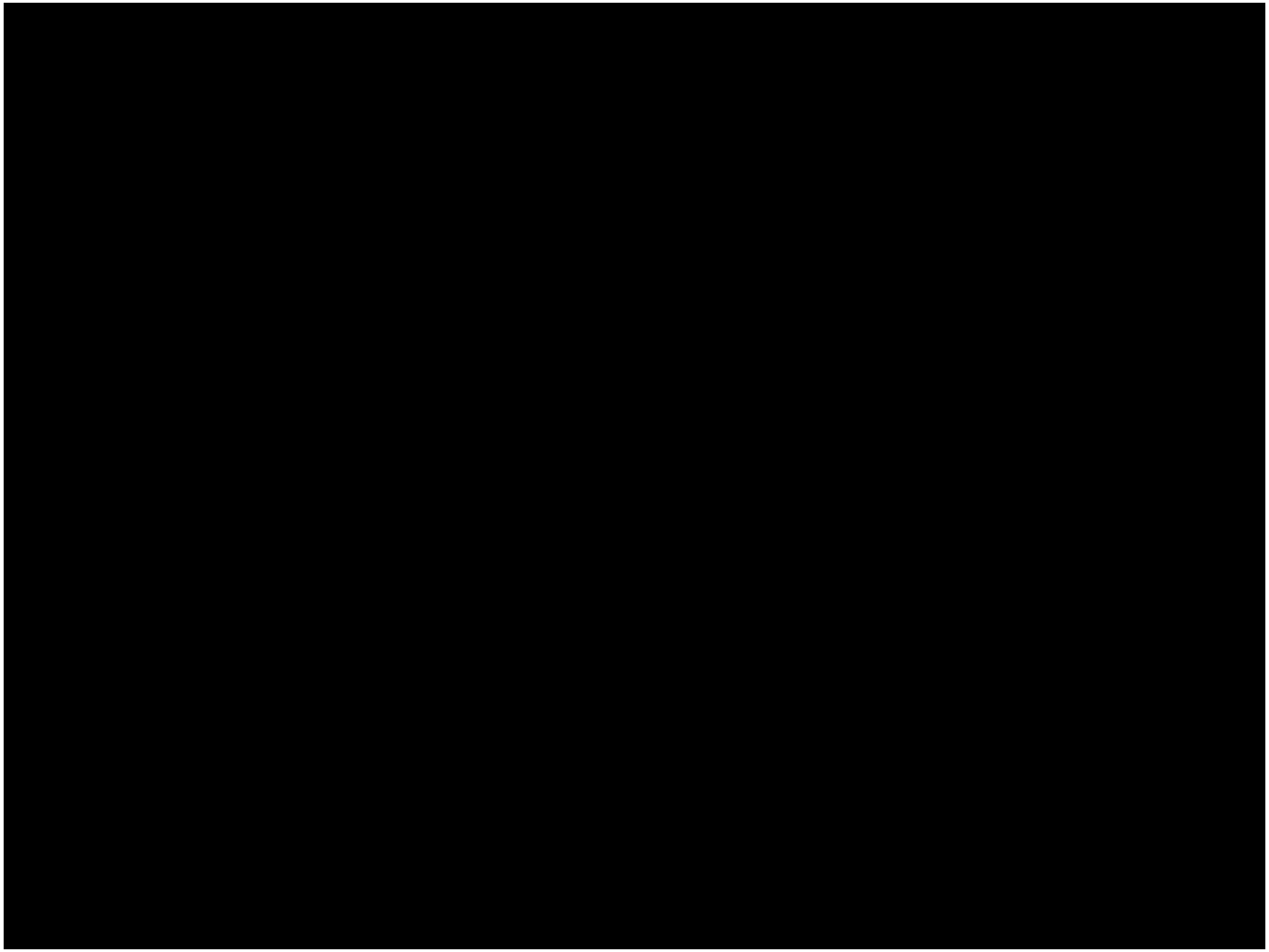




Water



Water



Take Away: Ammonia with Metals

Take away concepts:

1. At alkaline pHs above 9 ammonia has a partial negative charge and is volatile. Below pH 9 they have a positive charge and are not coordinating with metal
2. The negatively charged ammonia can coordinate with metals such as Zinc, Copper, etc.
3. It takes a high concentration of ammonia to metal to provide any significant amount protection to the metal
4. Ammoniated metals fail when diluted in water

Take Away: Zinc Citrates

1. Sufficiently strong enough to be mixed with water

Take Away: Zinc EDTA

1. Strong enough to be mixed with water

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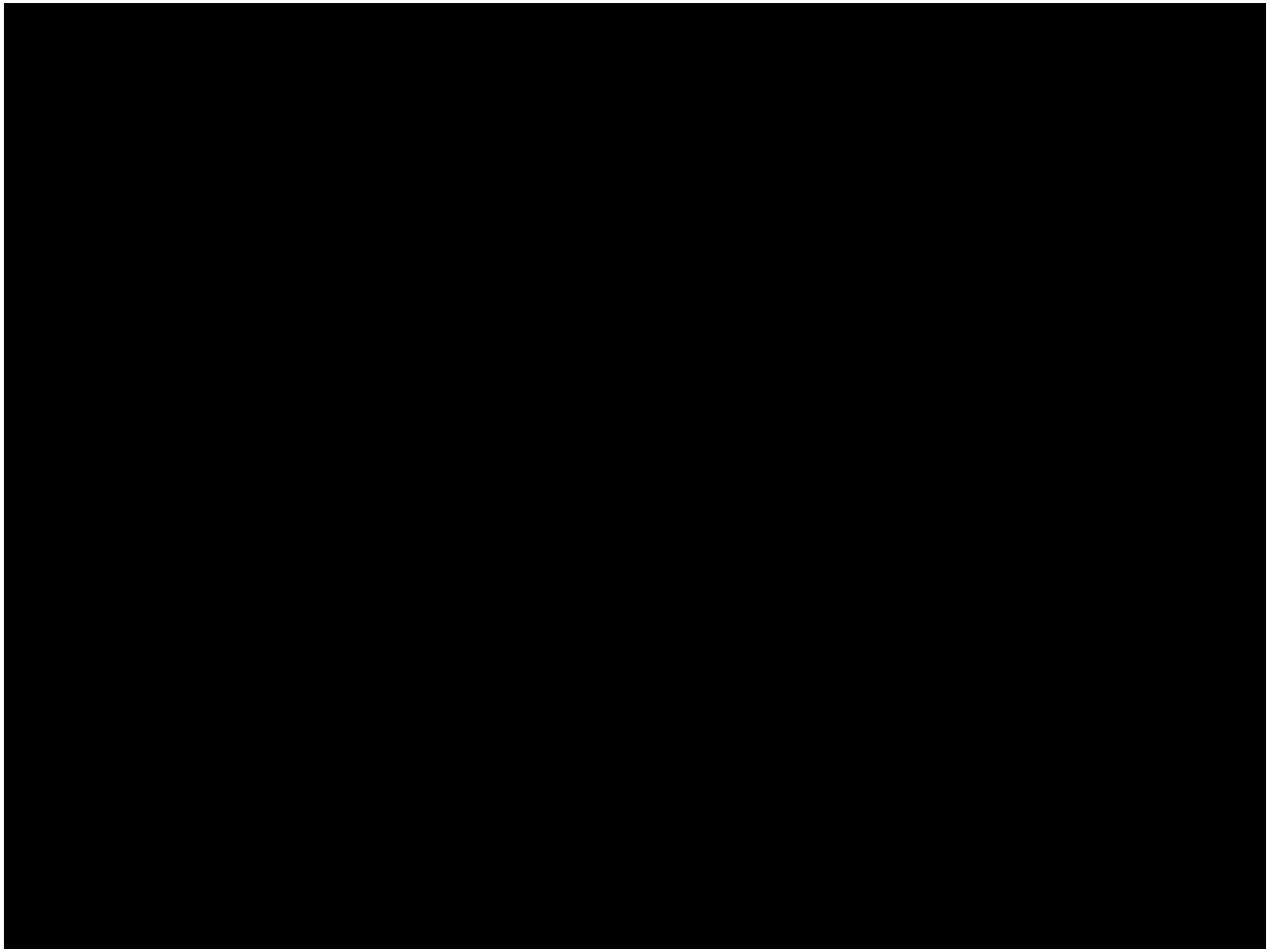
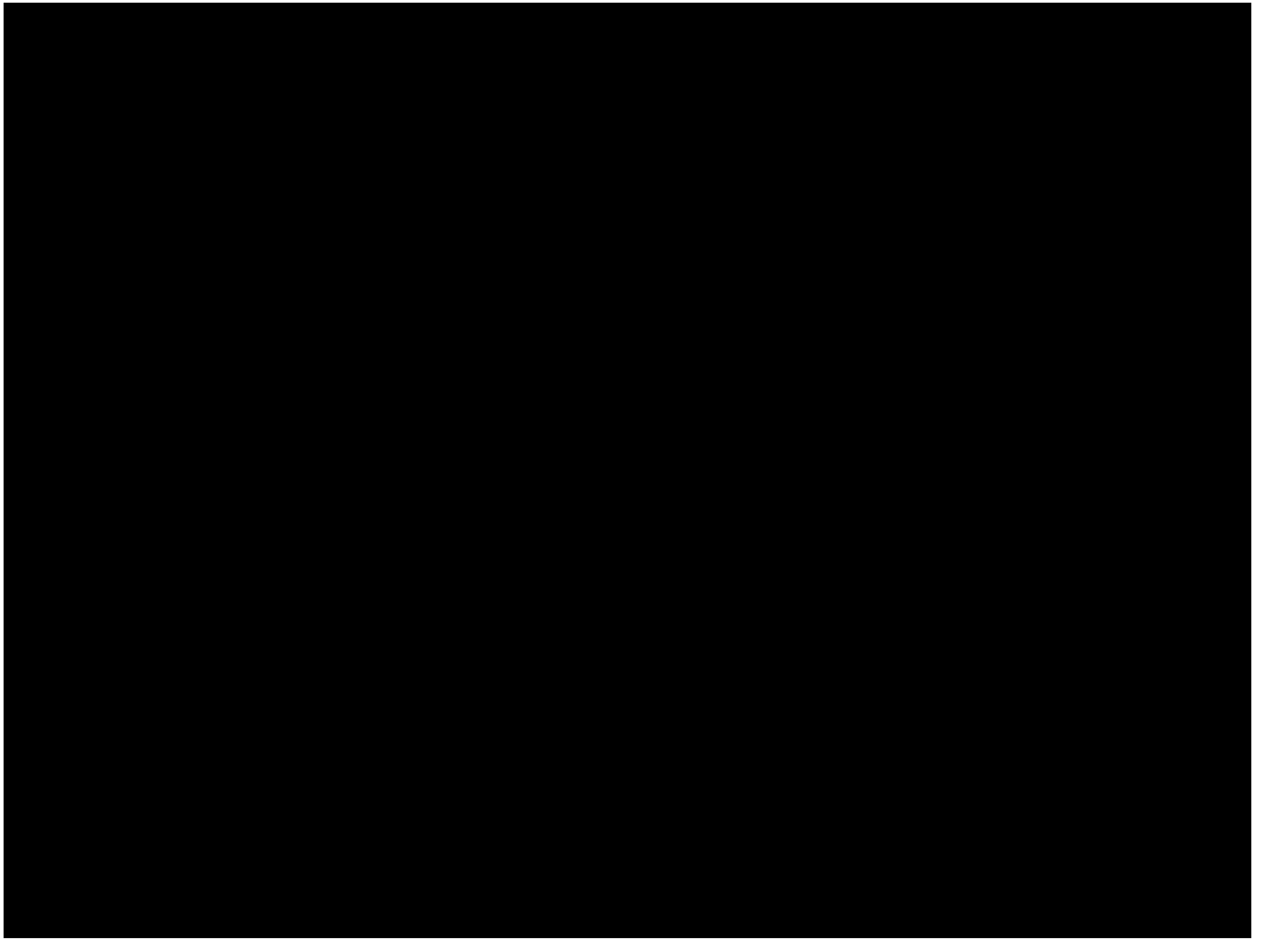
10-34-0



10-34-0



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5. Ammoniated Zinc should not be mixed and stored with 10-34-0 for long periods of time

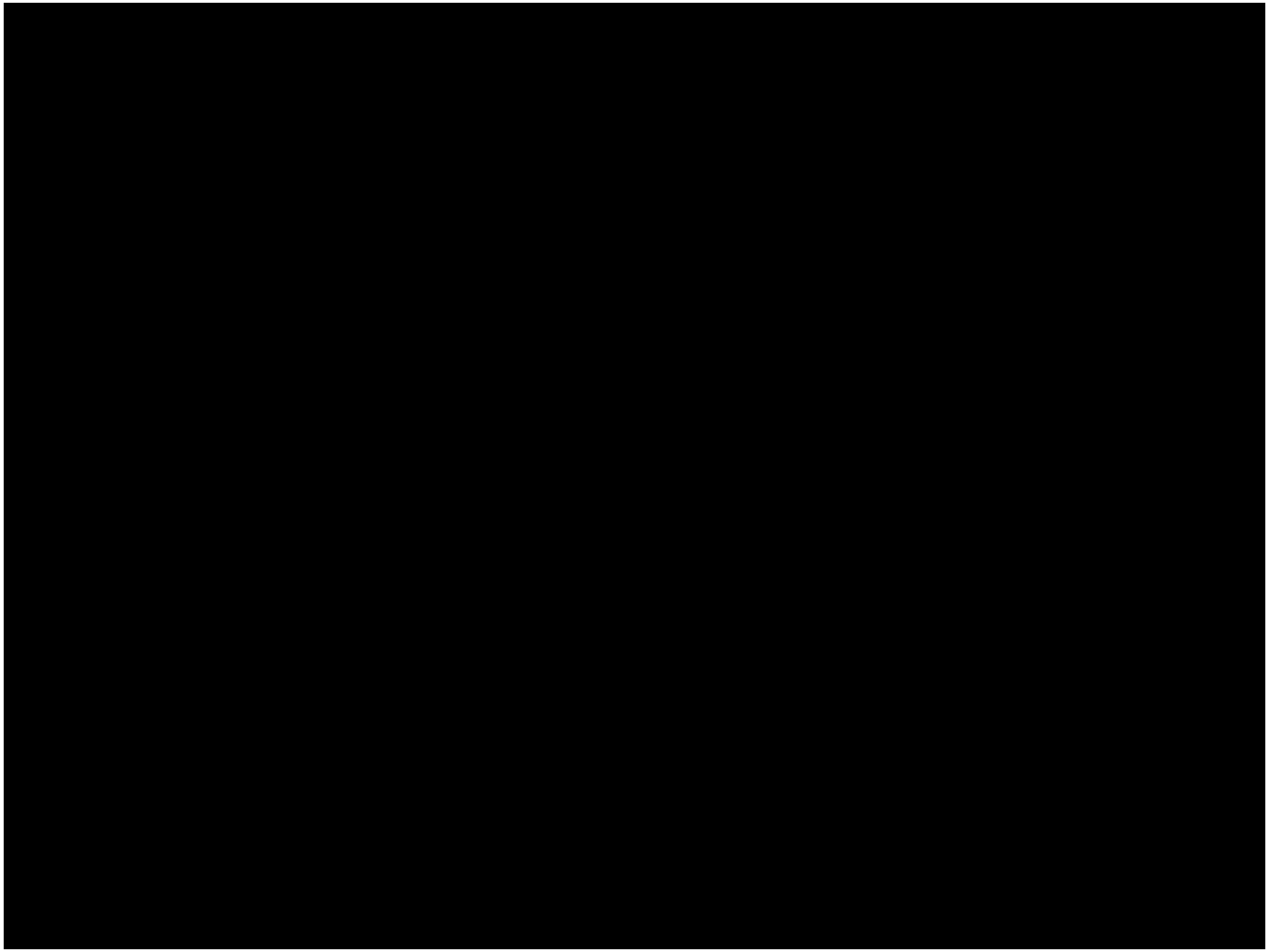
Take Away: Zinc Citrates

1. Sufficiently strong enough to be mixed with water
2. Sufficiently strong enough to be mixed with 10-34-0

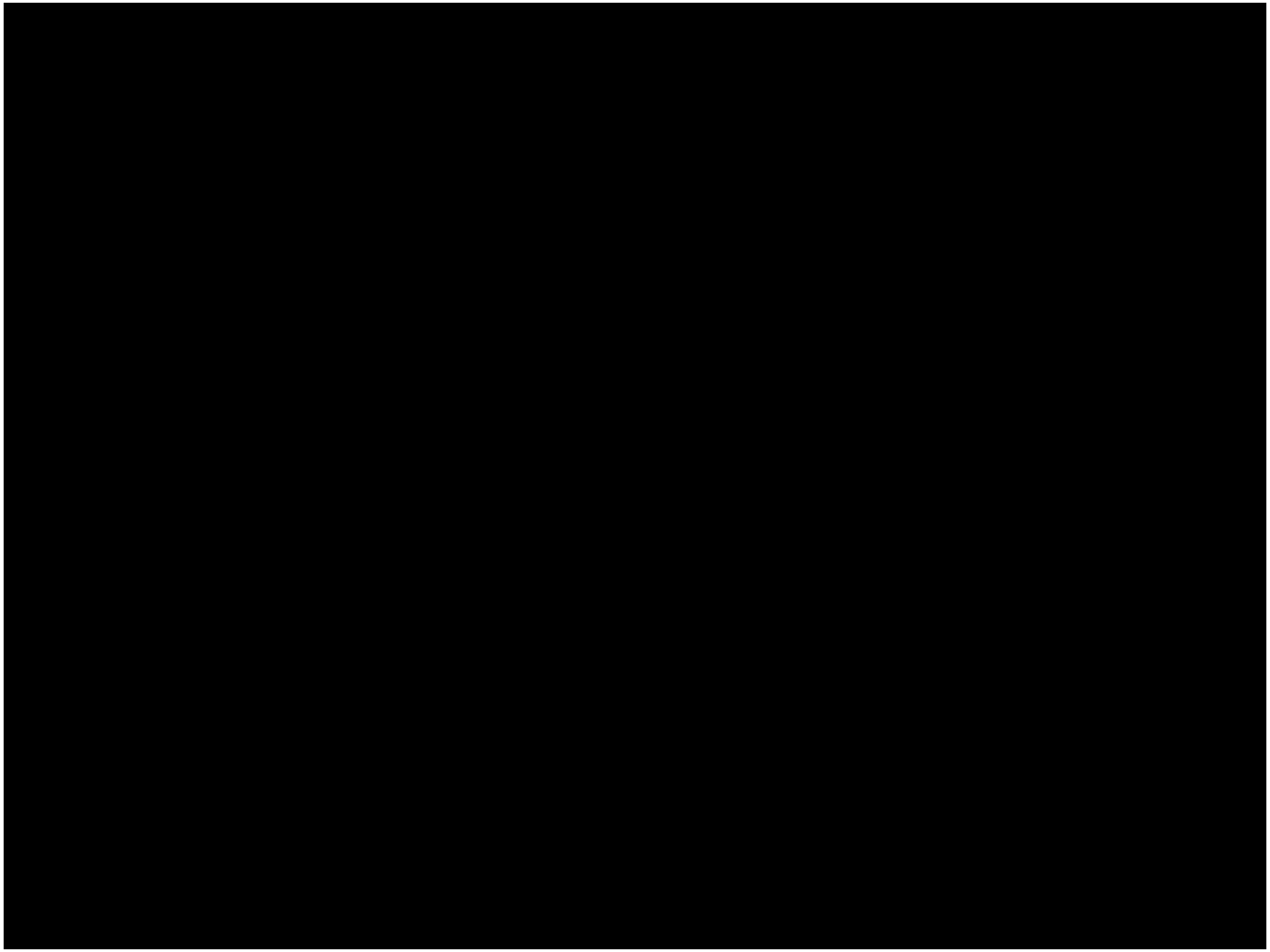
Take Away: Zinc EDTA

1. Strong enough to be mixed with water
2. Strong enough to be mixed with 10-34-0

3-18-18



3-18-18



Take Away: Ammonia with Metals

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3. It takes a high concentration of ammonia to metal to provide any significant amount protection to the metal

4. Ammoniated metals fail when diluted in water

5. Ammoniated Zinc should not be mixed and stored with 10-34-0 for long periods of time

6. Ammoniated Zinc fail in the ortho-phosphate solutions

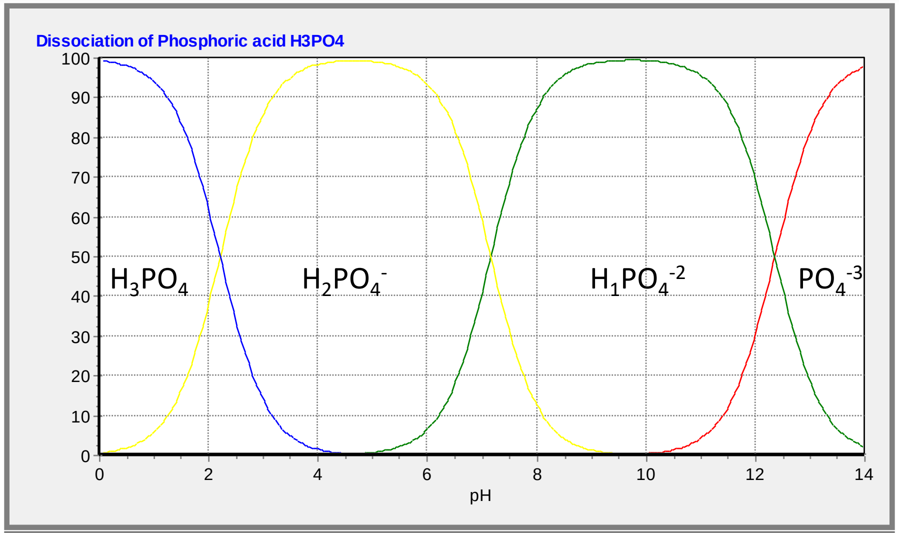
Take Away: Zinc Citrates

1. Sufficiently strong enough to be mixed with water
2. Sufficiently strong enough to be mixed with 10-34-0
3. Not strong enough to be mixed with ortho-phosphates. Reactions are not always immediate

Take Away: Zinc EDTA

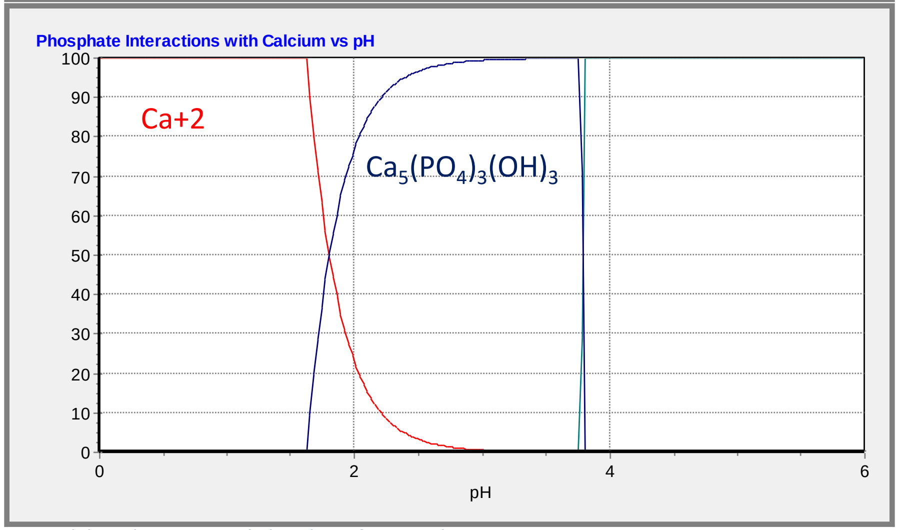
1. Strong enough to be mixed with water
2. Strong enough to be mixed with 10-34-0
3. Strong enough to be mixed with ortho-phosphates.

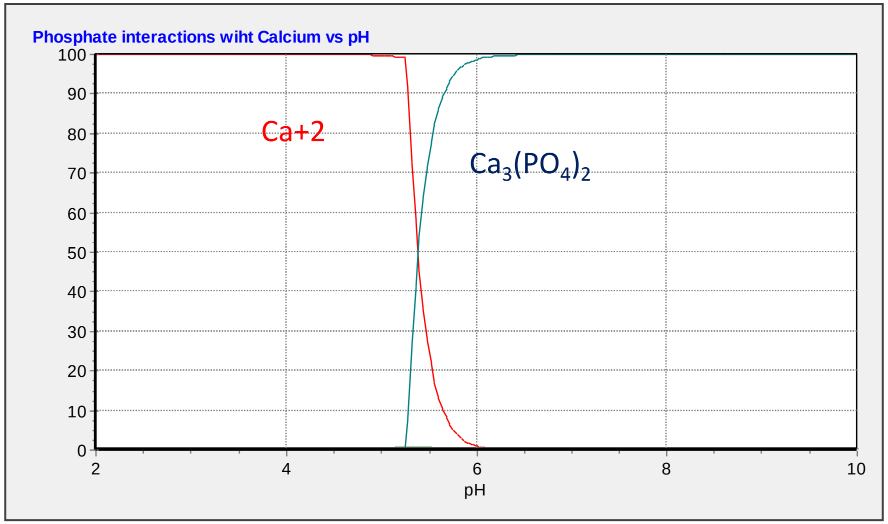
Phosphate Interactions
pH Dependence of Phosphate Binding



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	$Ca_3(PO_4)_2$	$1x10^{-26}$
	$Ca_2(PO_4)_2(OH)_2$	$1x10^{-27}$
	$Ca_5(PO_4)_3(OH)_3$	$1x10^{-57}$

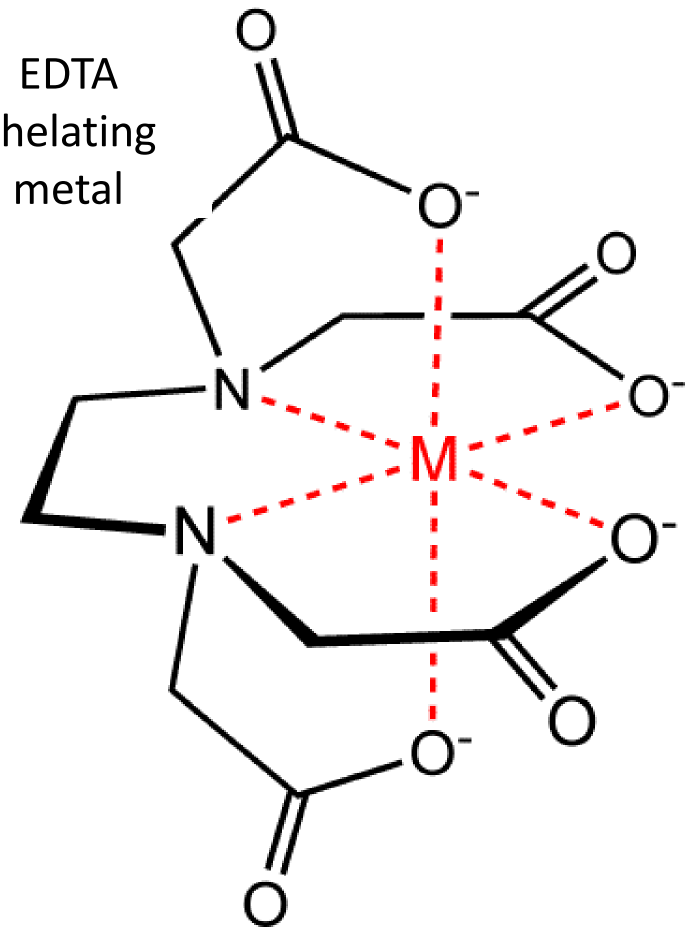




Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations
Graph based on 200mmol phosphate & 20mmol Ca+2 concentrations

EDTA Chelates – Efficiency Factors

EDTA chelating metal

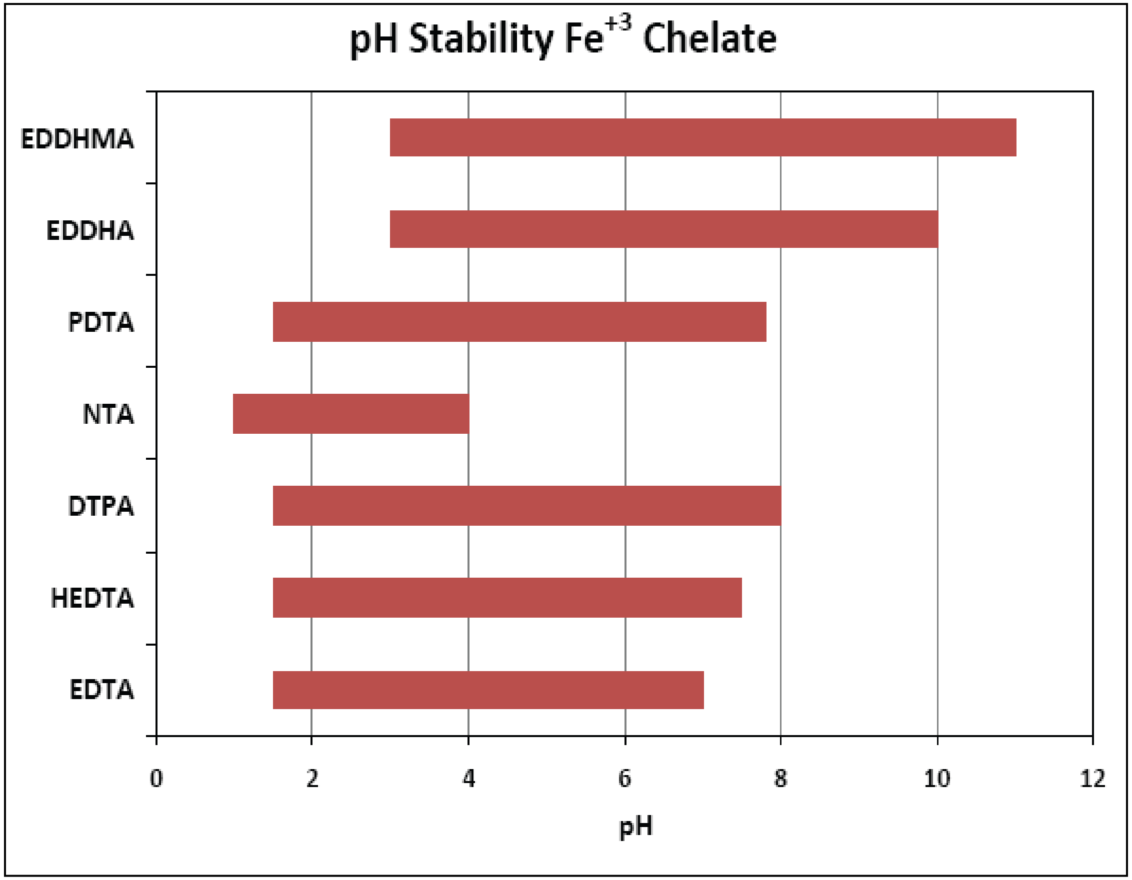


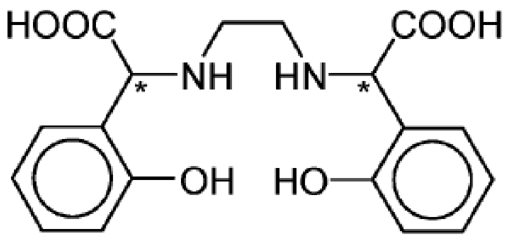
- EDTA chelates can with stand the harsh conditions of the soil
- Efficiency Ratios reported in literature vary depending on soil conditions and can go above 6x in harsh conditions
  - Zinc EDTA treatments had concentrations 5 times higher than other zinc treatments (Gangloff, 2004)
  - Up to 5x Zinc EDTA efficiency ratios over other sources (Alloway, 2004)
  - Zn EDTA increased zinc content of the crop twice as much as zinc sulfate in neutral solutions and up to 6 times as much in calcareous soil (Holden, Brown, 1965)
- Ideal for Liquid Starter Fertilizers
- Compatible with most all types of NPK solutions including orthophosphates and alkaline solutions

Brandt Sequestar Fe - EDDHA

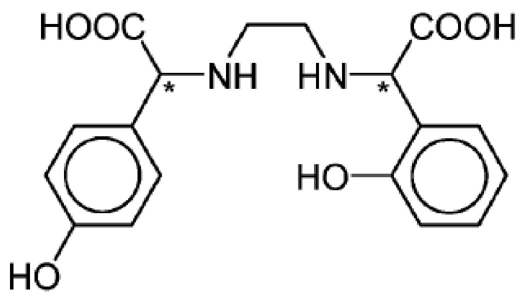
For alkaline conditions

A high-performance chelating agent used in Agriculture particularly with iron in alkaline soil conditions.





1 o,o-EDDHA



2 o,p-EDDHA

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Brandt Sequestar Fe   EDDHA

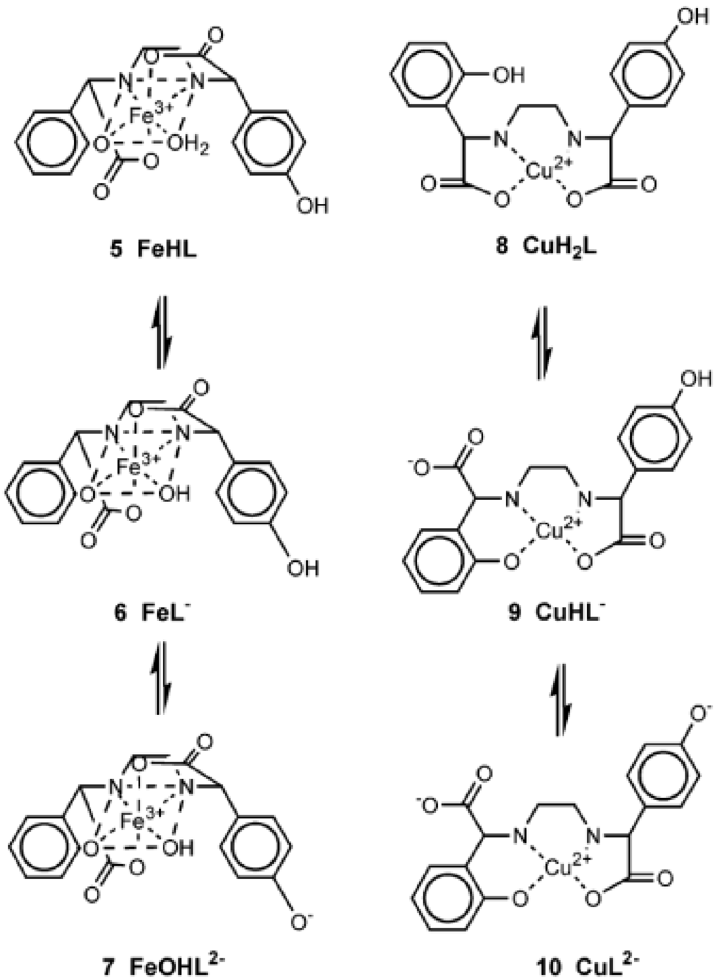


Figure 3. *o,p*-EDDHA/Fe^{3+} and *o,p*-EDDHA/Cu^{2+} species formed.

Table 1. log Protonation and log Ca^{2+} and Mg^{2+} Stability Constants[a] with *o,o*-EDDHA, *o,p*-EDDHA, and *p,p*-EDDHA

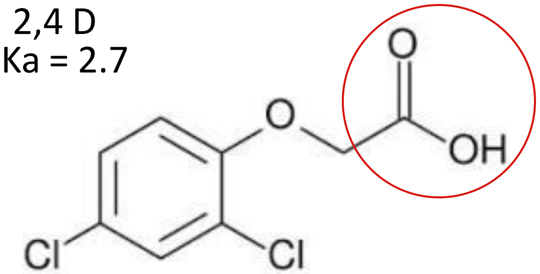
quotient	*o,p*-EDDHA	*o,o*-EDDHA[b]	*p,p*-EDDHA[b]
$[LH^{3-}]/[H^+][L^{4-}] \Longrightarrow K_1^H$	11.18	11.94	9.94 ± 0.04
$[LH_2^{2-}]/[H^+][LH^{3-}] \Longrightarrow K_2^H$	10.18 ± 0.04	10.73	9.07 ± 0.02
$[LH_3^{-}]/[H^+][LH_2^{2-}] \Longrightarrow K_3^H$	8.65 ± 0.05	8.66 ± 0.04	6.85 ± 0.06
$[LH_4]/[H^+][LH_3^{-}] \Longrightarrow K_4^H$	6.19 ± 0.02	6.18 ± 0.06	4.36 ± 0.07
$[LH_5^+]/[H^+][LH_4] \Longrightarrow K_5^H$	2.57 ± 0.02		
$[LH_6^{2+}]/[H^+][LH_5^+] \Longrightarrow K_6^H$	1.49 ± 0.07		
$[CaL^{2-}]/[Ca^{2+}][L^{4-}]$	4.12 ± 0.10	7.29 ± 0.30	3.54 ± 0.52
$[CaLH^{-}]/[Ca^{2+}][H^+][L^{4-}]$	14.27 ± 0.16	16.77 ± 0.33	12.93 ± 0.58
$[CaLH_2]/[Ca^{2+}][H^+]^2[L^{4-}]$	23.23 ± 0.32	25.95 ± 0.50	21.21 ± 0.65
$[MgL^{2-}]/[Mg^{2+}][L^{4-}]$	5.64 ± 0.16	9.76 ± 0.05	3.74 ± 0.57
$[MgLH^{-}]/[Mg^{2+}][H^+][L^{4-}]$	15.55 ± 0.03	18.18 ± 0.15	12.89 ± 0.39
$[MgLH_2]/[Mg^{2+}][H^+]^2[L^{4-}]$	23.83 ± 0.32	25.36 ± 0.24	20.79 ± 0.57
$[FeL^{-}]/[Fe^{3+}][L^{4-}]$	28.72 ± 0.05	35.09 ± 0.28	
$[FeHL]/[Fe^{3+}][L^{4-}][H^+]$	35.02 ± 0.05	36.89 ± 0.21	
$[FeH_2L^+]/[Fe^{3+}][L^{4-}][H^+]^2$	37.35 ± 0.10		
$[FeOHL^{2-}]/[Fe^{3+}][L^{4-}][OH^-]$	19.45 ± 0.19	23.66 ± 0.27	
$[CuL^{2-}]/[Cu^{2+}][L^{4-}]$	21.74 ± 0.38	25.13 ± 0.00	14.74 ± 0.06
$[CuHL^{-}]/[Cu^{2+}][L^{4-}][H^+]$	30.96 ± 0.09	32.61 ± 0.01	22.39 ± 0.06
$[CuH_2L]/[Cu^{2+}][L^{4-}][H^+]^2$	36.17 ± 0.12	37.31 ± 0.01	28.50 ± 0.04
$[CuH_3L^+]/[Cu^{2+}][L^{4-}][H^+]^3$	38.14 ± 0.07		31.09 ± 0.04

[a] μ = 0.1 M (NaCl); t = 25 °C. [b] Reference *14*.

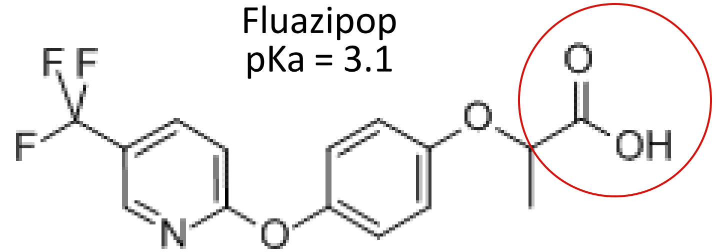
Phenoxy Herbicides
Do you recognize any functional groups?

Carboxyl groups

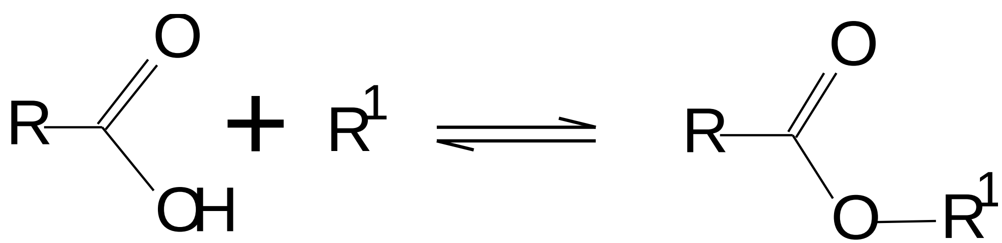
2,4 D
pKa = 2.7

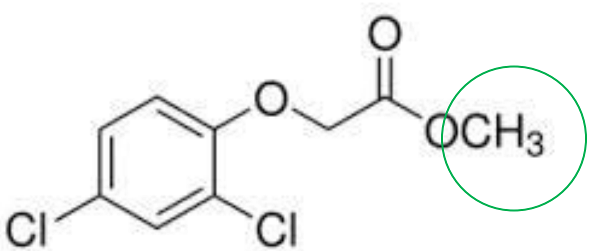


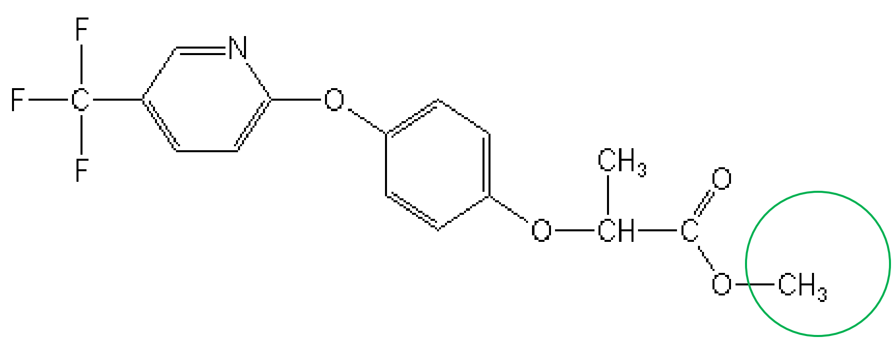
Fluazipop
pKa = 3.1



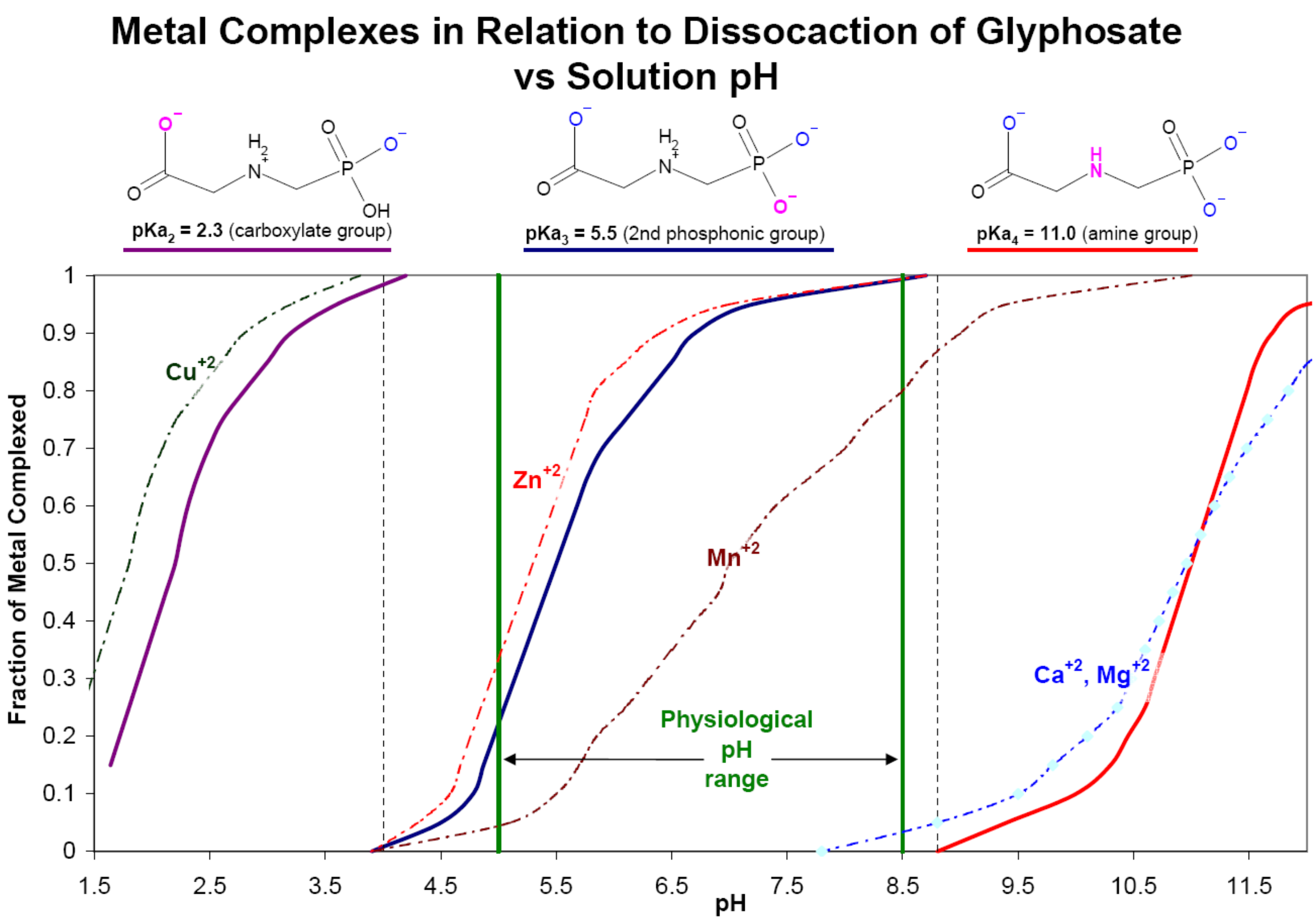
What about the ester formulation?







Glyphosate – Solution Chemistry
Interactions between Cations and Glyphosate

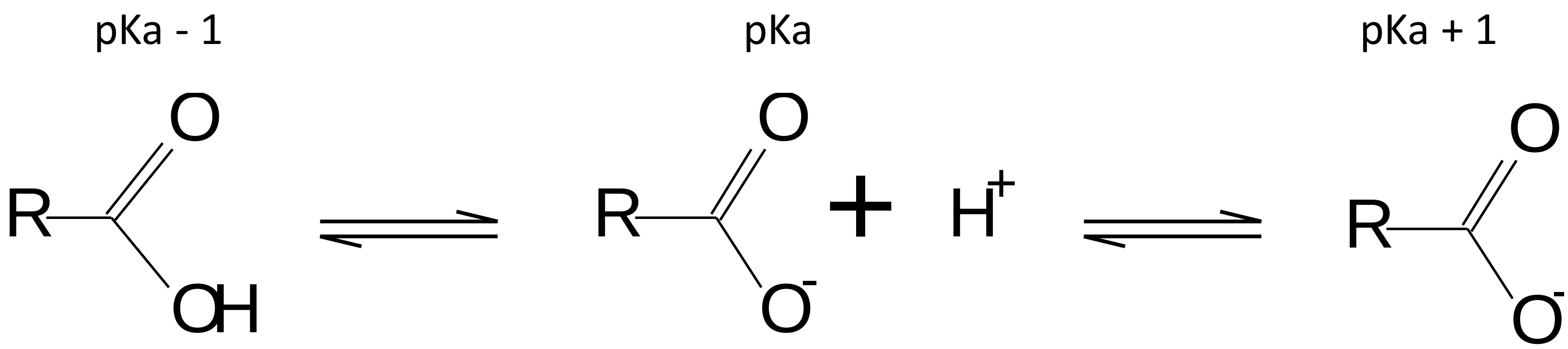


Stability Constants

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**

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

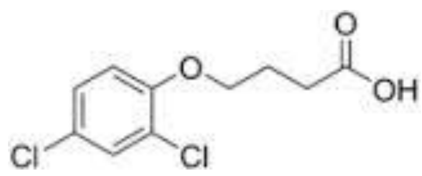
pKa + 1 is the pH value where the carboxyl groups has a negative charge 100% of the time

Phenoxy herbicides
Contain carboxyl groups

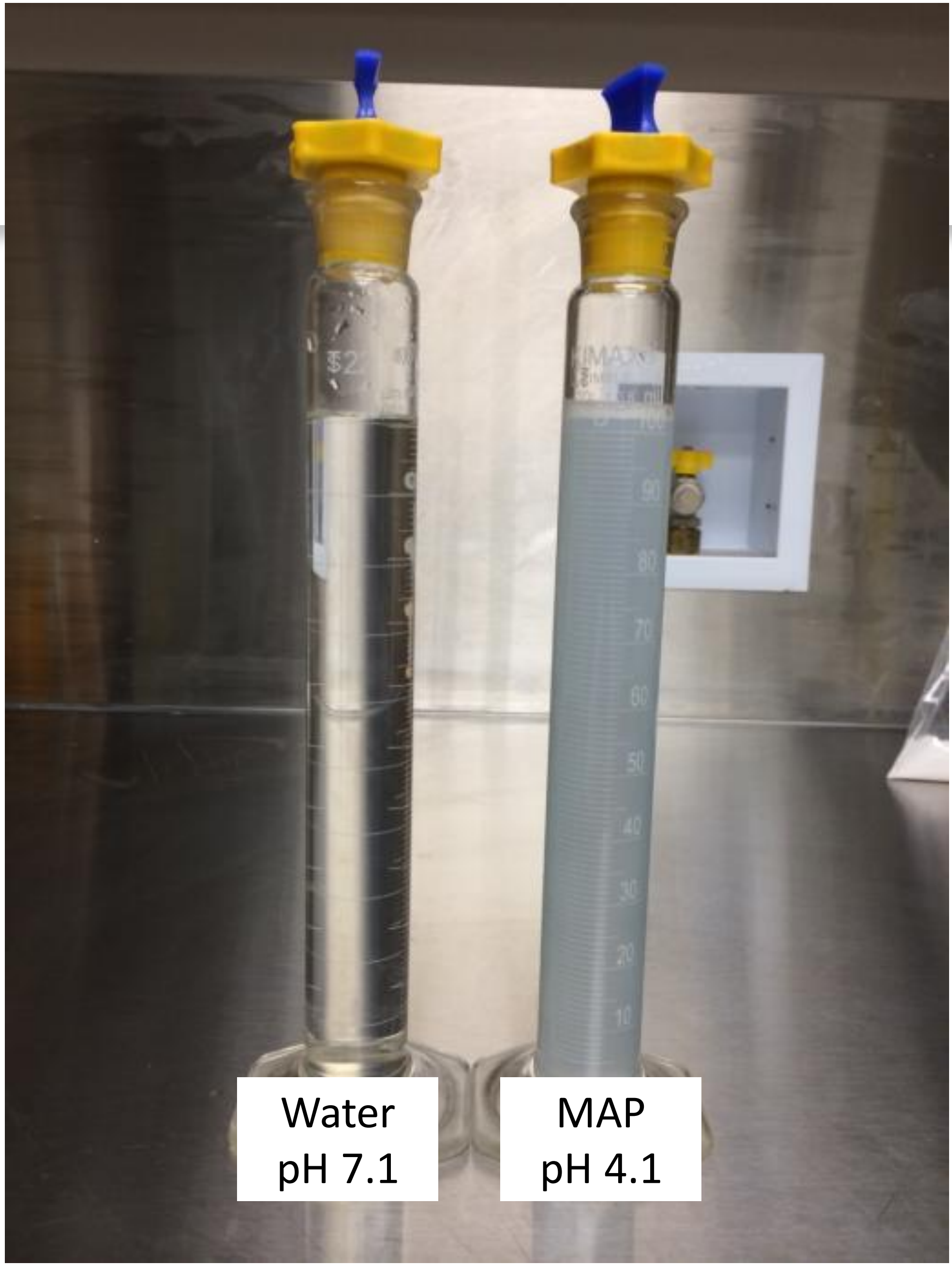
Active Salt / Ester	pKa	pka + 1	Formulation Type	Chemical Class	acid structure	Water Solubility Notes
2,4-D	2.7	3.7	SL	phenoxy acid	R_1-COOH	Acid and ester forms are sparingly soluble, the salts have high solubility. Formulated as both a water salt and oil soluble ester
2,4-DB	4.8	5.8	SL	phenoxy acid	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



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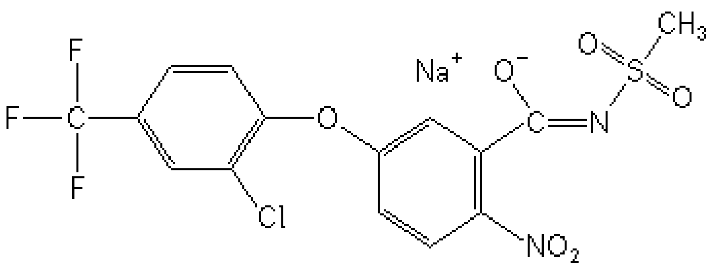
pH precipitation soluble liquid herbicide

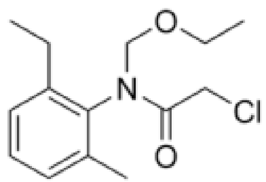
- Reflex Herbicide
- Active: Sodium Fomesafen



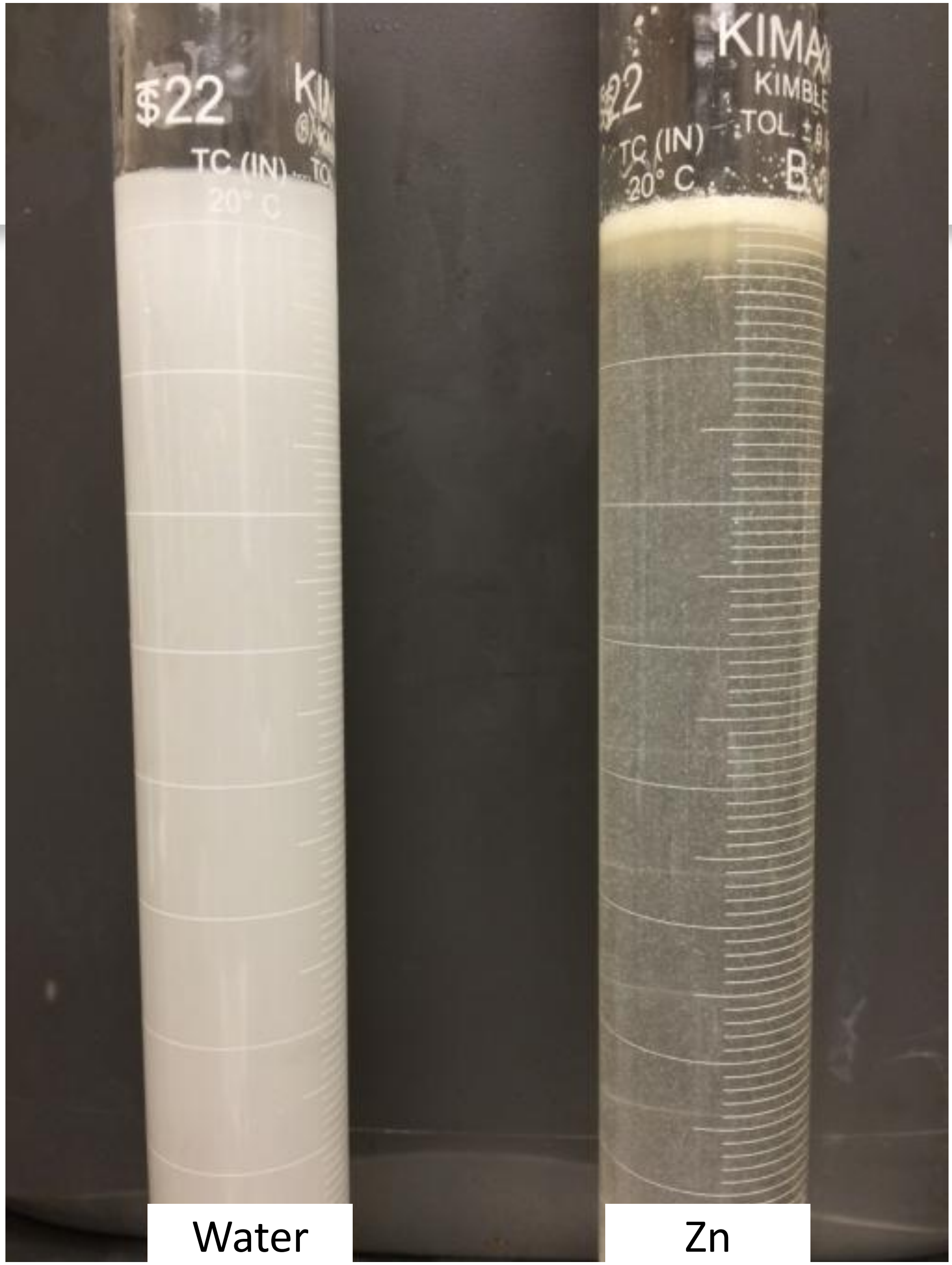
- SL Formulation
- pKa = 3.8
- Acid form is sparingly soluble, the salts have high solubility. Typically sold as a sodium salt

Suspension concentrate failure in presence of divalent cations

- Warrant Herbicide
- Active: Acetochlor

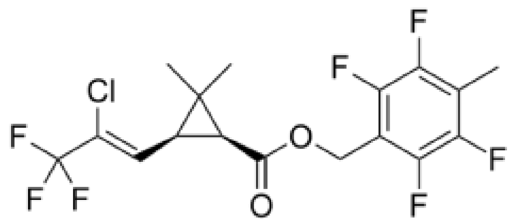


- SC Formulation
- Anionic dispersant fails do to binding divalent cations binding to the negative charged sites of the dispersant.

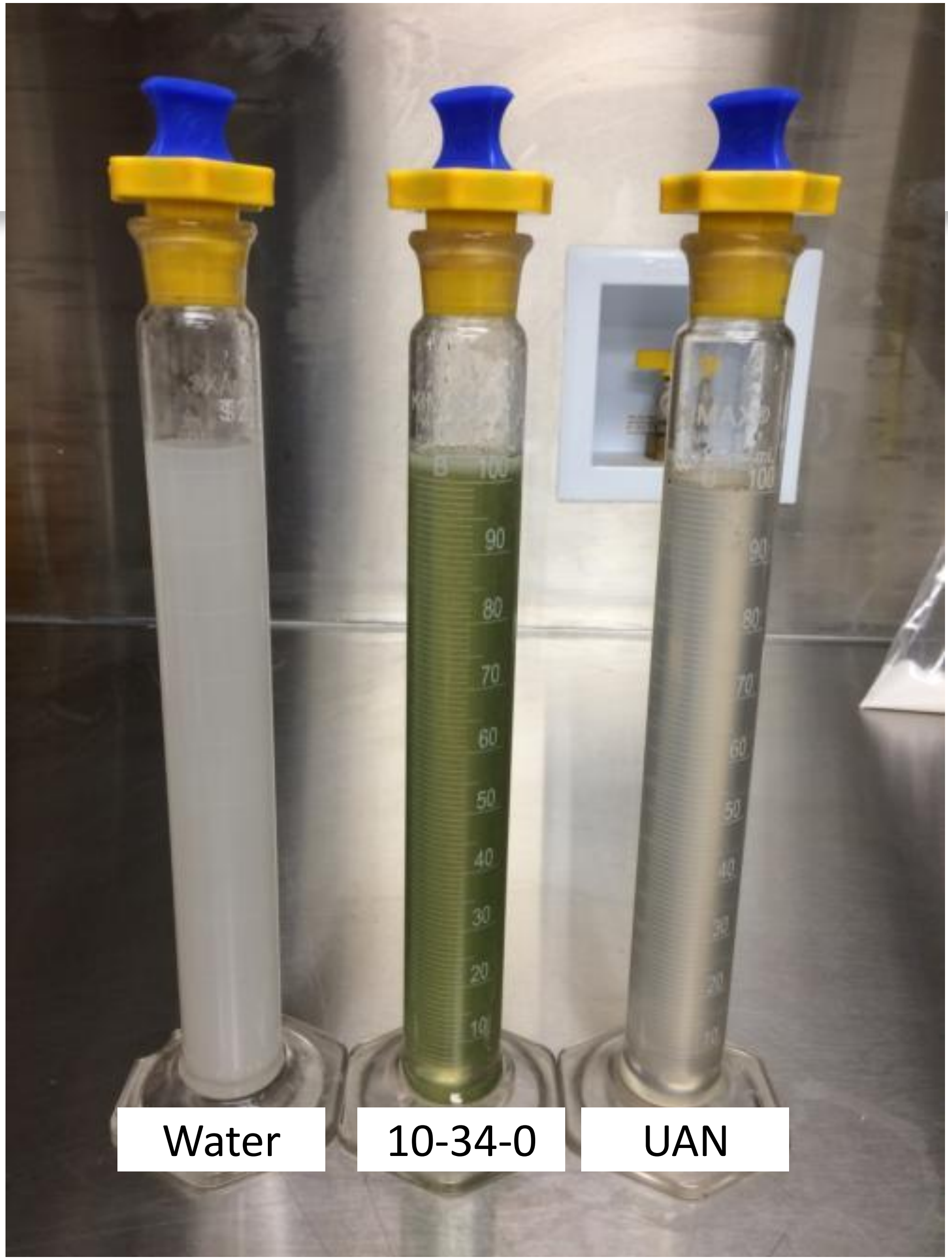


Suspension Concentrate failure in 10-34-0

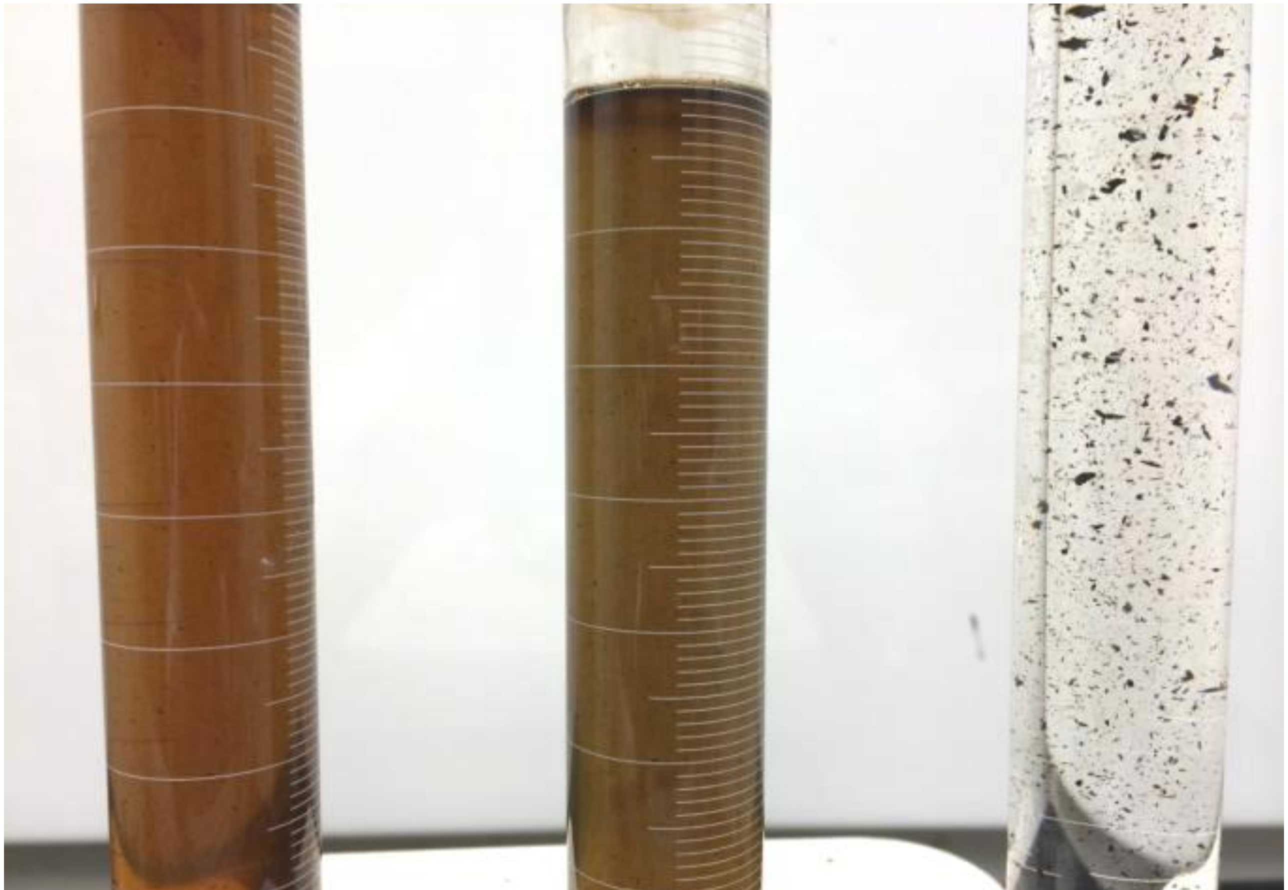
- Force Insecticide
- Active: Tefluthrin



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



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.

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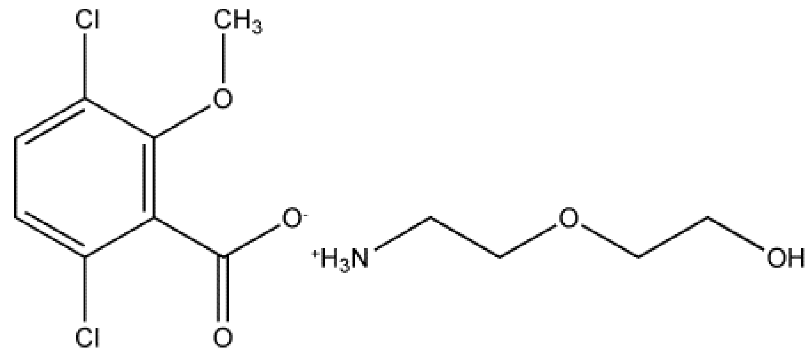
Counter Ion Affects Volatility of Dicamba
Ammonium can increase volatility

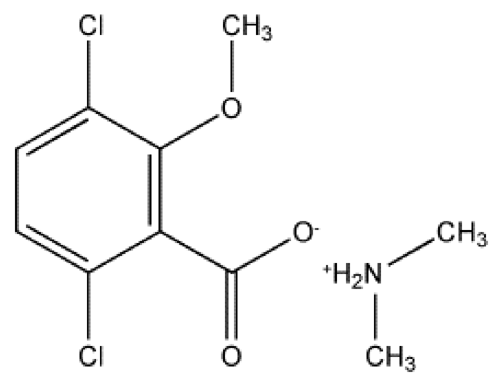
- Be caution of adding ammonium containing liquid fertilizers with Dicamba

NH_4^+

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

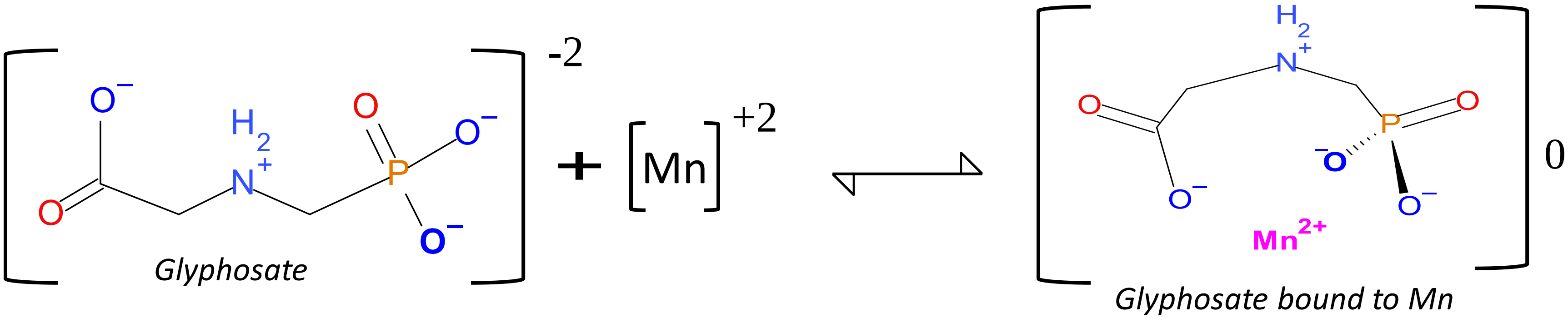


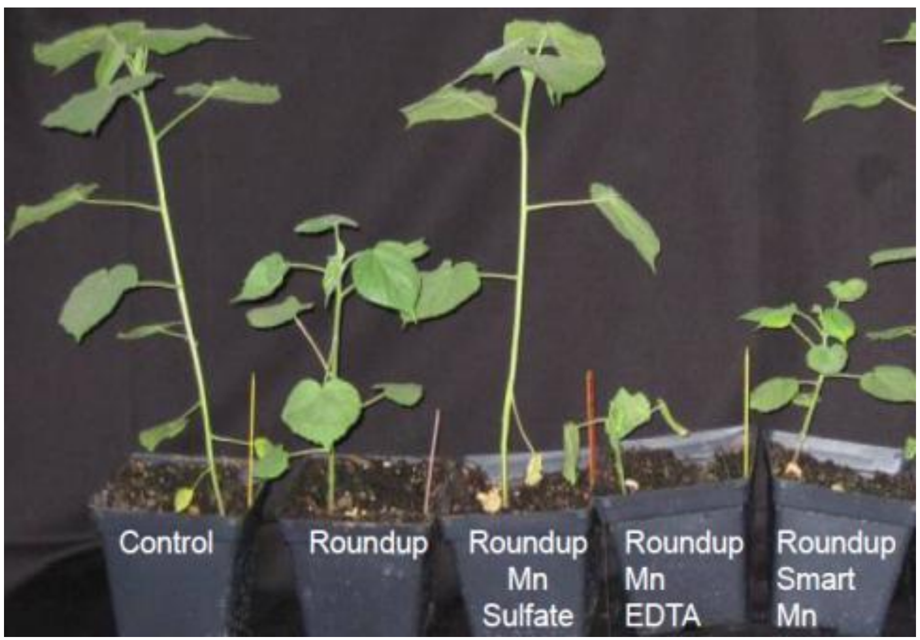
Dicamba, Diglycolomine salt



Dicamba, Dimethylamine salt

Glyphosate
Antagonized by Divalent Cations





Thank You

BRANDT 60 YEARS