# A Brief Overview of Humic Substances in Agriculture

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# Overview

- What are Humic Substances (HS)?
- Why are Humic Substances beneficial for agriculture?
- Standard Analytical Methods for Humic Substances

# What are Humic Substances?

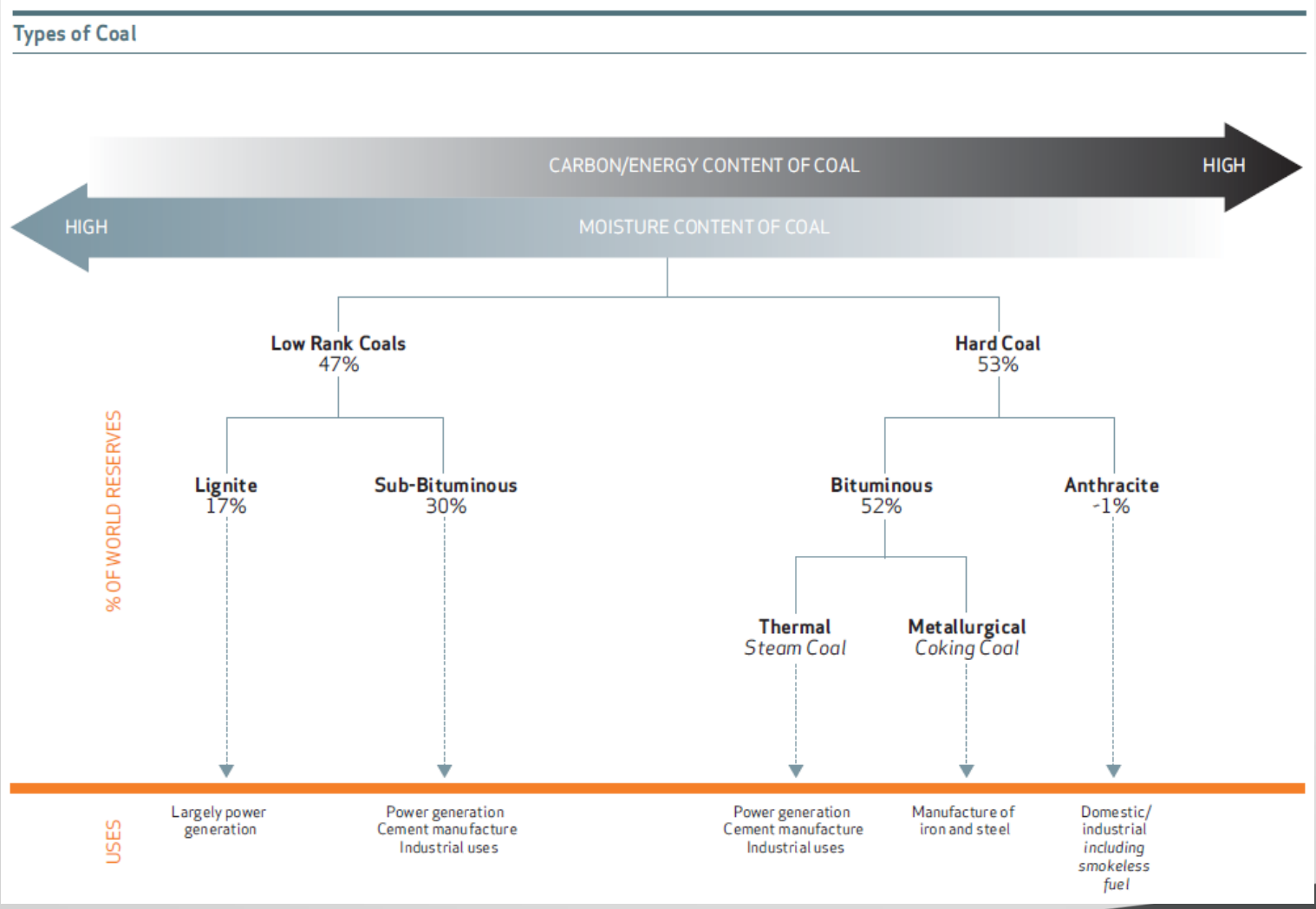
# What are Humic Substances (HS)?

- Result of the **nearly complete** microbial metabolism of plant and animal matter + geological forces (pressure, heat). A process known as "**Humification**"
- Biologically Refractory but Chemically Reactive Super Mixture
- Dominated by Carboxylic Acid and Phenol Chemistry

# Main Industrial Sources of HS - Brown Coal and Peat

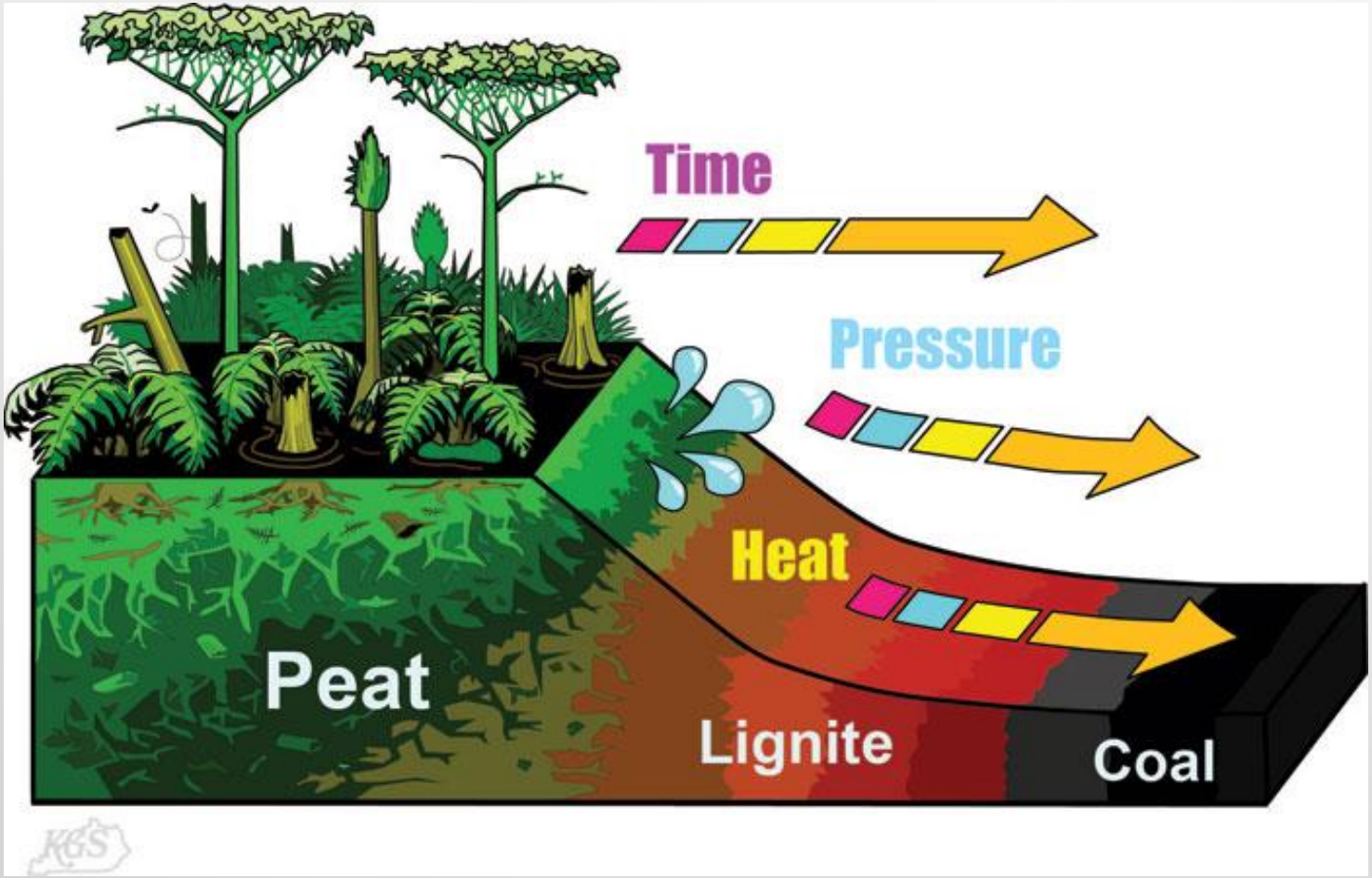

Actagro utilizes leonardite as its HS source.

# Types of Coal




https://www.worldcoal.org/

# Coal Formation




http://www.uky.edu/KGS/coal/coalform.htm

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# Leonardite – A Type of Brown Coal

An oxidation product of **lignite: a young brown coal with low energy content**


Leonardite is typically made up of **45-80% Humic Substances**. Known as the most **EFFICIENT/ECONOMICAL** source of Humic Acid.

# Humic Substances
# Historically: 3 Fractions

**Humic Acid** - acid insoluble

- 20,000 – 50,000 Avg. MW
- Colloidal

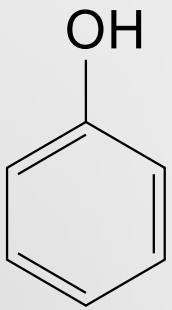
**Fulvic Acid** - acid/base soluble

- 1000 Avg. MW, do not aggregate into larger conglomerations
- Water Soluble

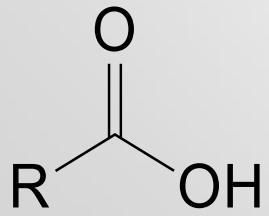
**Humin** - acid/base insoluble

- Up to 300,000 MW
- Insoluble

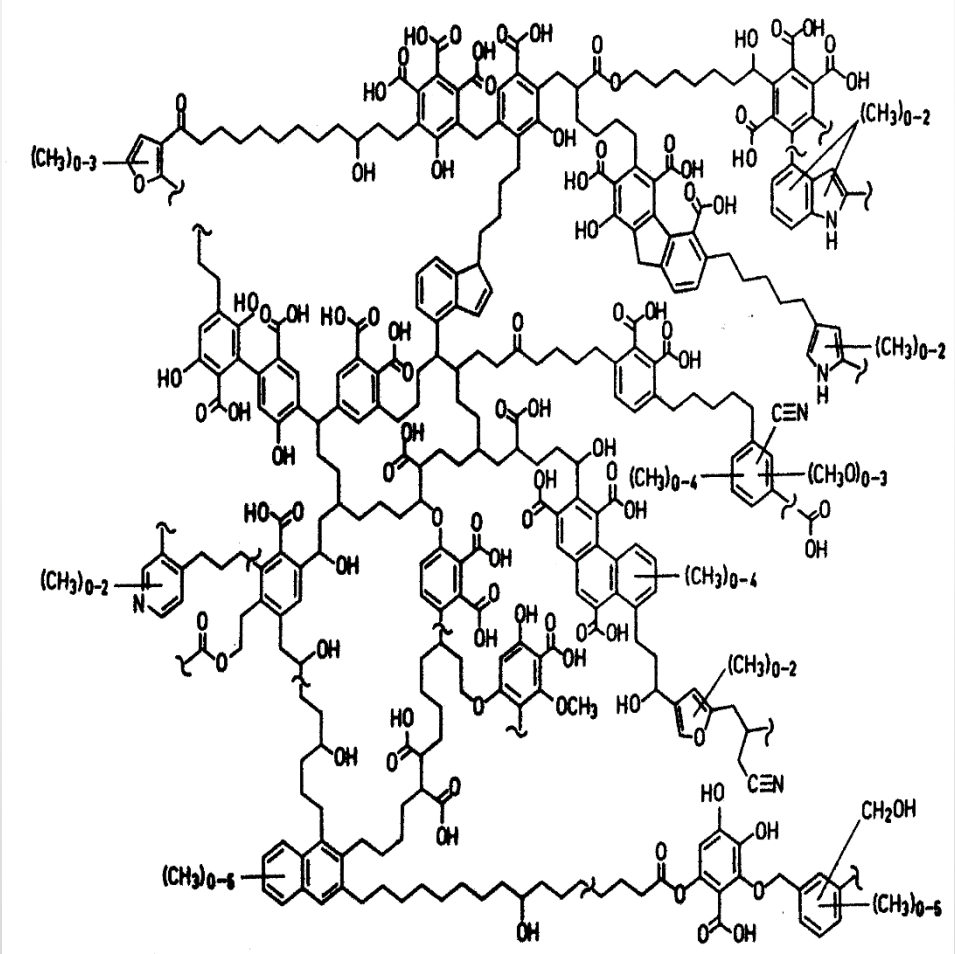
# Chemically, Humic Substances are Dominated by Phenols and Carboxylic Acids




**Phenol**




**Carboxylic Acid**



H.R. Schulten, M. Schnitzer, *Naturwissenschaften*, 1993, **80**, 27

# Why are Humic Substances beneficial for Agriculture?

# Benefits of HS for Agriculture

**CHEMICAL**, **BIOLOGICAL** and **PHYSICAL**

Salt Mitigation

Cation Exchange Capacity

Soil Structure & Consistency

Metal Complexation/Chelation

Nutrient Availability

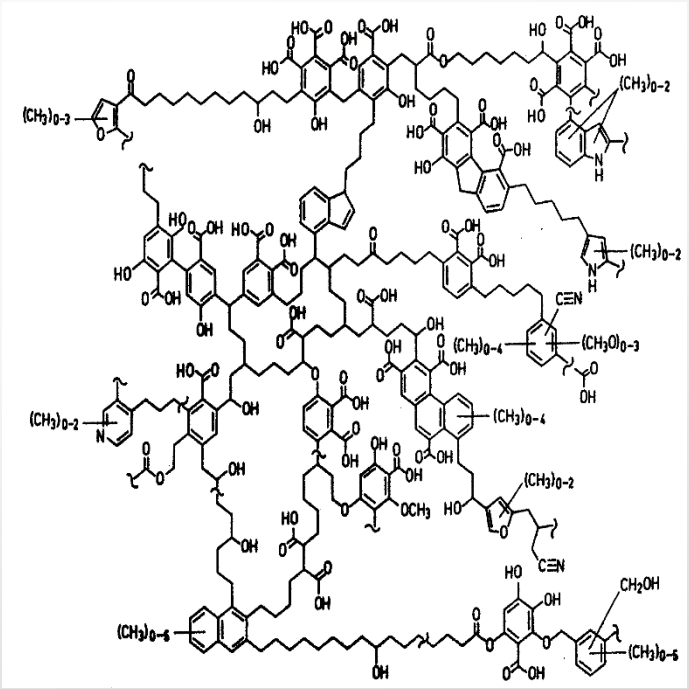
Water Holding Capacity

Reducing Agents/Antioxidants

Cyclic Redox

Plant Physiology & Metabolism

Beneficial Microbial Growth Environment



**…to name a few**

H.R. Schulten, M. Schnitzer, *Naturwissenschaften*, 1993, **80**, 27

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# Soil Structure Improvements with HS

HS can improve **soil structure** via:

**Cation Bridges**

**CLAY-Si-O-····+METAL+····-O-HUMIC-O-····+METAL+····-O-Si-CLAY**

**Anion-Ligand Exchange**

**2 HO-Si-CLAY + HO-HUMIC-OH → CLAY-Si-O-HUMIC-O-Si-CLAY +2 $H_2O$**

Soil Use and Management (1996) 12, 209-213
European Journal of Soil Science, August 2006, 57, 426–445

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# Soil Structure Improvements with HS

- Microbial exudation of secondary metabolites and binding agents
- Particle enmeshment by fungal communities increasing adhesion and particle aggregation
- Gaseous release of $CO_2$ from microbial respiration creates micro-cracks and large pore formation

**Microbes** are a **CAUSE** and **CONSEQUENCE** of **Soil Structure** improvements

Soil Biology and Biochemistry 74 (2014): 138-147.

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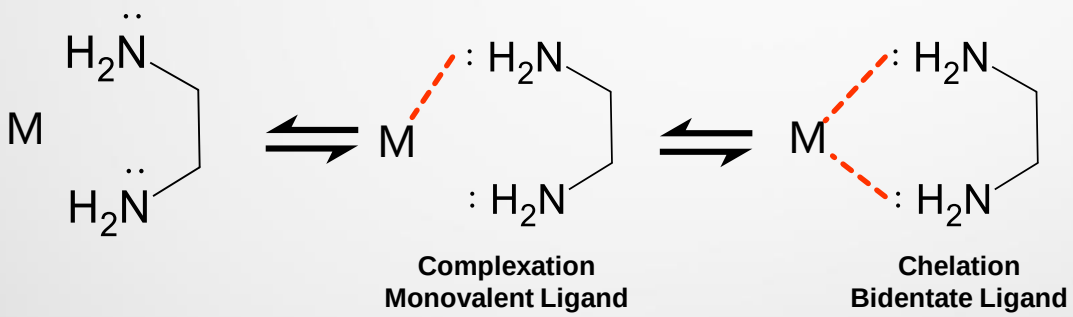
# Metal Complexation/Chelation with Humic Substances

- Metal Chelation/Complexation requires a donor ligand with a lone pair of electrons and a Metal Cation




- Sequestration: chelation/complexation that leads to a water soluble complex that can be more plant available.

# Antioxidants/Reducing Agents

HS may reduce insoluble metals and allow for dissolution (making them more available).

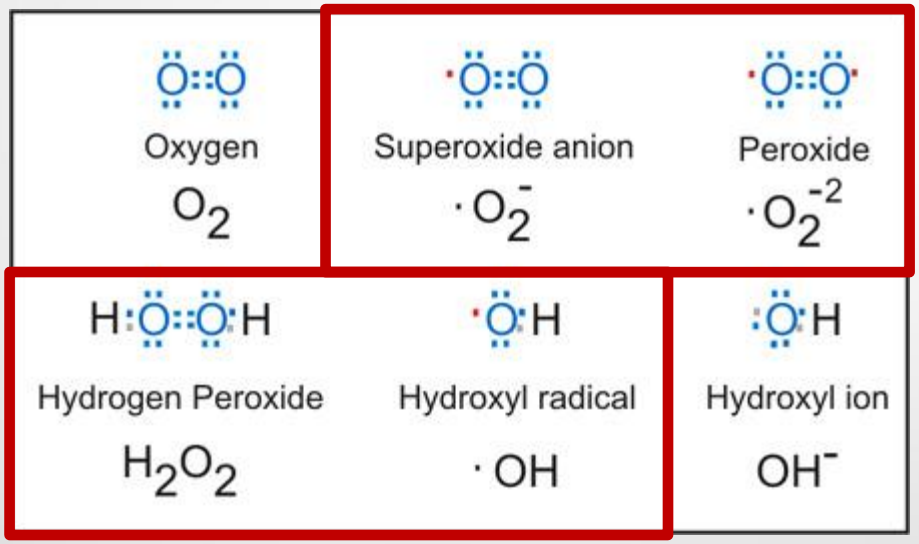
$$\text{Fe (III) Oxide} + HS_{reduced} \rightarrow \text{Fe (II) Oxide} + HS_{oxidized}$$

Ferrous (II) forms of Iron are more soluble than Ferric (III) forms of Iron.

Tan, Kim H. *Humic matter in soil and the environment: principles and controversies*. CRC Press, 2014.

# Antioxidants

Free Radicals - Reactive Oxygen Species



# Antioxidants

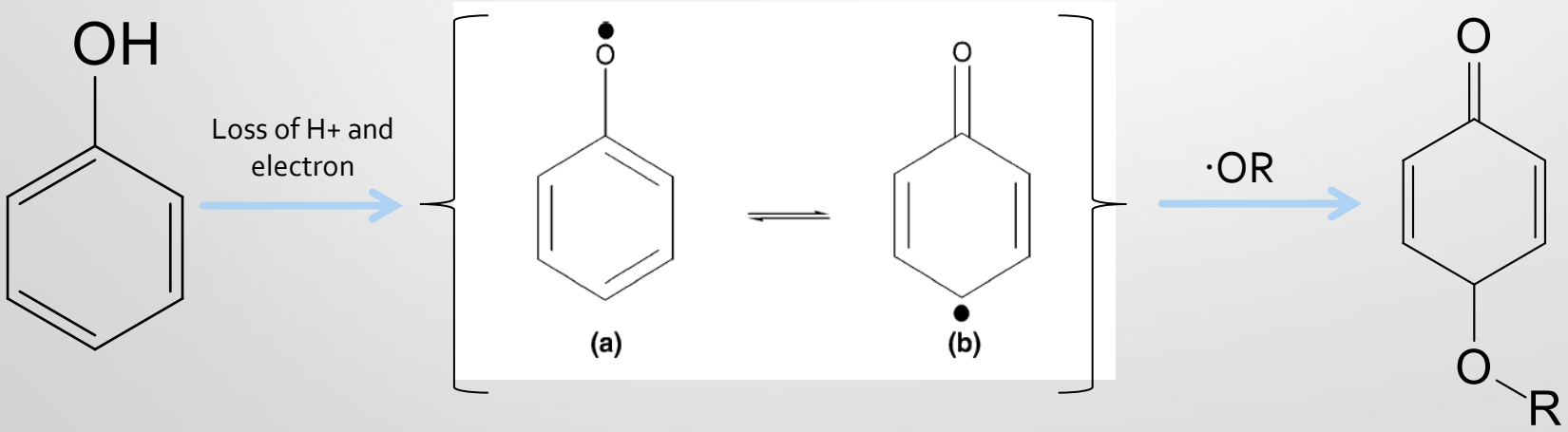
**Chemically ROS are:**

- Oxidizing Fatty Acids – Undermining the Structure of Lipid Membranes
- Oxidizing Amino Acids – Denaturing Proteins
- Oxidizing Nucleic Acids – Causing Breaks in DNA/RNA
- Oxidizing Sugars – Structural Damage
- Oxidizing Metal Cofactors – Inactivating Enzymes that rely on Cofactors

# Antioxidants

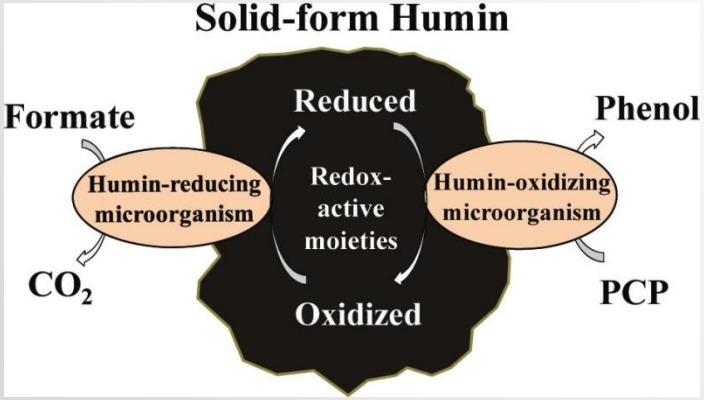
## Naturally Occurring Plant Antioxidants

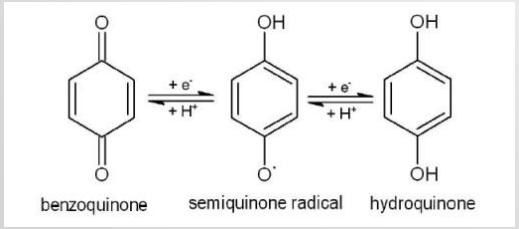
- Ascorbate (Vitamin C)
- **Phenolic Compounds** (Tocopherol)
- Glutathione



# Humin and Cyclic Redox Benefits for Microbial Growth

## Cyclic Redox Center




## Resistant To Degredation

- Acid (2%HF, 0.1M HCl 48 hours)
- Alkaline (0.1M NaOH)
- Oxidation (30% H2O2 30 min)
- Reduction (0.1M NaHBH4 for 15 hours)
- Heat (autoclaving 121°C, 30 min)

Environ. Sci. Technol. 2012, 46, 6575−6583

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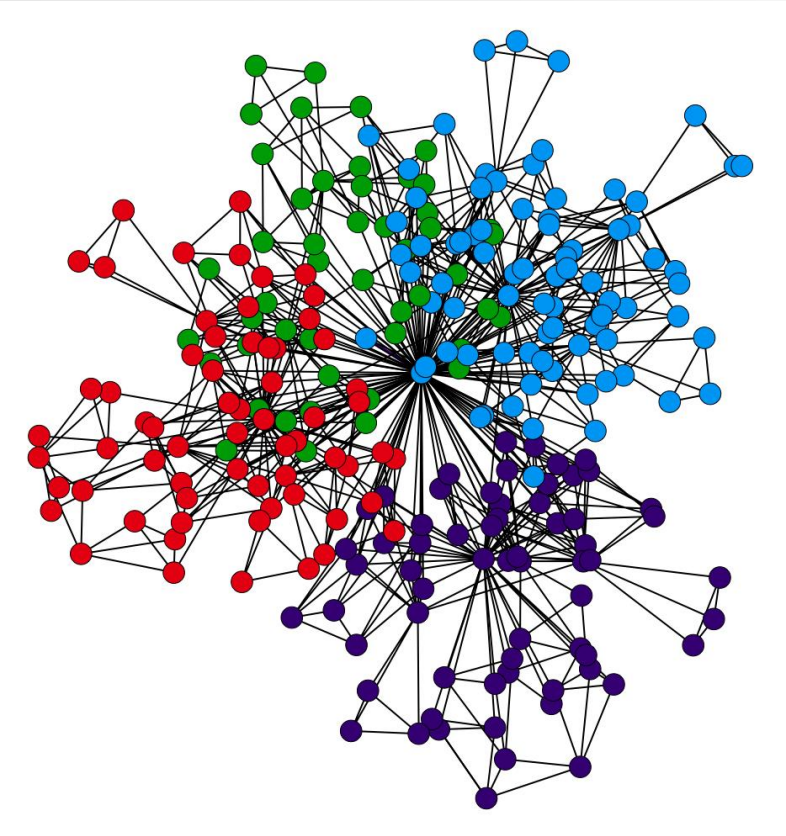
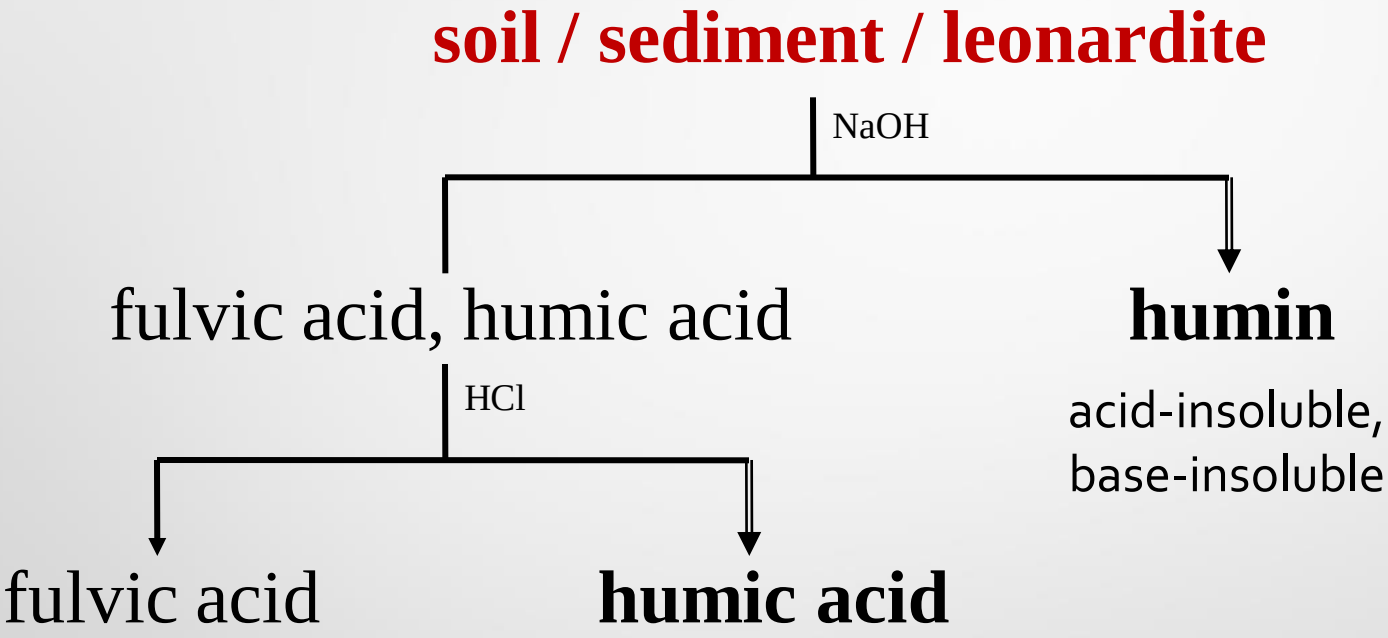
# Systems View of the Effects of Humic Substances



Microbiology, Plant Biology, Chemistry and Environmental Interactions all involved in Producing a Measurable Effect on the Plant.

# Standard Analytical Methods for HS

# CDFA Analytical Method Defines the Fractions (Functional/Physical Definition)



# Market Perception

Compost and Manure are not true sources of HS!

| Humic Substance | % Humic Acid |
|---|---|
| Leonardite | **40-85** |
| Black Peat | 10-40 |
| Compost | 7.9 |
| Manure | 3.5 |
| Coffee | 23.44 |

…yet they do generate Humic Acid values with the CDFA Test.

# New Standard Humic/Fulvic Method

- Humic Acid
- Hydrophobic Fulvic Acids (Genuine HS)
- Hydrophilic Fulvic Acids (Additives)

All Measured on a Dry, Ash Free Weight Percentage

Lamar, Richard T., et al. "A new standardized method for quantification of humic and fulvic acids in humic ores and commercial products." *Journal of AOAC International* 97.3 (2014): 721-730.

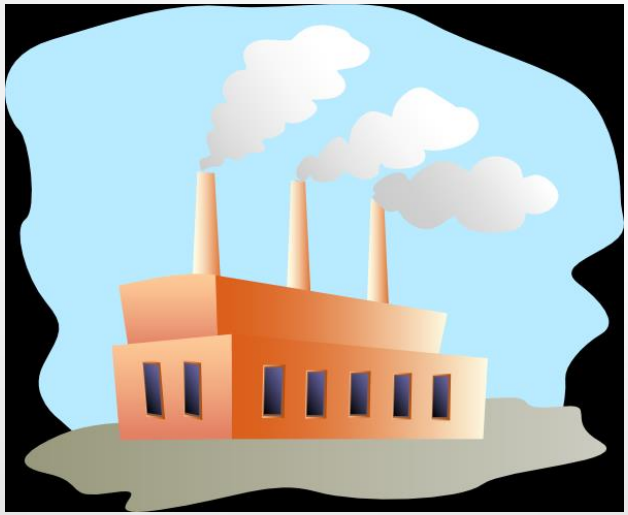
# Actagro Organic Acids® are **NOT** Humic Acids

- Actagro Organic Acids®
  - Contain Disaggregated Humin
  - Contain Customized Carbohydrates
  - Produced through Proprietary Extraction Processes
  - Contain a Humic Component
  - Contain a Fulvic Component
- Actagro Organic Acids® have additional agronomic benefits over standard Humic Substances
- Advanced Chemical Analysis clearly differentiates AOA® Chemistry from standard HS.

# Why are Actagro Organic Acids® Unique?

**Actagro Process**

**Humic**
**Fulvic**
**Humin**
**Carbon**



**Actagro Organic Acids®**

**Humic Substances are Chemically Reactive!**

# Summary

- HS are Biologically Refractory, Chemically Reactive Super Mixtures
- HS have many beneficial effects on agricultural systems
- Improved Standard Analytical Methods are being developed for liquid HS
- Actagro Organic Acids® are NOT Humic Acids