



Understanding The Impact Of Water On Glyphosate Effectiveness

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Outline



No-Till

Structures of Several Herbicides

Problems with Glyphosate

Freshmen Chemistry Solubility Rules

Rate of Glyphosate Consumption

Typical Set up for Spray Supply Sources

A Better Approach to Managing Water

Going Beyond Ammonium Sulfate



No-Till



A way of growing crops year to year with minimal to no disturbance of soil.

The minimal soil disturbance has numerous advantages

Removal of unwanted vegetation is a launching point for the no-till practice

Herbicides accomplish this but over the past few years, we have seen resistance of weeds to particular herbicides



Why Do We Use Herbicides?



Increased Yield

Increased Profit

Rapid Response

More Effective vegetation removal when compared to manual removal

You Don't Have to Break Your Back Killing Weeds

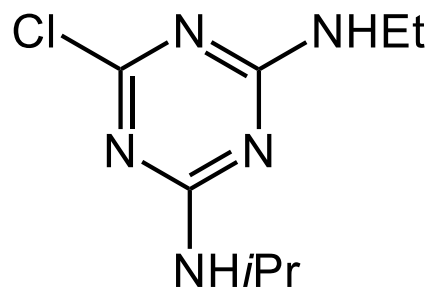
Herbicides kill the plant, tillage can leave plants intact and viable.



Example Molecules (herbicides)

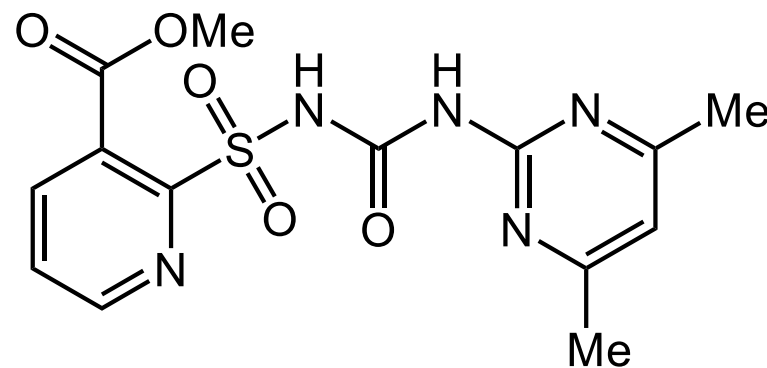


- 1,3,5-Triazines



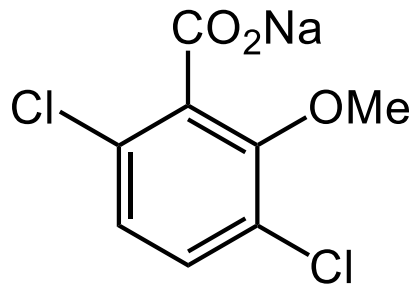
Atrazine

- Sulfonylureas



Sulfometuron Methyl

- Benzoic Acids



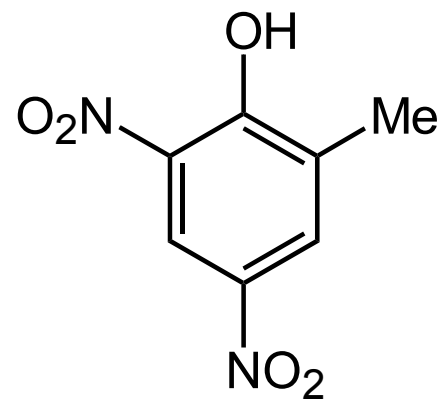
Dicamba



Example Molecules (herbicides)

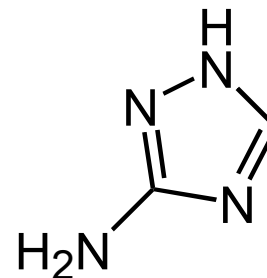


- Dinitrophenols



DNOC

- Triazols



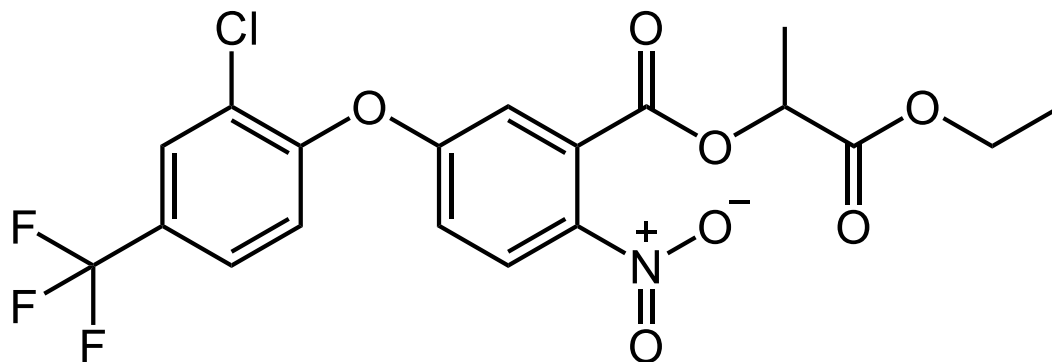
Amitrole



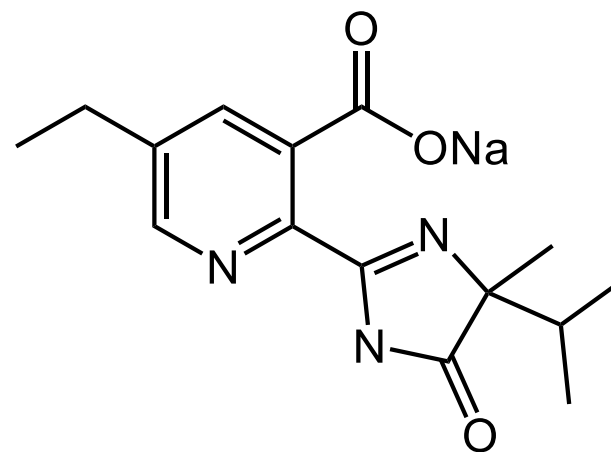
Example Molecules (Herbicides)



- Classic (LACTOFEN)



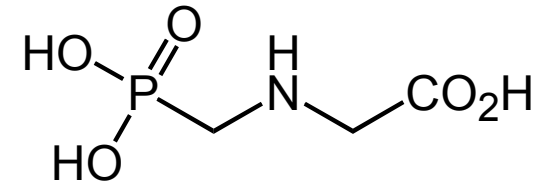
- Pursuit (Imazapyr)



Round Up[®]



- Round Up[®]
- Glyphosate
- Broad spectrum burn down herbicide
- Genetic modification of plants has lead to glyphosate resistance
- #1 herbicide



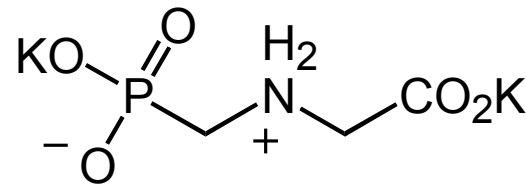
Glyphosate



What is the problem with Glyphosate



- Being number 1 has caused it be the go to herbicide
 - “I use glyphosate every pass over the field”
 - “if glyphosate wont kill it, I don’t know what I’ll do”
- Several plants are becoming resistant



Glyphosate



Glyphosate Resistant Plants



- Maretail
- Pigweed
- Waterhemp
- Whats next?
 - Johnson grass?
 - Cocklebur?
 - Ragweed?



Glyphosate Mode of Action



- Glyphosate is a Metal attractor
 - It attaches easily to most M^{2+} ions (free or in biological systems)
- Glyphosate is a schimate inhibitor
- These schimate enzymes are responsible for synthesis of several amino acids
- These necessary amino acids aid in a plants natural defense mechanisms
- Plant dies



Glyphosate Resistance



- Plants gain the ability to synthesize amino acids other ways
- Plants fight off disease utilizing other methods
- But why have some plants become resistant over night with little pattern or explanation as to why and why not



Recommendations Farmers Have Given to Fix the Problem



- Add more water
 - Move from 10 gallons per acre to 20
 - Move from 15 gallons per acre to 25
- Change your nozzels
 - You need micro-fine droplets
 - Cone coverage is better than fan
- Buy a new sprayer
 - Self-propelled do better
 - Your booms are allowing for too much drift



Growing Trend



- Regions of the world are showing resistant weeds
- The growing trend I see is in areas of hard water, greater glyphosate resistant is manifested.
- Why is hard water an issue



Water Samples



- 5 water samples
- Pick which one you would use.
- Simple solution to your problem
 - Hardness tester
 - pH meter



Water Samples cont



- Sample 1
 - Hardness 71 ppm
 - pH 6.3
- Sample 2
 - 194 ppm
 - pH 5.17
- Sample 3
 - 921 ppm
 - pH 4.85



Water Samples cont



- Sample 4
 - Hardness 0 ppm
 - pH 6.4
 - DI water
- Sample 5
 - Unreadable (over 1000) ppm
 - pH 5
 - Water and AMS



Calcium Carbonate



- Calcium carbonate in water
 - Hardness 25 ppm
 - pH 6.4
 - DI water



What is Hard Water?



- A build up of minerals in soluble form in a solution water
- What minerals are present?
 - Calcium (Ca^{2+})
 - Magnesium (Mg^{2+})
 - Iron (Fe^{2+})
 - Other metals in minute quantity (ppb levels)
- Why does this matter?



Solubility is the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.

TABLE 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds

Exceptions

Compounds containing alkali metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and the ammonium ion (NH_4^+)

Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)

Halides (Cl^- , Br^- , I^-)

Sulfates (SO_4^{2-})

Halides of Ag^+ , Hg_2^{2+} , and Pb^{2+}

Sulfates of Ag^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Hg_2^{2+} , and Pb^{2+}

Insoluble Compounds

Exceptions

Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-})

Hydroxides (OH^-)

Compounds containing alkali metal ions and the ammonium ion

Compounds containing alkali metal ions and the Ba^{2+} ion

Organic vs Inorganic



- Organics (typically referred to as oil) are usually **Insoluble in Water**
- To increase solubility of an organic molecule in water it takes a group of atoms that will increase solubility the organic material
- Water Solubilizing Groups
 - -OH, -NH₃⁺, -SO₃²⁻, -PO₃²⁻
 - Charges aid in Solubility on Organic



Organic vs Inorganic Cont.



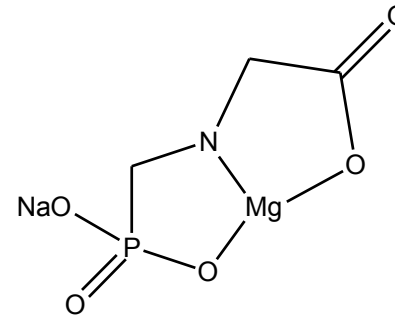
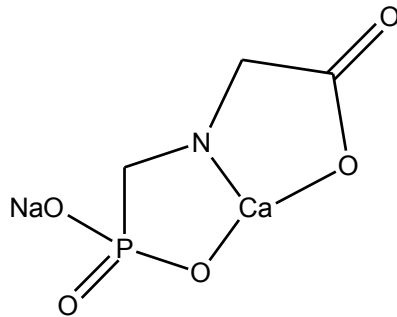
- Since $-\text{PO}_3^{2-}$ is a Cousin to PO_4^{3-} their Interaction with Alkali and Alkali Earth Metals are similar
- Additionally $-\text{SO}_3^{2-}$ is a Cousin to SO_4^{2-} their Interaction with Alkali and Alkali Earth Metals are similar
- The Difference is that Phosphates have a Higher Affinity for Calcium than Sulfates



What Happens when we put Glyphosate into Hard Water



- Calcium has a high affinity for glyphosate
 - The phosphonate group binds rapidly
 - Chelate



- Glyphosate is tied up by Calcium and therefore becomes inactive

Potential chelate structures for glyphosate, calcium and magnesium



What Loss of Activity of Glyphosate will You Accept?



- What is “Good Enough” activity?
 - 90%
 - 80%
 - 50%
- Or will you just double the rate of glyphosate to “Fix the Problem”



Hardness Chart and Percentage of Glyphosate Lost



Gallons per acre of water	% loss at 100ppm	% loss at 400ppm	% loss at 1000 ppm
1	100	99	97
2	99	98	94
3	99	96	91
4	99	95	88
5	98	94	85
10	97	88	70
15	95	82	54
20	94	76	39
25	92	70	24



But We Treat our Water with AMS



- Freshmen solubility rules revisited
 - Calcium Sulfate is Insoluble
 - pH will be acidic
- AMS has not fixed the problem
- Are you using it correctly



Order of Addition



- Water started into sprayer
- Put the AMS in first
 - Liquid is better than Solid
 - Allow solid to agitate well
- Put in Surfactants (if spraying)
- Put in other Chemicals
 - Insecticides
 - Herbicides
 - Fungicides
- Glyphosate last!



Typical Spray Rig Supply Set Up



Problem with Set up



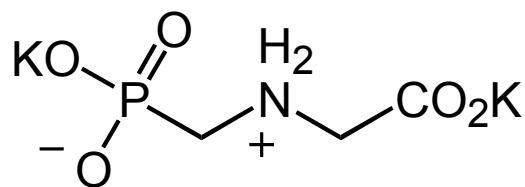
- Induction tank
- Water supply is untreated
- Hardness is still in full effect



Our Research



- Measure the rate which glyphosate is consumed by Ca^{2+}
- Method of measurement
 - ^{31}P NMR
 - Subject glyphosate to Calcium Chloride for selected times then quench with a competitive anion (sulfate and carbonate)



Glyphosate



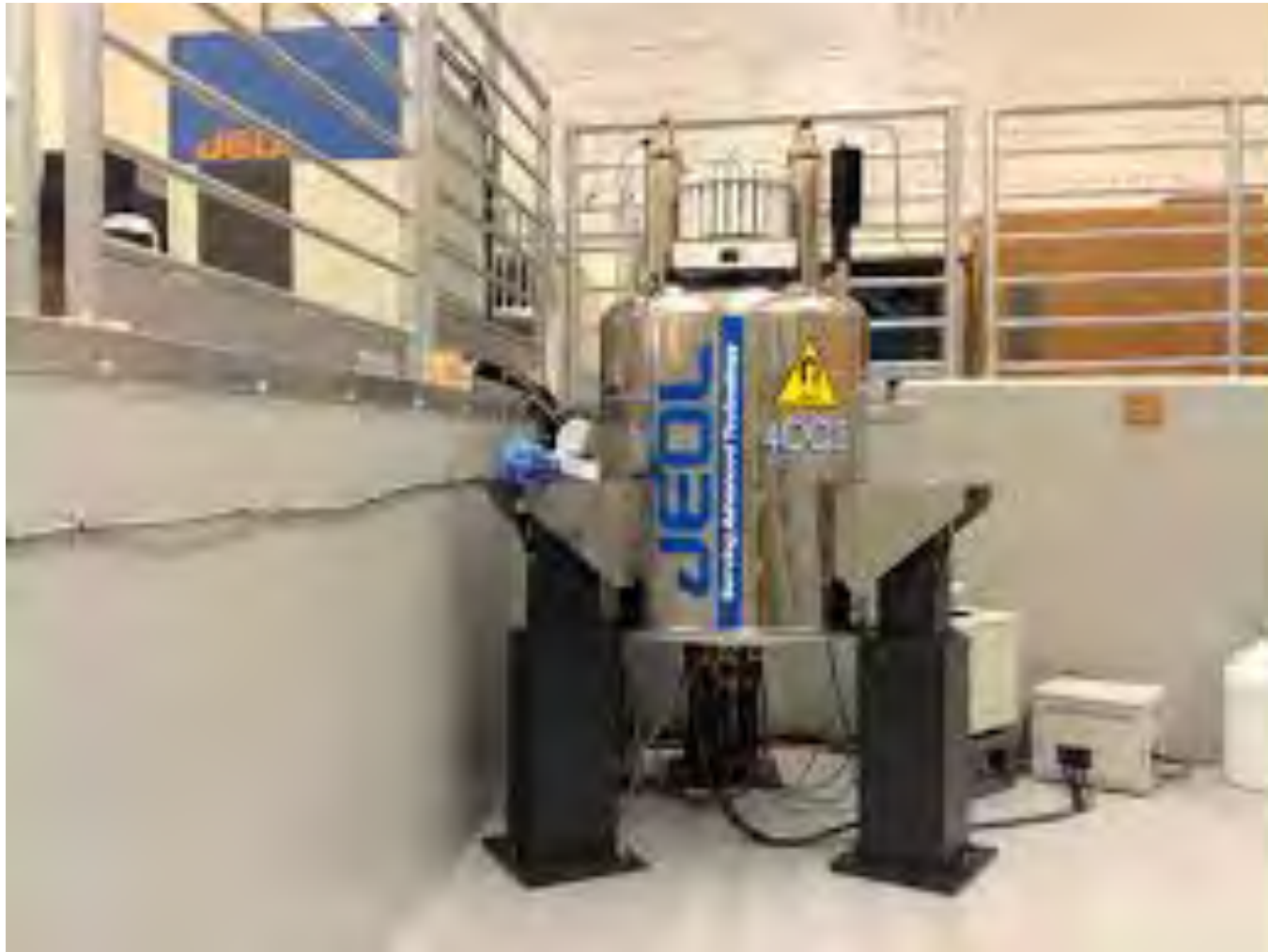
What is NMR?



- Nuclear Magnetic Resonance
- Can evaluate a particular atom in a molecule based upon its interaction with radio waves
- Quantitative when compared to an internal standard



What is NMR cont.?



Results to date



- Equal quantity of glyphosate and calcium result in complete loss of ^{31}P
- The ration of Calcium to Glyposate should be 1:1 in complex when calcium is in equal quantity to glyphosate
- Rate of consumption
 - Less than 1 second total loss of ^{31}P from sample



Results to date



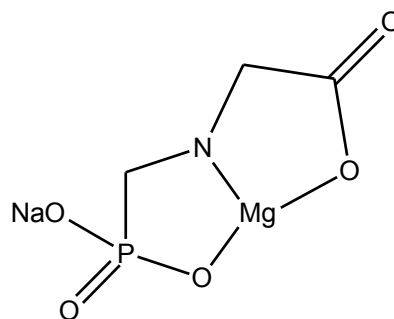
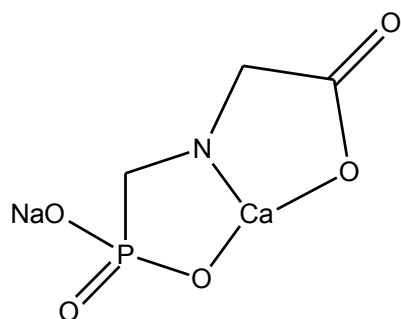
- Bulk synthesis of calcium glyphosate efforts to recover glyphosate
- Subjection of solutions to the following competitive anions and results:
 - CO_3^{2-} No displacement
 - SO_4^{2-} No displacement
 - PO_4^{3-} No displacement
- All efforts to recover glyphosate from calcium have been unsuccessful



Explanation as to Why Displacement Will NOT Work



- Chelate ring sizes 5 and 6 are super stable
 - Thermodynamic
 - Kinetically favored



- In other studies involving pH variances (5-8), up to 4 glyphosate molecules can coordinate to a single calcium (Raymond 1998 Inorg. Chem.)

Potential chelate structures for glyphosate, calcium and magnesium



If Two Glyphosates Coordinate to Calcium....



Gallons per acre of water	% active at 100ppm	% active at 400ppm	% active at 1000 ppm
1	100(98%)	99(97%)	97(94%)
2	99(97%)	98(96%)	94(88%)
3	99(96%)	96(92%)	91(82%)
4	99(96%)	95(90%)	88(76%)
5	98(95%)	94(88%)	85(70%)
10	97(94%)	88(74%)	70(40%)
15	95(90%)	82(64%)	54(8%)
20	94(88%)	76(52%)	39(0%)
25	92(84%)	70(40%)	24(0%)



Typical Spray Rig Set Up Revisited



A Better Approach



- Pre-treat water with softening agent prior to exposure to glyphosate
- Recommendation of 1 hour prior to usage
- Never expose glyphosate to water that has not been softened
- Realize an induction tank does create easy fill options but can kill herbicide before it ever gets to the sprayer



Going Beyond AMS



- Ammonium Sulfate is a water soluble salt that is used as a softening agent
- Not the best approach in acidifying the water
- Has been known to give yield drag in soybeans
- Is there a better approach?



So-Il Boost Plus



- The only AMS alternative that I will back
 - Scientifically Sound
 - Proven
 - The best of the best
- Soften your water the right way with the right product at the right time!

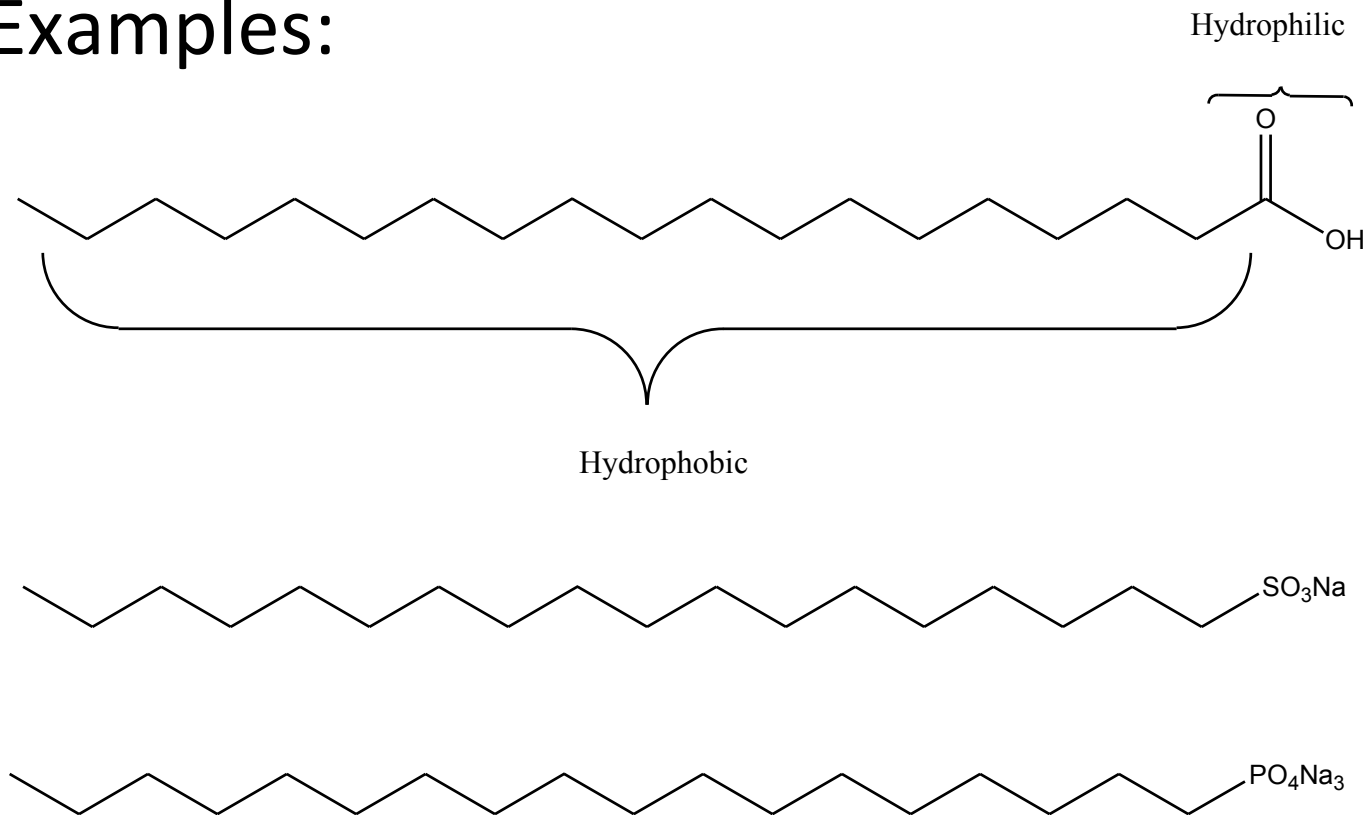


Going Beyond AMS

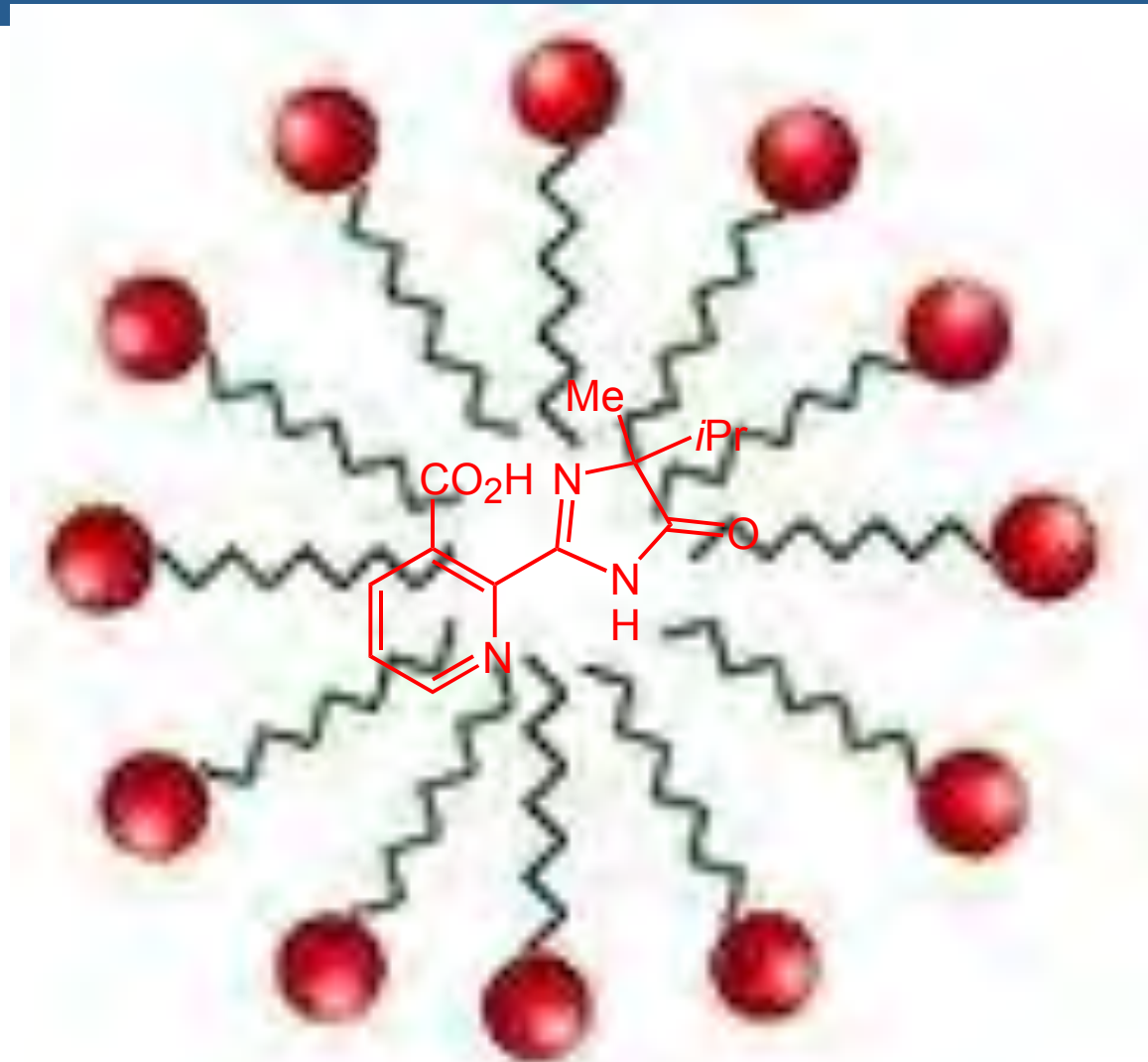
Surfactants



- Surfactants can aid in keeping Organic herbicides soluble in water
- Examples:



How Surfactants Work



Plant Based Surfactants



- MSO (methylated seed oil)
- Soybean oil based

SO-IL SERVICE

LANDOIL

Your "Homegrown" COST CUTTER

 CONTAINS SOYOIL



Acknowledgments



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