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A Practical Approach Review of Humic and Fulvic acids.

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Aim of the Talk

- a general oversight of what humic and fulvic acids are;
- a comparison of the 2 compounds
- where they come from
- what their benefits are
- Exaggerations and pitfalls
- Regulation and registration
- How to choose the right product

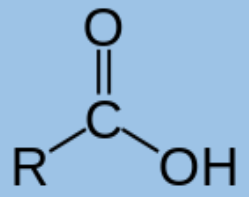
What are humic and fulvic acids?

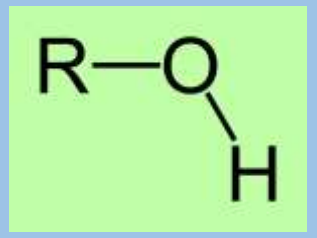
Active soil organic matter that forms the key component of sustainable agricultural practices.

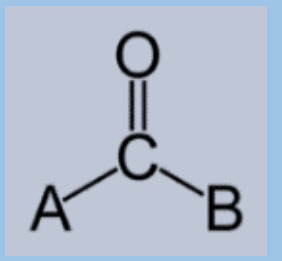
Consist of **C, H, O, N** and **S**.

Activity mainly determined by **Functional** chemical groups:

carboxylic acid (COOH), hydroxyl (-OH), carbonyl (C=O),





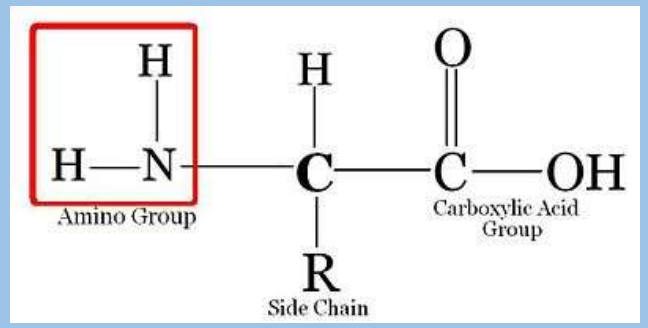


Functional groups allows humic and fulvic acids to form complexes/chelates with cations such as Mg^{2+}, Ca^{2+}, Fe^{2+} etc. to keep them available for crop utilization.

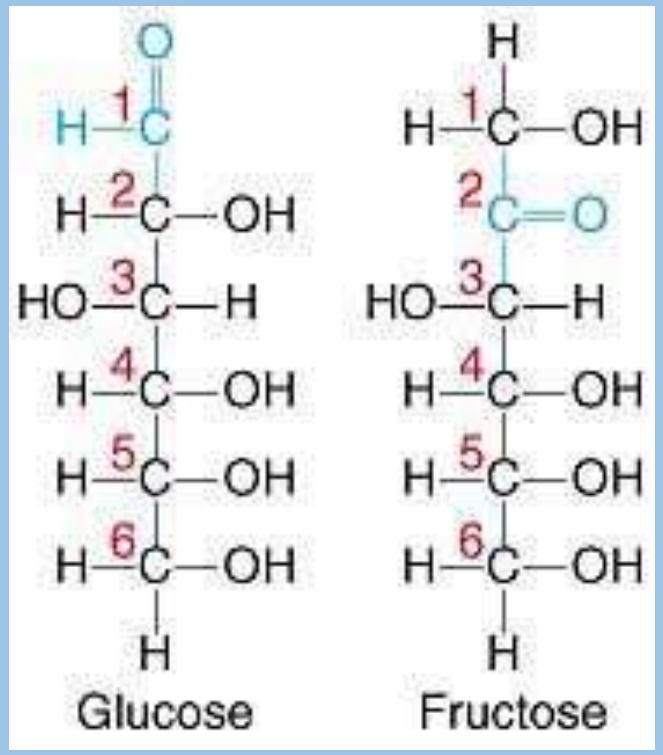
Important aspect is the role of these molecules in regulating bioavailability of nutrient ions and its effect on crop performance.

Non-Humic Substances with the same active functional groups that often part of HA and FA aggregate structures:

amino acids,



sugars



organic acids like citric acid.

HCOOH – Formic acid,

CH_3COOH – Acetic acid

Comparison between Humic and fulvic acid

Humic

- Relatively large molecules >35 Kdalton weight and 150 – 300 nM size
- Lower chemical reactivity – less functional groups or ionic charges
- A solution at a pH above 10, alkaline
- Precipitate in productive agricultural soils, with the pH between 5 and 7
- Precipitate when reacted with divalent $^{2+}$ cations
- Cannot be absorbed by plant roots or leaves.
- Cannot shuttle complexed nutrients into the plant.

Fulvic

- Relatively small molecules <35 Kdalton weight and 80 -100 nM size
- Higher chemical reactivity – higher number of functional groups or ionic charges
- Water soluble at any pH
- No precipitation at any pH. Always in solution, especially in productive agricultural soils
- No precipitation when reacted with divalent $^{2+}$ cations
- Can be absorbed by plant roots and leaves
- Fulvic acid complexed nutrients shuttled into the plant.

Comparison between Humic and fulvic acid

Humic

- enhance utilization of nutrients via ion exchange sites and prevent reaction with phosphate anions which will form insoluble phosphate compounds.
- at sufficient concentrations contribute towards cation exchange capacity (CEC) of soil.
- Humic acids CEC: 400-870 meq/100g

Fulvic

- Enhance utilization of mineral nutrient fulvate complexes which are in solution can be taken up by plant roots and therefore utilized by the plant – serve as a shuttle to carry nutrients into the plant.
- contribute towards CEC of the soil at sufficient concentrations.
- Fulvic acids CEC: 900-1400 meq/100g

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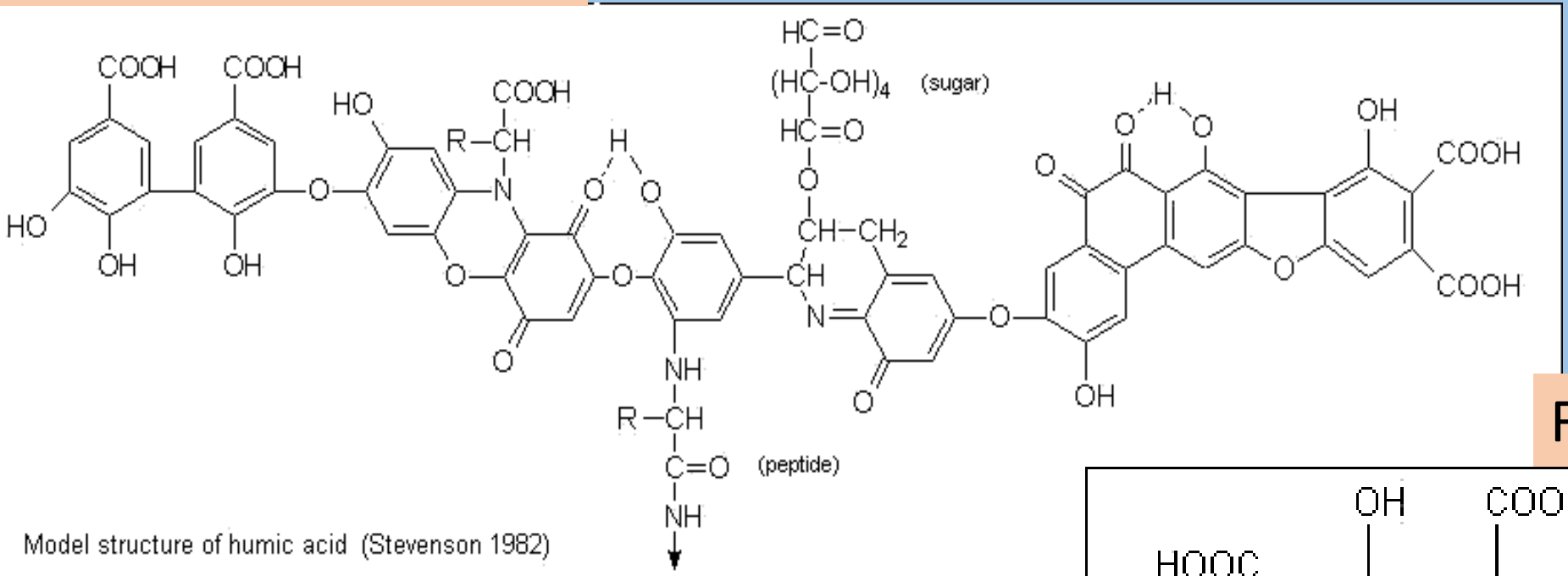
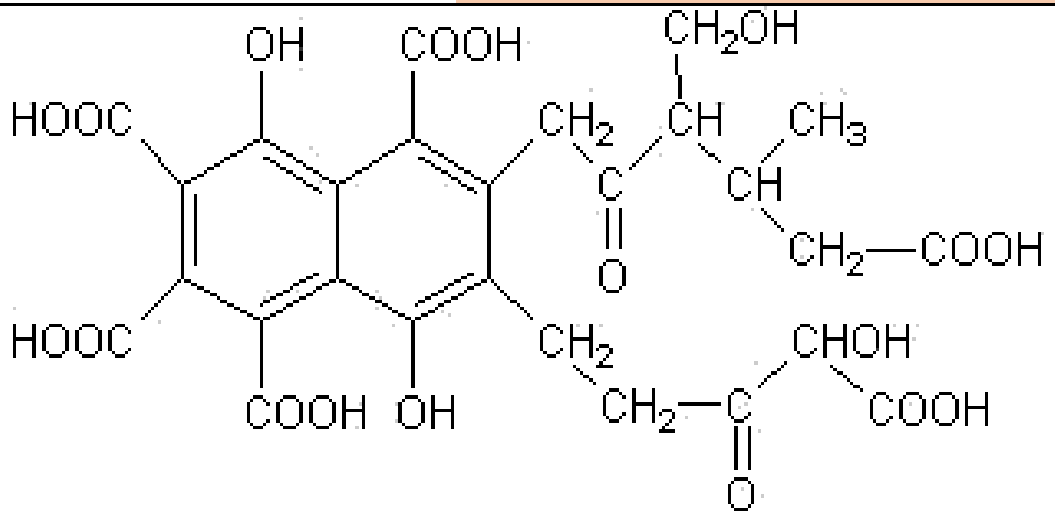
Proposed molecular structures: **molecular aggregates**

Humic acid structure



Model structure of humic acid (Stevenson 1982)

Fulvic acid structure



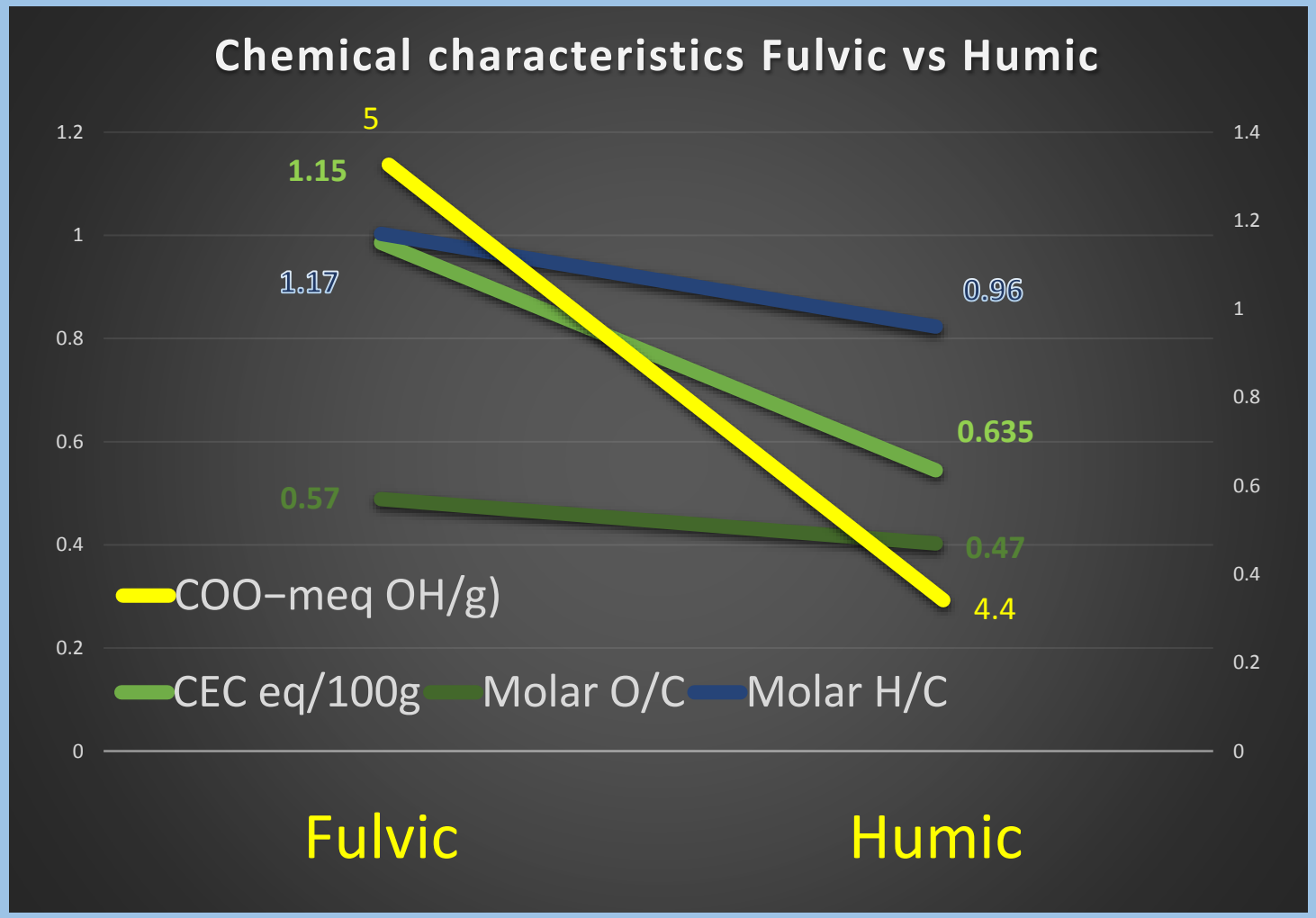
Model structure of fulvic acid by Buffle

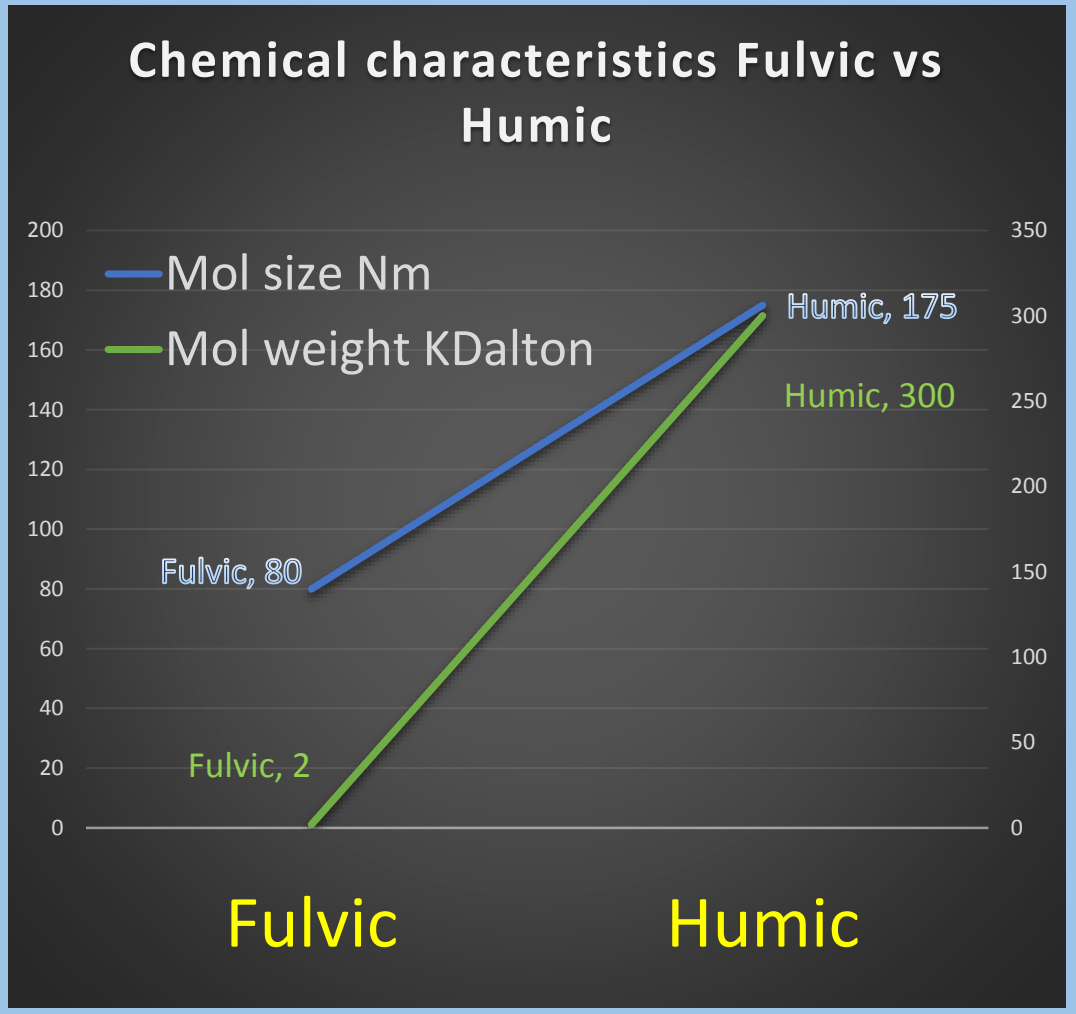
HS are practically classified based on solubility at an acid and alkaline pH.

Humins **consist of plant and animal material resistant to decomposition (solid material not soluble in water at any pH);**

Humic acids are substances in the process of decomposition (large molecules that are alkaline extractable) but not soluble at productive soil pH;

Fulvic acids are a complex mixture of smaller size organic molecules resulting from humic acid decomposition through microbial action and soluble in water at any pH.





Summarized chemical characteristics of humic and fulvic acids (Stevenson, 1982 and Helal,2007).

C and O contents, acidity and degree of polymerization all change with increasing molecular weight.

Chemical characterization of humic fractions (Helal, 2007).

	Molar H/C ratio	Molar O/C ratio	COO−(meq OH/g)
FA	1.17 **(+22%)**	0.57**(+21%)**	5**(+14%)**
HA	0.96	0.47	4.4

Fulvic acids contain more functional groups of an acidic nature, particularly COOH ➡ more reactivity towards reacting with cations .

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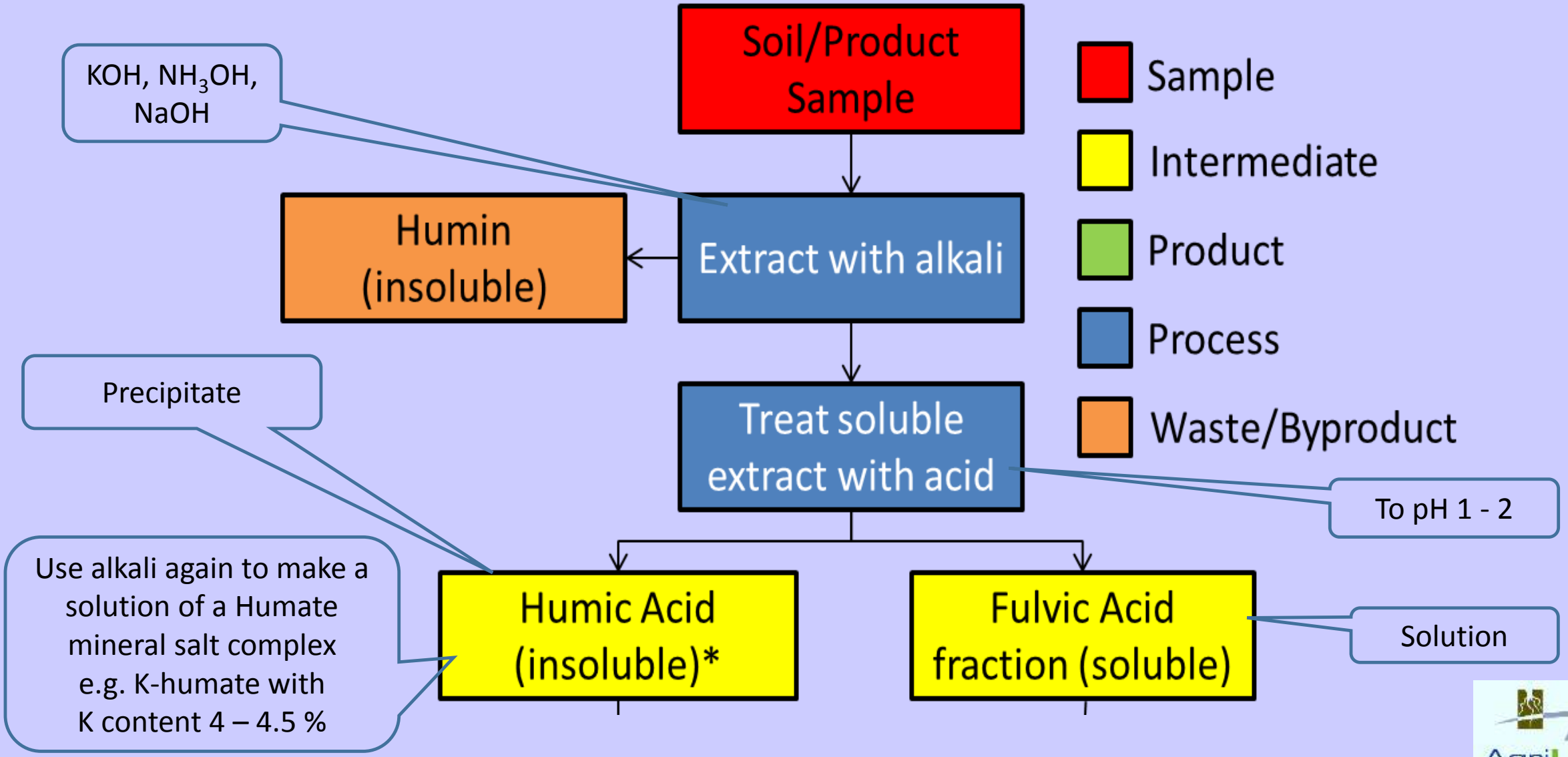
Extraction of humic and fulvic acids.



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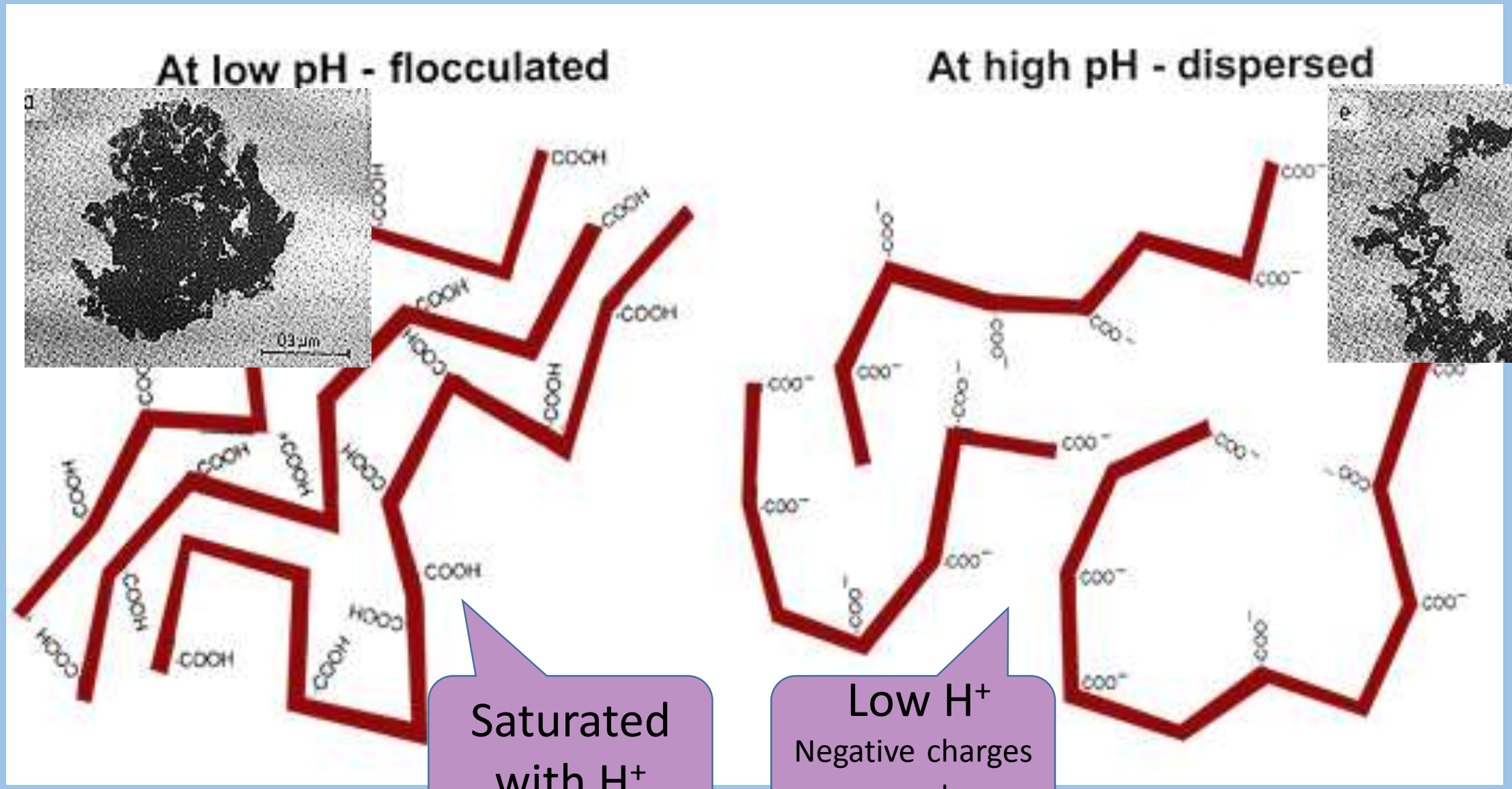
Electron microscope photographs below shows the polymeric or aggregate structures of HS



Chemical characteristics

Functional carboxyl (COOH) + hydroxyl (OH) groups (on the outside of the polymers) dissociate (expel) hydrogen ion.

Once the hydrogen ions are dissociated a negatively charged anion (COO^- or CO^-) results

Two anions can bind to positive divalent metal cations, (Fe^{++}), (Cu^{++}), (Zn^{++}), (Ca^{++}), (Mn^{++}), (Mg^{++}).

Reaction

($2COO^- + Fe^{++}$ → $2COOFe + 2H^+$) binds two anions.

Chemical characteristics

Humic and Fulvic acids neutralize cations

Ca^{2+} +
Mg^{2+} +
Zn^{2+} +
Fe^{2+} +
Cu^{2+} +
Mn^{2+} +

PO_4^{2-}

Insoluble

$Ca_3(PO_4)_2$	0.0002g/100mℓ
$MgPO_4$	0.00026
$ZnPO_4$	0
$FePO_4$	0
$CuPO_4$	0
$MnPO_4$	0

Physical characteristics

HS profoundly influences the structure of soils.

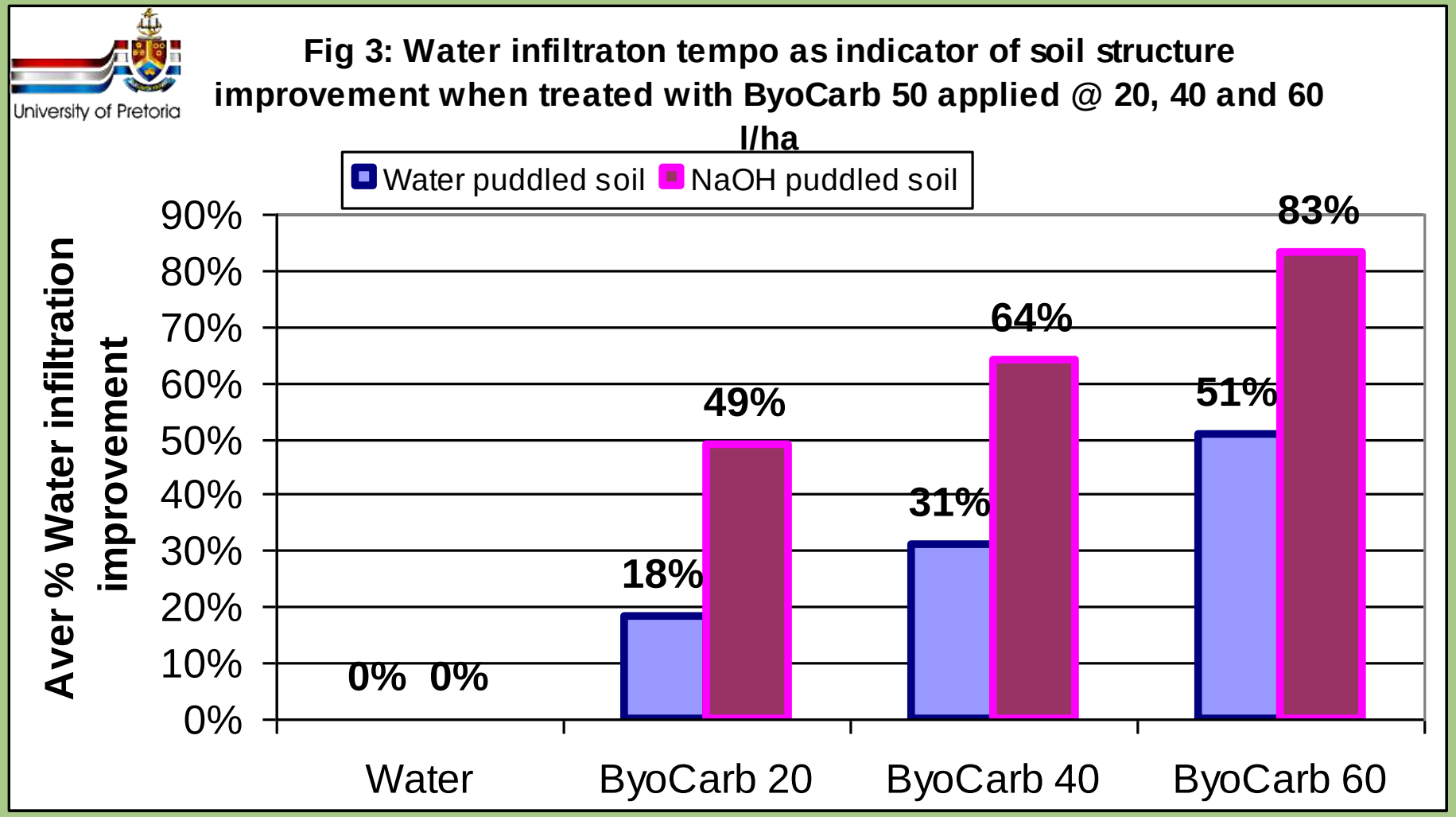
Important – concentration related

Intensive tillage of soils results in loss of humus that leads to:

- hard and compact soils,
- poorly aerated soils
- poor water-permeability
- Poor water holding capacity.

Physical characteristics

Effect of high concentration (20%) renewable resource extract FA on water permeability in soil where structure was destroyed by puddling with water and more severely with NaOH.



Humic Substance physical benefits:

- bind soil particles into ***structural aggregates*** that plays a major role in ***managing soil erosion***.
- Estimated that up to 70% of the exchange capacity of soils is the result of the colloidal HS aggregates.
- Aggregates help maintain a loose, open, granular condition of soils with improved ***aeration and water holding capacity***.

Humic substance biological benefits- impact on plant metabolism

Direct effects:

- HS can **contain auxin or auxin-like molecules – Growth stimulation**.

Indirect effect:

- **Hormone production enhancement** - improved uptake of Zn that catalysis natural auxin formation.
- hormone production by improved growth and multiplication of **Rhizosphere synergistic bacteria**.
- Improved nutrient uptake SUPPORT **total metabolism stimulation**.

All stimulatory effects like the increase CO_2 uptake, ATP synthesis, mitochondrial respiration and enhanced photosynthesis can be an indirect consequence of the all of the above.

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Biological characteristics

Take note that crop growth improvement **claims made for commercial HA and FA products** should be questioned because,

The effect of the equivalent nutrient portion (e.g. K in K-humate, 4,5 – 5% K) must be tested separately from the humic or fulvic acids.

Such a product used in a soil deficient in K, the K in the product will have an effect on crop performance.

Combined use should show synergism.

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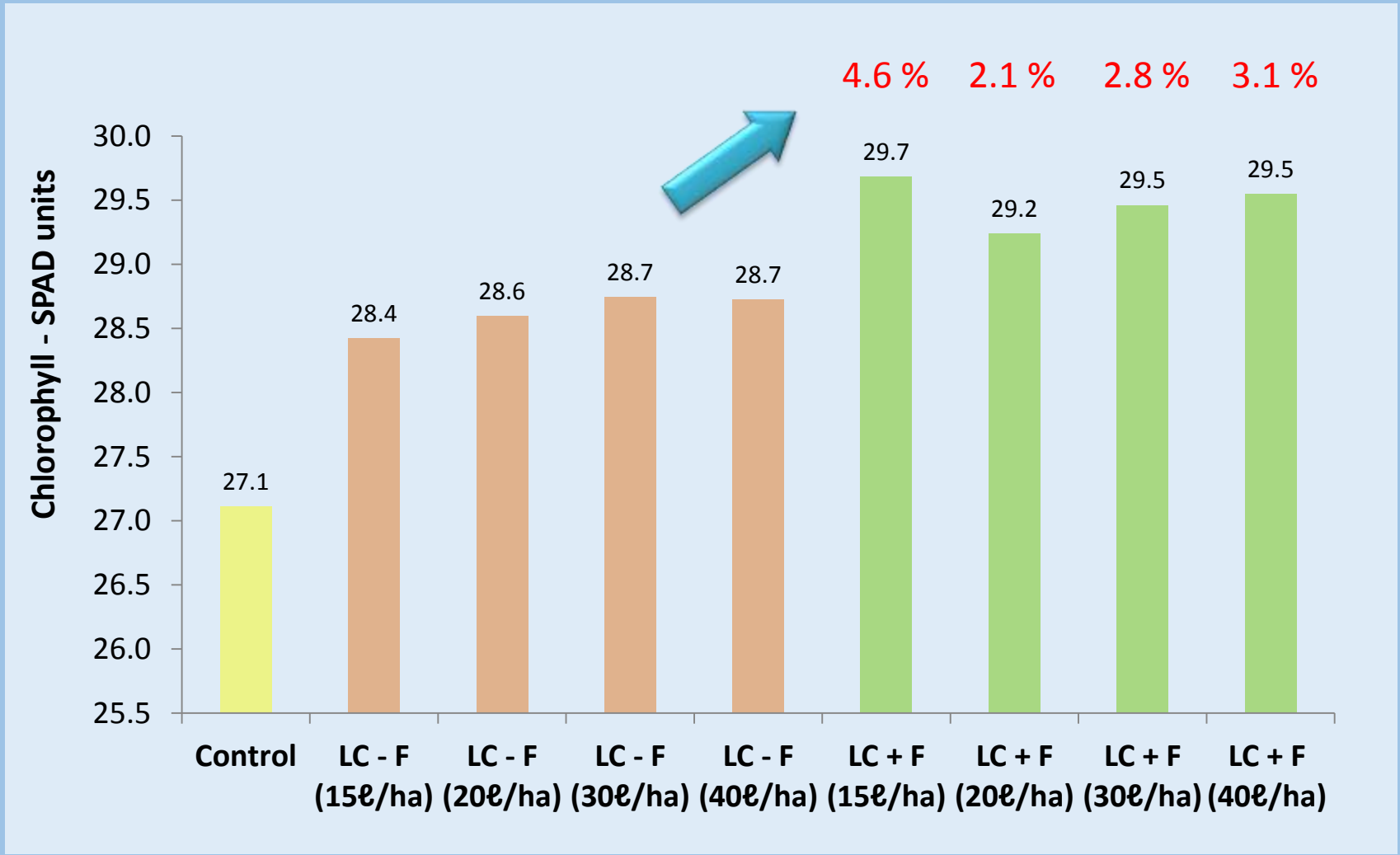
1. Nutrient vs Fulvic acid synergistic effect:

Differential effect on **chlorophyll** in maize grown under controlled conditions and treated with the **equivalent** amount of **nutrient** alone (LC-F) compared to nutrient plus Fulvic acid (LC+F)



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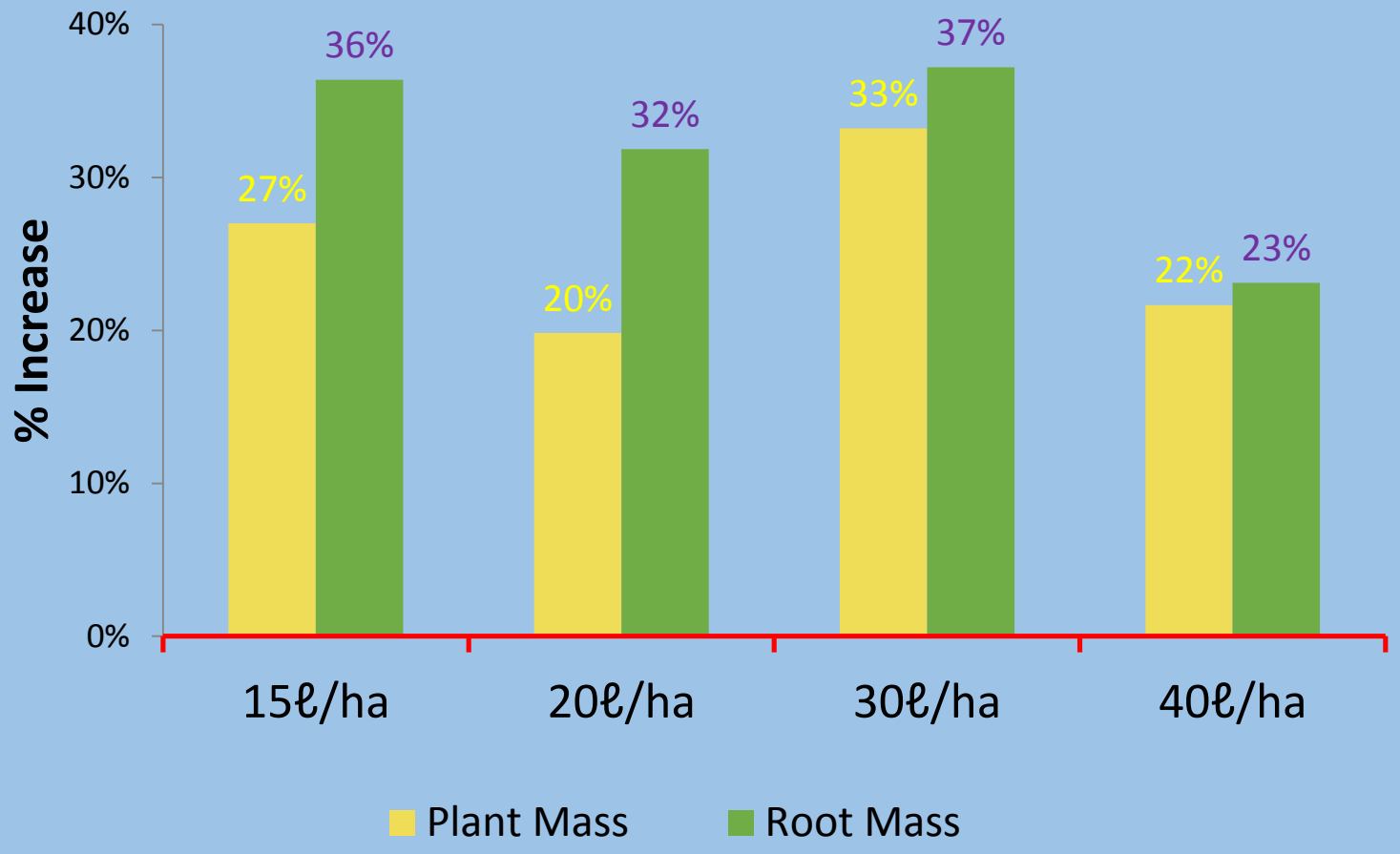
1. Nutrient vs Fulvic acid synergistic effect:

Likewise much more drastic synergistic differential effect on **root and top growth mass**

Fig 15: % Increase in root and top growth mass: nutrients plus Fulvic acid compared to nutrients alone (0%)

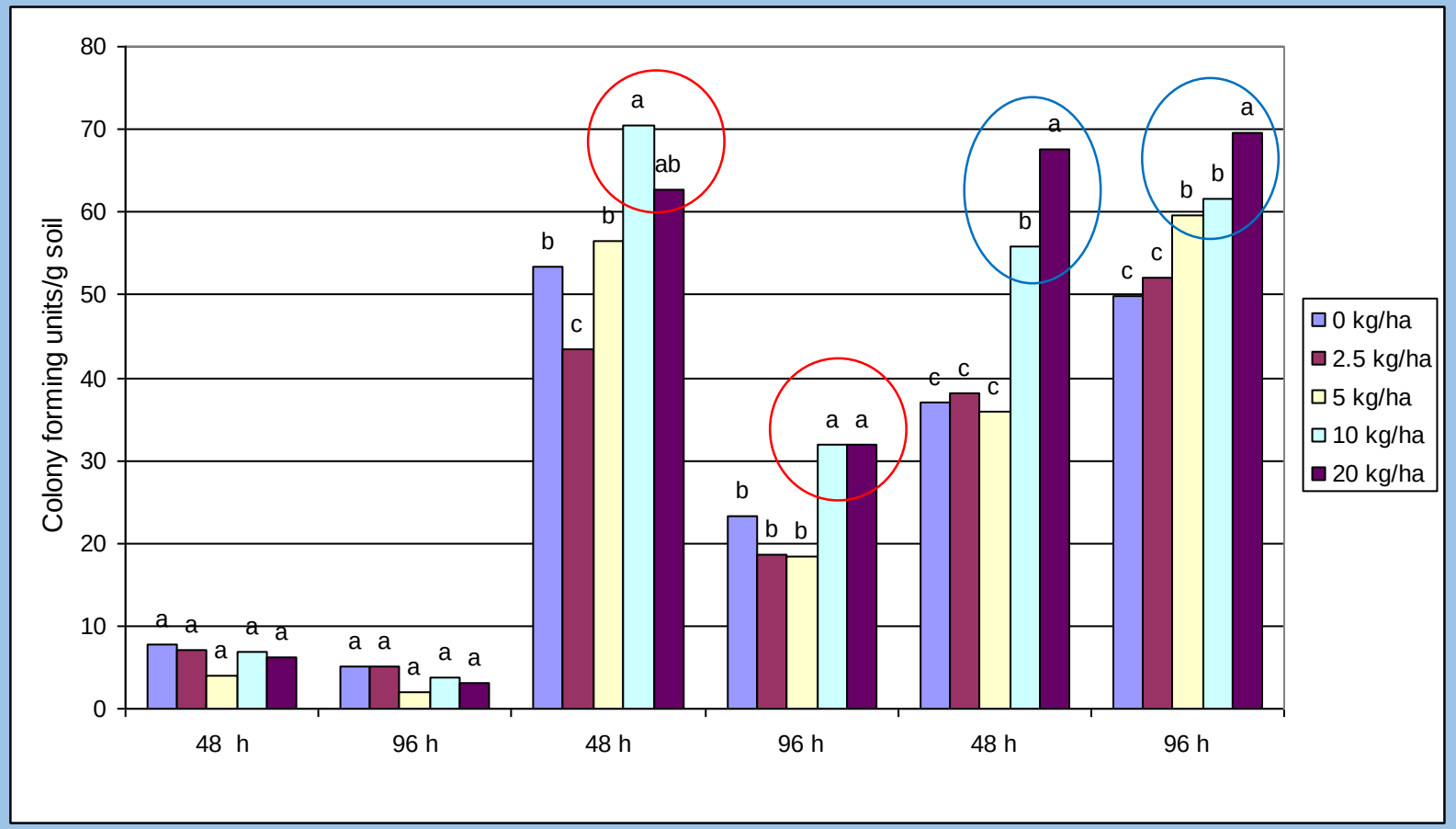


2. Bacterial hormonal effect:

Effect of a high concentration FA (ByoCarb50) treatment on the nr of fungi, bacteria and yeasts retrieved from soil.

No significant growth promoting effect on fungi within a 96 hour incubation period.

Bacterial and yeast growth stimulation occurred from 48 hours after incubation, specifically at the 10 and 20 kg /ha equivalent dosages.



Fungi | Bacteria | Yeast

[Mean of three replicate plates of two dilution series]

University of Pretoria, 2007

Common exaggerated HA and FA product claims that often are the reason for failure of these products:

- **Overstated active ingredient content** of products
- Soil chemical, physical and biological **activity** properties at **application rates** and **product content** that are **too low** to have any effect and without any valid experimental results to prove it,
- Claims that humic acids are more bio-active than fulvic acid as a soil application.

Reasons for using either Humic or Fulvic acids or both must be clear:

Change CEC or physical structure of soil

long term at sufficient dosages can be expensive and has to be compared to using compost or manure at a lower cost and will achieve the same goal

Neutralize charges of nutrient ions to improve uptake

dependent on concentration ai and application method

Stimulate microbial action

Depends on what the *concentration active ingred*ient is and *how it is applied*

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Note:

Not all black or dark brown liquids/suspensions/powders are humic or fulvic acids.

For example, black coal dust sold to uninformed farmers as “slow release humic acid” is not oxidized at all and therefore are totally insoluble and inactive.

Sources and characteristics of products from different sources.

Humic acid sources as K, Na, Ammonium, Mg humate powder, granules or liquid.

Leonardite/lignite, peat, pecan nut shells, compost, manure , wood or fermented fresh plant material extracts. The higher the oxidation state the more active it is.

Fulvic acid sources.

Due to **solubility** of fulvic acids it easily leaches out of source material,

- present in low concentrations (0.2 – 1% w/v) in leonardite, peat, compost sources.
- In South Africa, novel high concentration fulvic acid extracted from a **sustainable renewable resource** has shown to have high ion charge neutralizing and biological activities.

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Analysis of humic and fulvic acids.

BemLab implemented an internationally accepted chemical analysis procedure to analyse commercially available humic and fulvic acid products in South Africa in order to assist to better control and regulate the chemical quality of HS products and also to assist in the registration of such products.

HA concentration is determined **gravimetrically**, while the **FA** that remained in solution is determined **spectrophotometrically**.

The method was developed using the procedure described in two publications, namely,

GAN, D., KOTOB, S.I. & WALIA, D.S., 2007. Evaluation of a Spectrophotometric Method for Practical and Cost Effective Quantification of Fulvic Acid. Annals of Environmental Science. 1, 11-15.

THURMAN, E.M & MALCOLM, R.I., 1981. Preparative isolation of aquatic HS. Environ. Sci. Technol. 15, 463-466.

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Analysis of humic and fulvic acids.

All HA and FA products made up of an ***organic portion*** and an ***inorganic mineral portion***.

What must be analyzed?

- Total macro- and micronutrients including S.
- Humic and fulvic acid concentration (%) using standardized internationally accepted methodology.
- % Carbon
- Moisture %
- Specific density - kg/l

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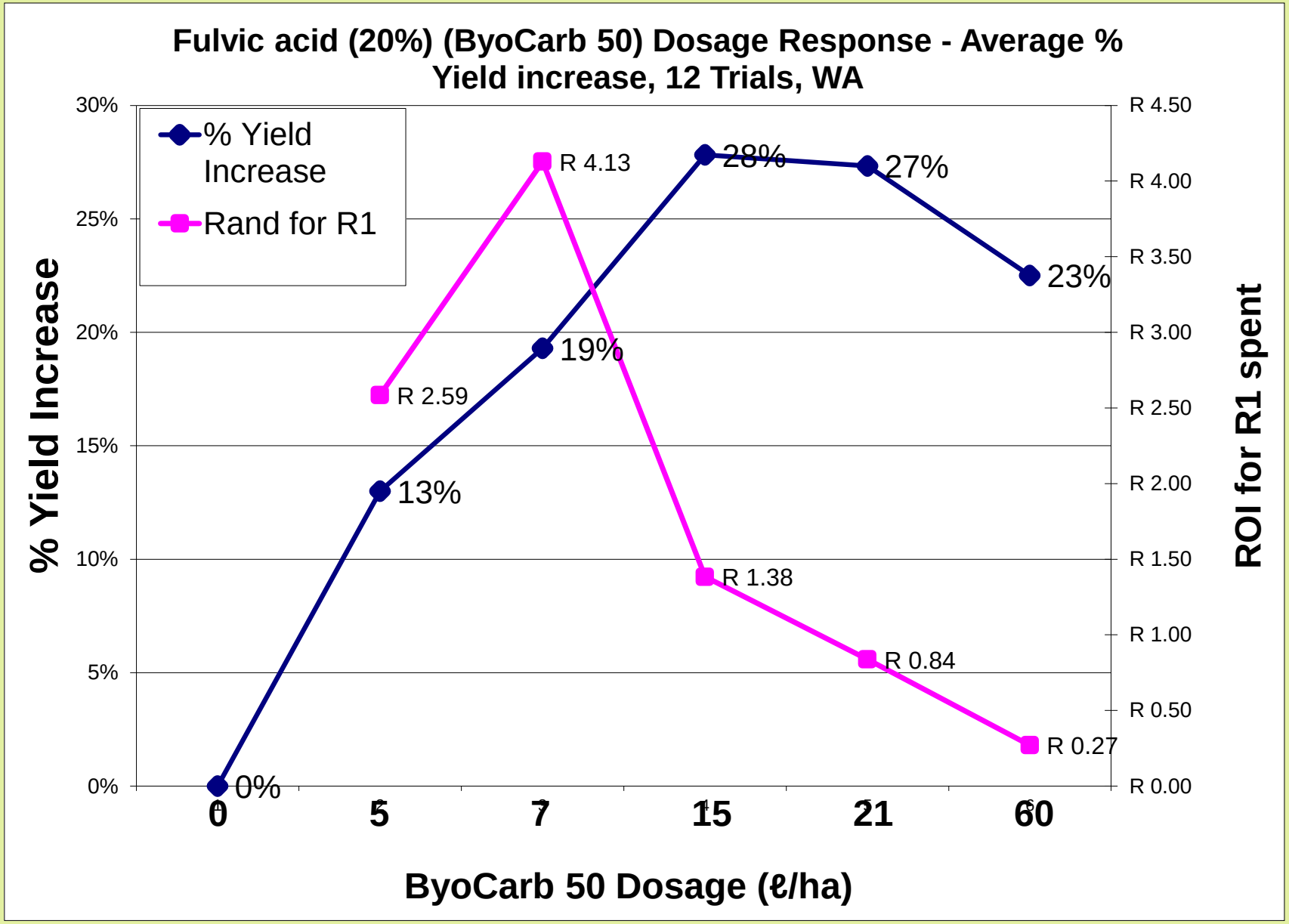
Proof of activity: Dosage response and optimal dosages



Results of field trials done on wheat in Western Australia, repeated on 12 farms, was combined and the dosage response curve was plotted to establish the *in situ* concentration range where the highest yields were obtained.

A high concentration renewable resource fulvic acid (55 – 55% dry matter, 18 – 22% pure fulvic acid) used.

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Dosage response and optimal dosages

I. Data analysis by Rose et al (2014), where 89 papers (700 analysis points) relevant to the question of, **to what extent Humic substances will result in plant growth responses**, showed an optimum growth response at a dosage of approximately 20 kg/ha.

II. The WA field trials shows that the **optimum application dosage** is between 15 and 21 liters/ha based on yield alone but based on ROI, it was between 5 and 7 liters/ha.

III. Chen et al. (2004) used the data of a number of studies to calculate the optimum dosage of HS and arrived at a figure of approx. 22.5 kg/ha **as a** soil application.

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Humic and fulvic acids (HS) ***as synergists – farm benefits***

Improved nutrient use efficiency with the use of FA was observed **on wine grapes in the Western Cape** .

The 20% FA product at 30 ℓ/ha (3x10 ℓ split over a 2 month period) was used on 4 vineyard cultivars (8 blocks, separate adjacent control and treatment blocks).

Chlorophyll % relative to controls, measured in SPAD units.	
Vineyard blocks	% Increase relative to control
Cabernet	6.1%
Chardonnay	13.5%
Shiraz	12.0%
Viognier	1.2 %

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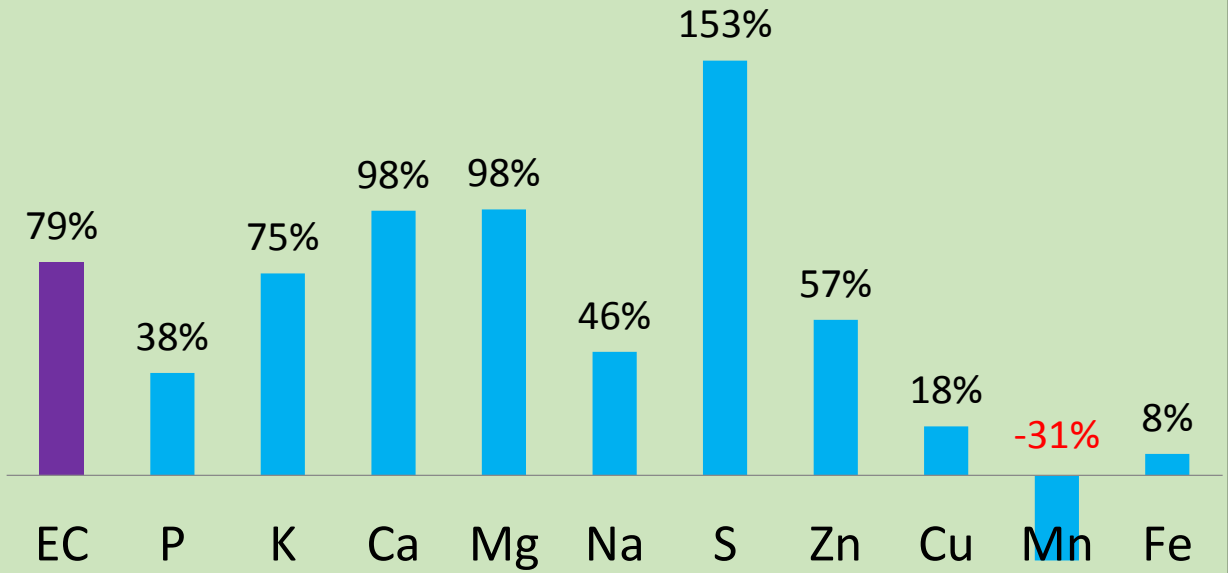
Humic and fulvic acids (HS) ***as synergists – farm benefits***

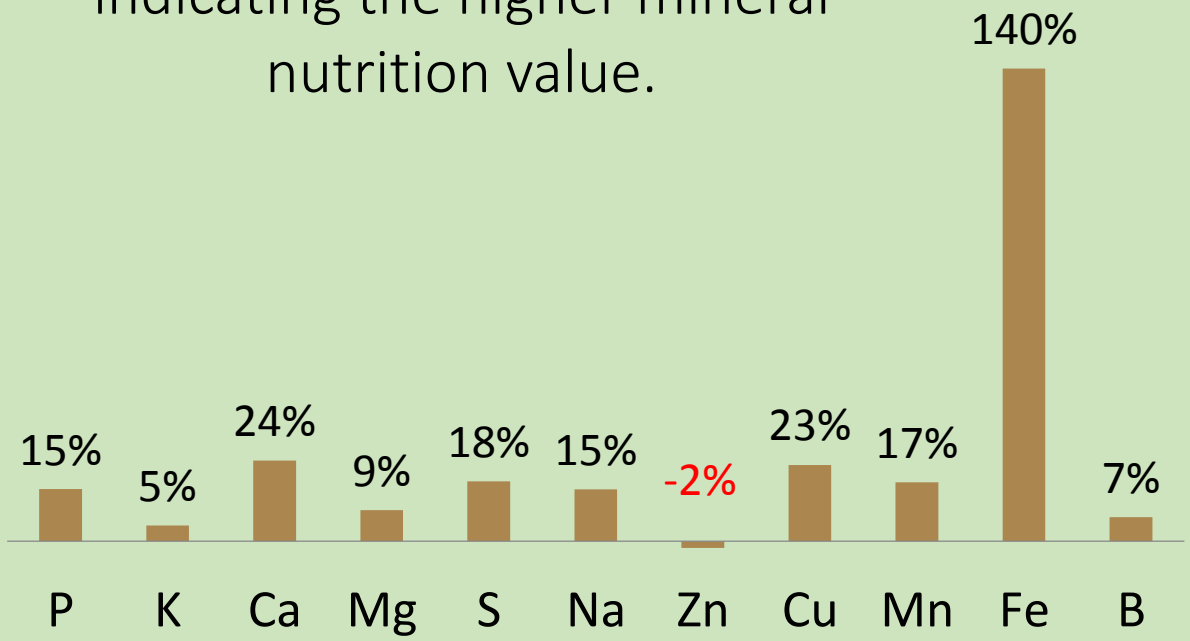
1:2 Water extract soil analysis

Average results for 4 cultivars: **% Increase in water soluble nutrient concentration relative to control.**



Average wine mineral content

% relative to control for 4 cultivars indicating the higher mineral nutrition value.



These results show the direct synergistic benefit in using FA in conjunction with nutrients in the soil.

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How to choose between different Humic and fulvic acid products = Information required for registration purposes.

- **Active ingredient** of the product? Humic or fulvic or both?
- **Concentration** as per analysis of the active ingredient/s?
- **Source** of the humic and /or fulvic acid extraction?
- Which **mineral** **nutrients** are in the product and at **what concentrations** as per analysis? Products oxidized Nitric acid will contain a high concentration of N but comparible low amounts of humic and/or fulvic acid. This is an expensive N product instead of supplying N as conventional fertilizers and the small amount organic material in these products does not contribute to the intended goal.

How to choose between different Humic and fulvic acid products = Information required for registration purposes..

- What is the **pH of the product**? Water soluble: humates pH>10 and fulvic below 6.
- What is the **specific density** of the product? Generally a good quality product with high organic active content will have a density higher than approximately 1.2 kg/ℓ.
- What is the **carbon content** of the product, can be a good indication of concentration and potential activity.
- Fulvic acid products: Does it have water **dispersing** (water surface breaking), **wetting and re-wetting** (hygroscopic) characteristics that both for soil and foliar applications, beneficial enhanced infiltration, uptake and utilization of nutrients.

Conclusions

The **compounding benefits** for using Humic Substances to ensure sustainability in crop production are:

- ❑ improvement of soil chemistry and structure
- ❑ improvement of biological status of soils
- ❑ improved utilization of nutrients supplied and obvious cost savings
- ❑ improved water utilization and possible cost savings
- ❑ improved yield – higher income/ha
- ❑ improved quality – higher income/ha

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Conclusions

The **amount of research data** that proves its significant positive impact on a broad spectrum of agricultural situations, should be proof enough to consider these products for their intended use,

provided attention is given to the quality of products, correct dosages and how being used,

otherwise poor results will make the name “snake oil” stick and the true on-farm benefits will not be realized.

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Thank you

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What are the intended benefits required?

List of Intended benefits of organic amendments from Bünemann et al (2006), amended.

Reasons for organic amendment
(a) Supply bulk nutrients for plant production
(b) Increase availability of existing soil nutrients
(c) Increase the availability of applied fertilizers
(d) Fix N from air
(e) Improve soil chemical fertility
(f) Improve soil physical condition
(g) Improve soil biology
(h) Plant growth promoters
(i) Direct suppression of plant disease
(j) Indirect suppression of plant disease
(k)Decontamination of polluted soils.
(l) Break down crop residues and other compostable materials