Fluid Fertilizer Workshop

IPNI
International
Plant Nutrition
Institute

Calcium in the West:

Sorting it out ?

Rob Mikkelsen
Director, Western Region, North America Program

Calcium

- Calcium plays two distinct roles in crop production

Adequate Ca in the plant is essential for

  - Reduction of physiological diseases
  - Suppression of pathogenic diseases
  - Reduction of environmental stress

- Adequate Ca in the soil is critical for good soil chemical and physical conditions

Calcium in short:

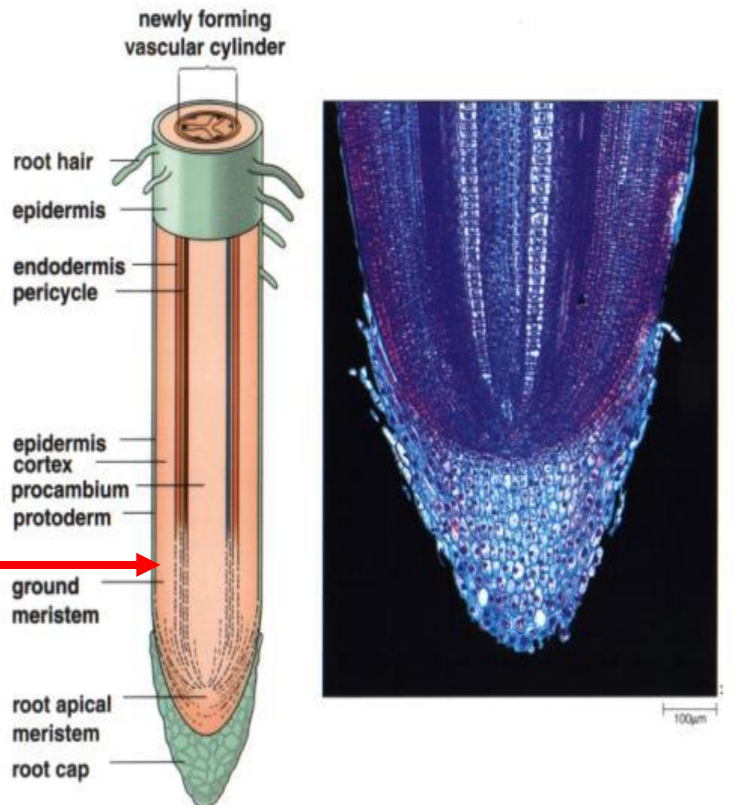
- Calcium is important for cell strength and the working of the membranes.
- Calcium uptake process is closely linked with water uptake.
- Calcium redistribution in the plant does not happen.
- Plant parts which do not evaporate water quickly show deficiency symptoms.
- Calcium is <u>not</u> the same as Chalk, Lime or Gypsum.

Function and behavior of Ca^{2+} in the plant

Ca^{2+} uptake: Passive process(?)

Uptake only though young root tops as the cell membranes of the epidermis are still very permeable.

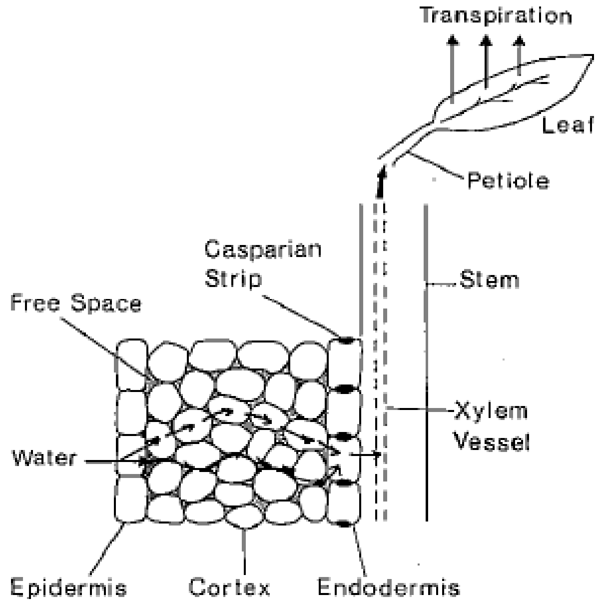
Ca^{2+} uptake



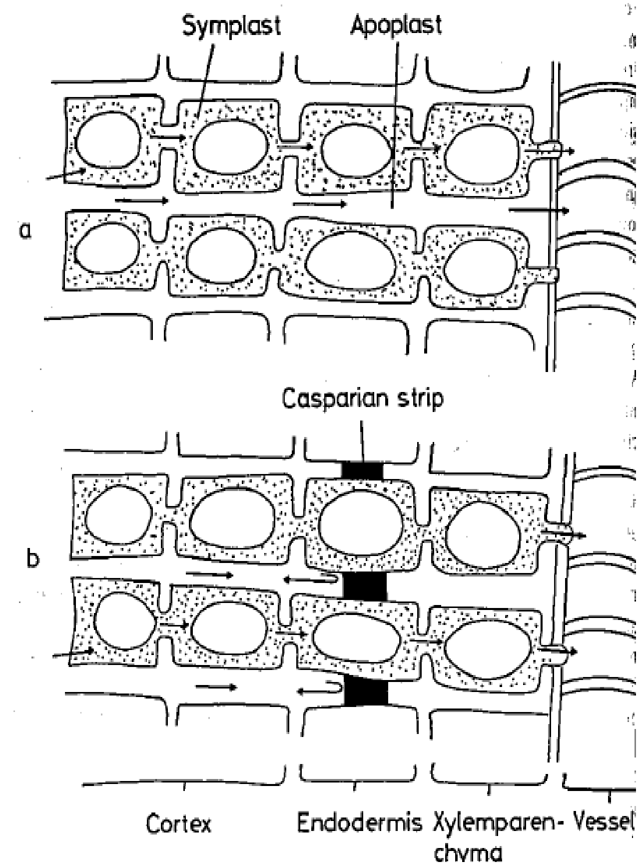
www.rmutphysics.com/charud/general/1/silviculture/root-cap.gif

Function and behavior Ca^{2+} in the plant

- Ca^{2+} transport through apoplast.
- Young roots do not have Casparian strips.
- In older roots Casparian strips block the transport of water with ions through the apoplast.



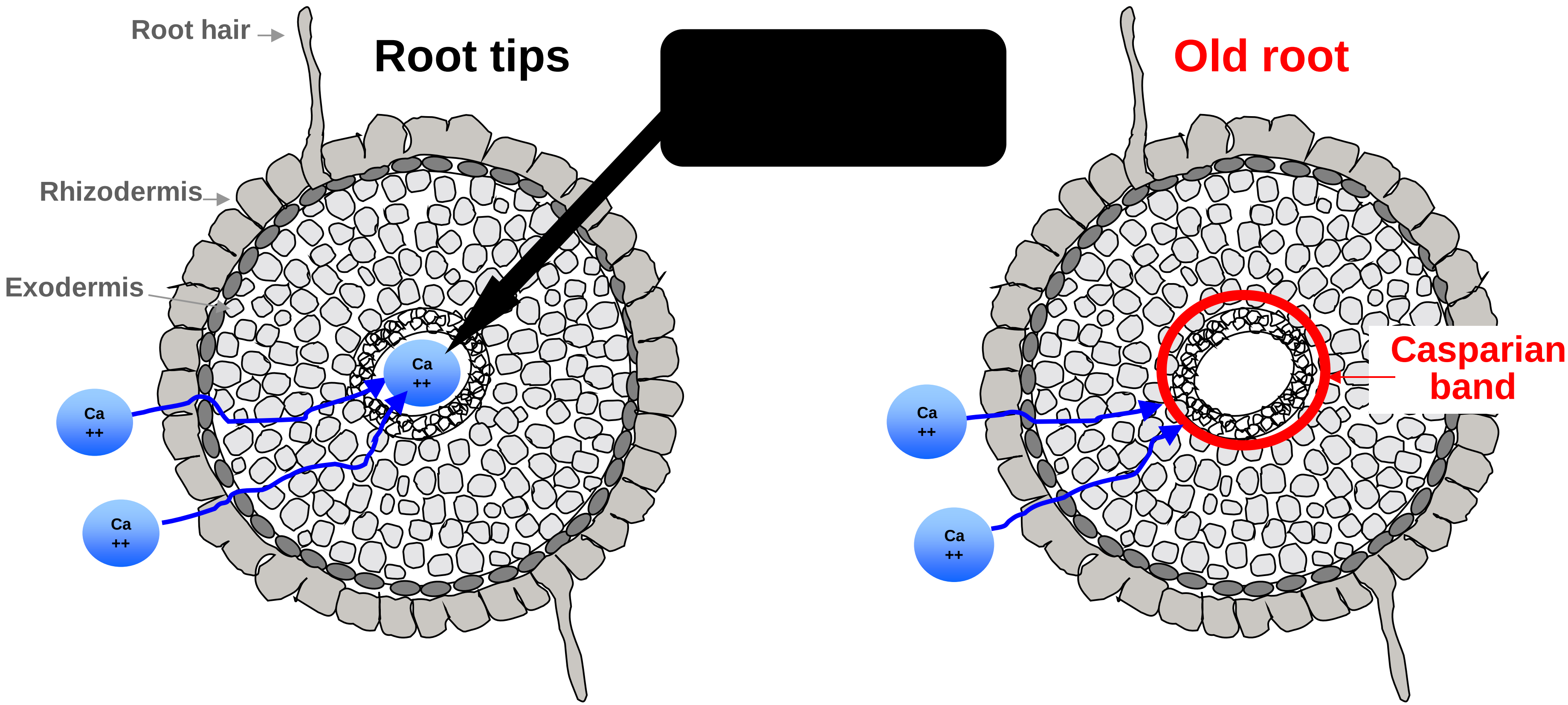
Principles of plant nutrition. Mengel and Kirkby 1987



Principles of plant nutrition. Mengel and Kirkby 1987

High Ca uptake by roots tips, where the Casparian band is not yet developed

Microscopical cross section of a root

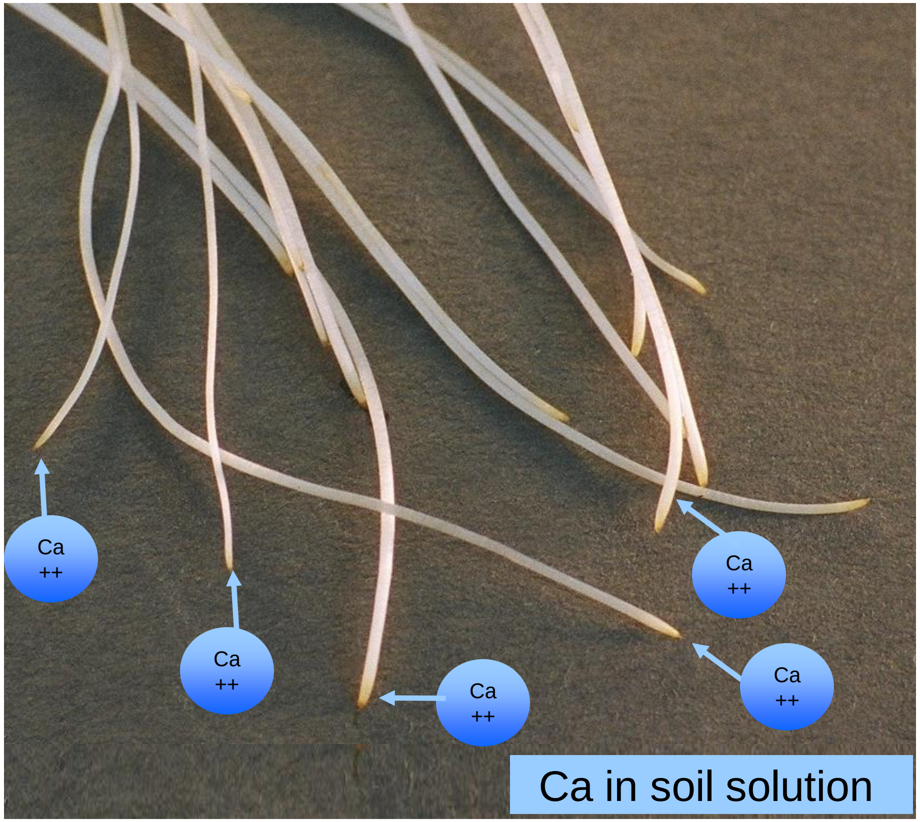


In older roots the Ca transport is hindered by a physical barrier, the "Casparian band".

Ca uptake by plant roots

- Ca is mainly taken up by root tips.
- Therefore root growth is a prerequisite for good Ca uptake.
- As a Ca transport back to the root tips is impossible, root growth depends on continuous Ca supply from the soil.

Ca uptake mainly by root tips



REF: Kwast, Research Centre Hanninghof, Yara - Head lettuce roots

Root growth depends on a continuous calcium supply by the soil solution

Root tips die in a short term when there is not enough calcium in soil solution.

Because calcium transport

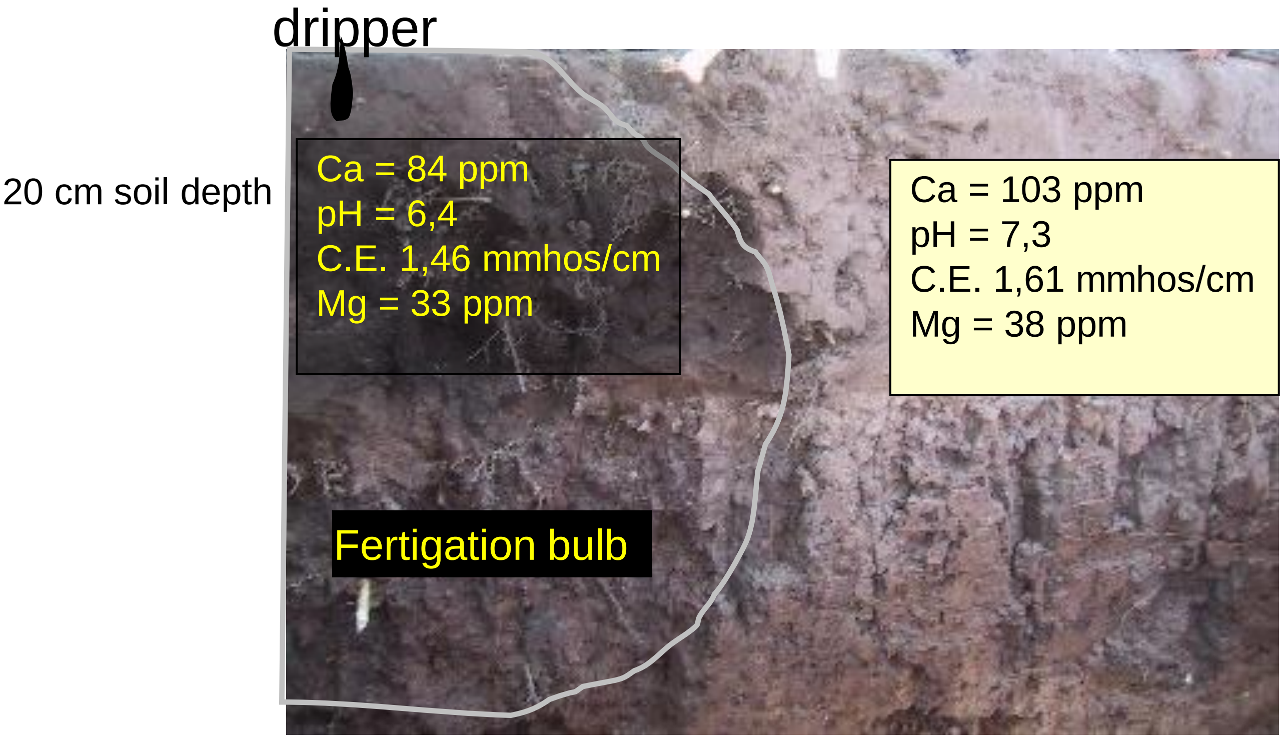
"back to the roots"

is not possible.

(Yara Brazil/Adubos Trevo; Citrus)

Is it important to include calcium in the fertigation solution?

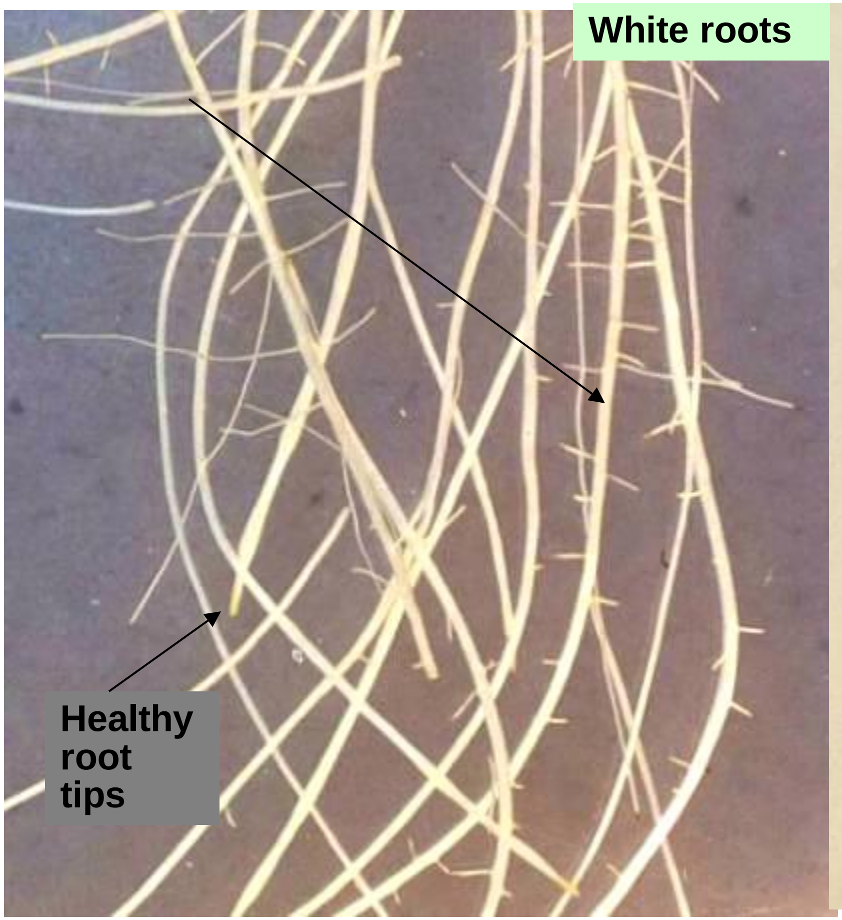
Even on a calcareous soil, one year of fertigation with a Ca-free solution resulted in declining Ca availability in the wetted zone



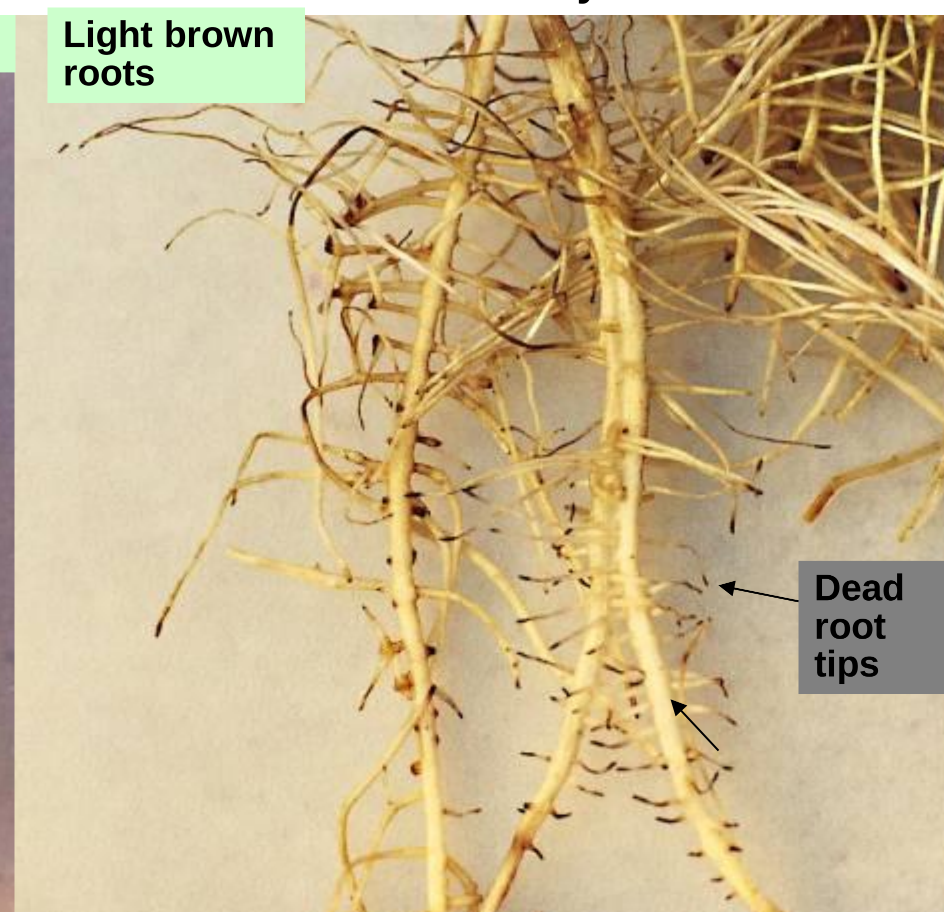
Citrus orchard in Argentinia, 2004, Juan Palma SQM

With Ca deficiency, root growth is stunted- more branching and tip death

Healthy Roots

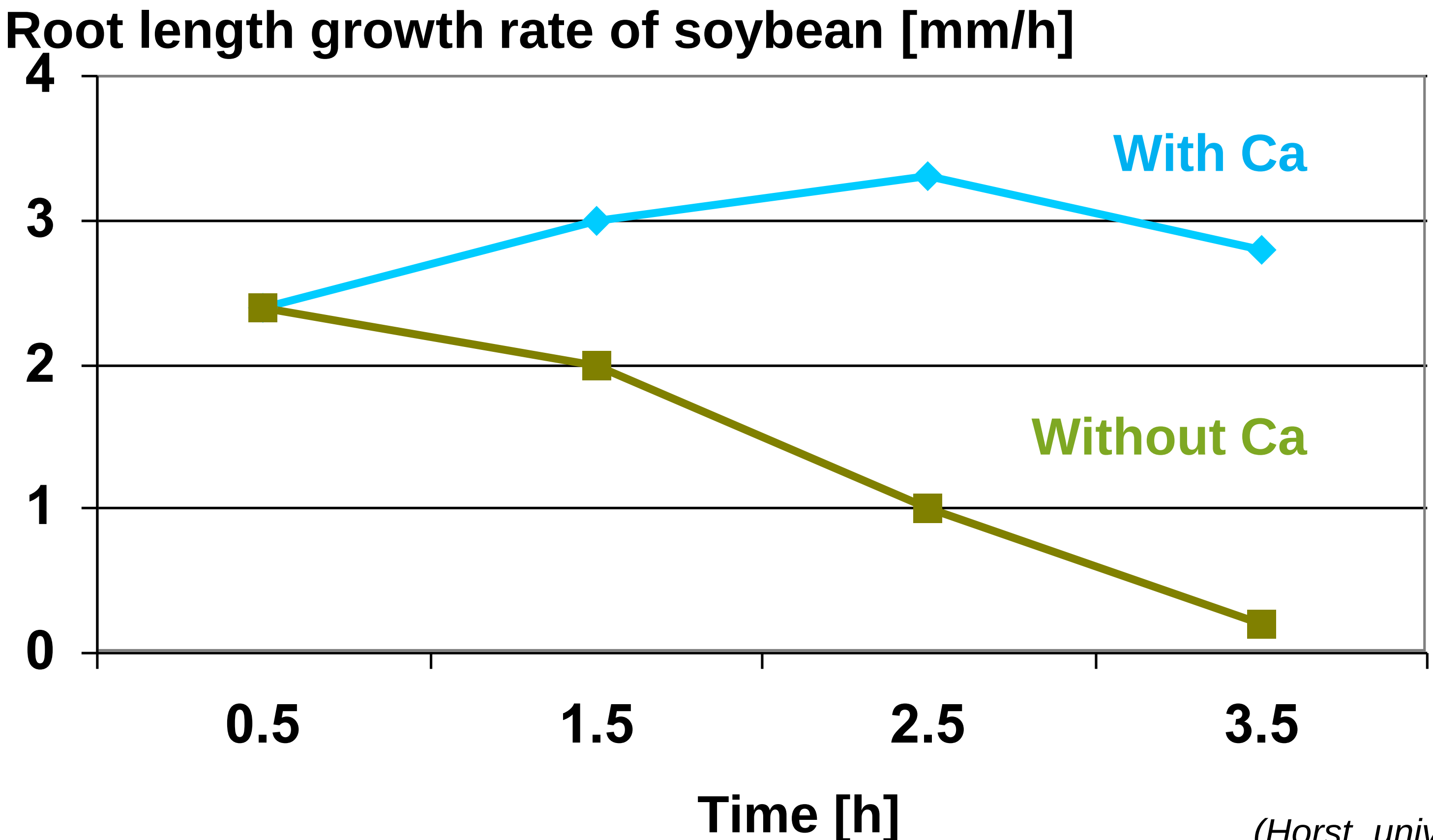


Ca Deficiency



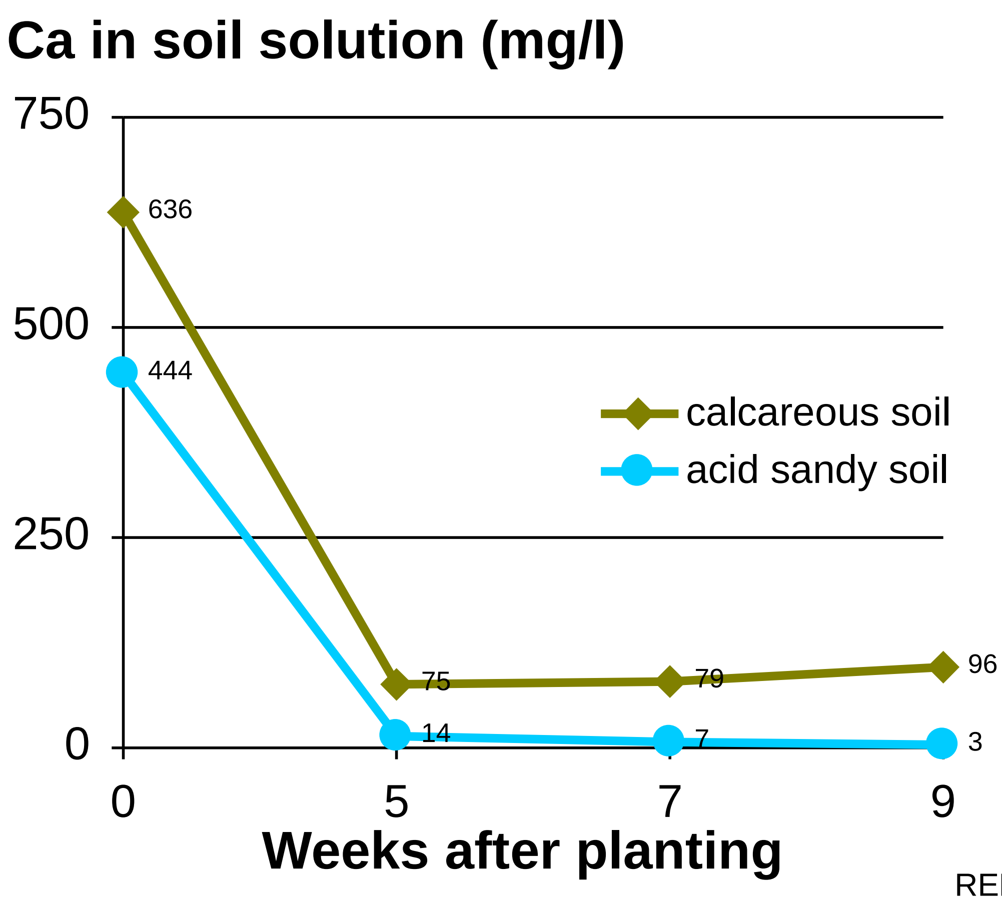
(Head lettuce roots; Kwast, Research Centre Hanninghof, Yara)

Root growth requires continuous Ca supply



(Horst, university Hannover)

Crops can dramatically reduce the soil solution Ca concentration



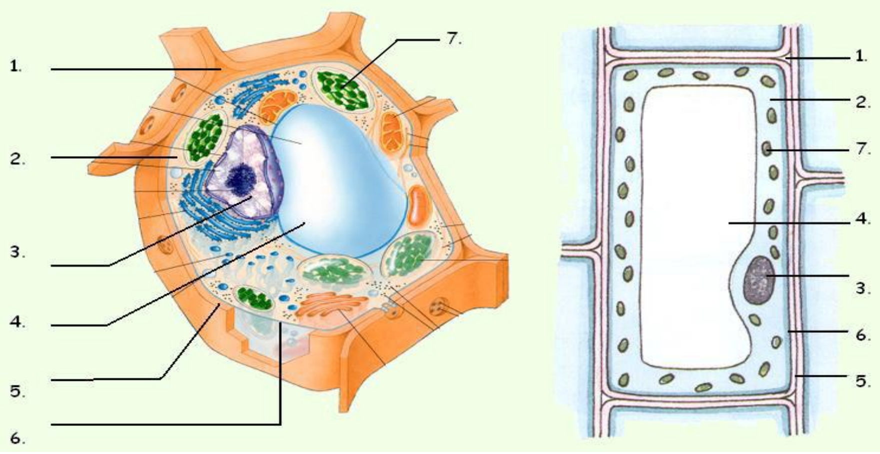
Trial code: 2008-DE-CAL-G-31

(pot trial with broccoli in calcareous soil from Spain and acid sandy soil from East Germany; suction cups were placed in top soil layer 0-5 cm; without Ca supply).

REF: Pot trial, Research Center Hanninghof, Yara

Function and behavior of Ca^{2+} in the plant

- Ca^{2+}: mainly present in apoplast and vacuole.
- Some cell parts contain Ca: mitochondria, endoplasmatic reticulum.
- Ca^{2+} is actively moved from cytoplasm in the vacuole.
- Ca^{2+} ; low concentrations in cytoplasm and chloroplast:
  - Ca^{2+} slows down enzyme activities.
  - Ca^{2+} reacts with phosphate and forms calcium phosphate (precipitation)
  - Ca^{2+} competes with Mg $^{2+}$

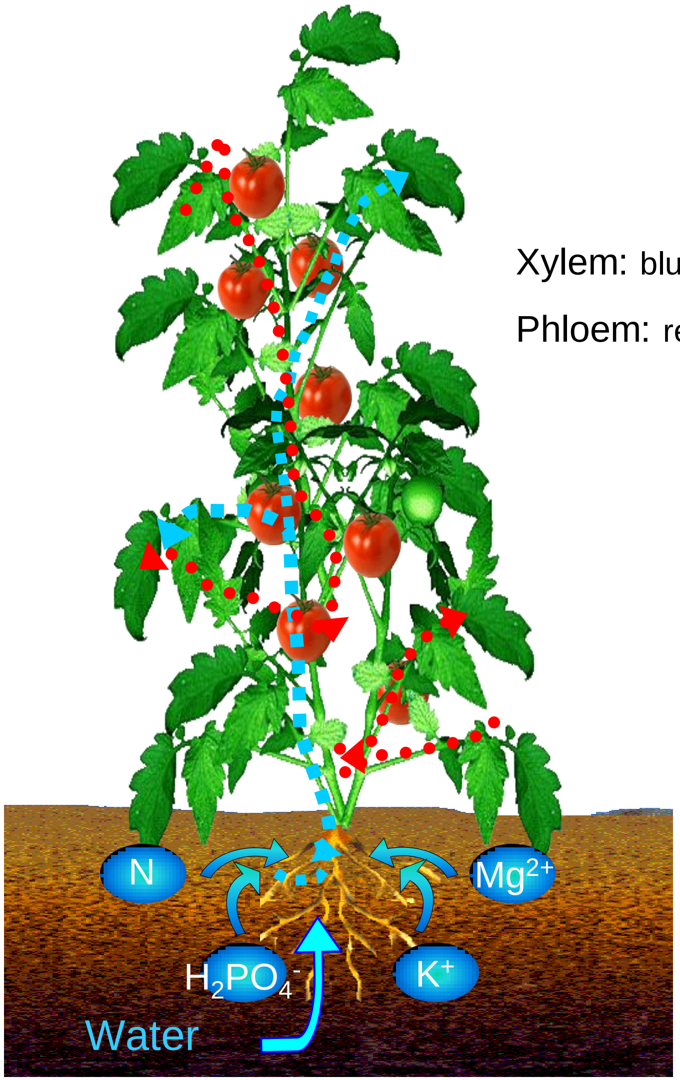


1. Inter cellular space
2. Cytoplasm
3. Cell nucleus
4. Vacuole
5. Cell wall
6. Cell membrane
7. chlorophyl

www.biologiesite.nl/plantenceldelen.jpg

Function and behavior of Ca^{2+} in the plant

- Ca^{2+} moves through xylem to the evaporating parts of the plant (leaves).
- Ca^{2+} remains present in leaves.
- Redistribution through phloem is very limited.
- Fruits dependent on Ca^{2+} supply through phloem are lacking sufficient quantity
- Calcium in abundance present as calcium oxalate



Xylem: blue

Phloem: red

Deficiency symptoms

Calcium deficiency:

- Deficiency in non evaporating- and young plant parts.
- Plant strength of tissue and membranes is reduced. Development of weak spots and important material (fluids) can leak away.
- Meristem tissue can be affected.
- Quick ageing of plant (tissue, leaves etc).
- Physiological problems:
  - Tip rot (tomato, paprika)
  - Glassiness (lettuce)
  - Heart rot (celery)
  - Pit (apple)

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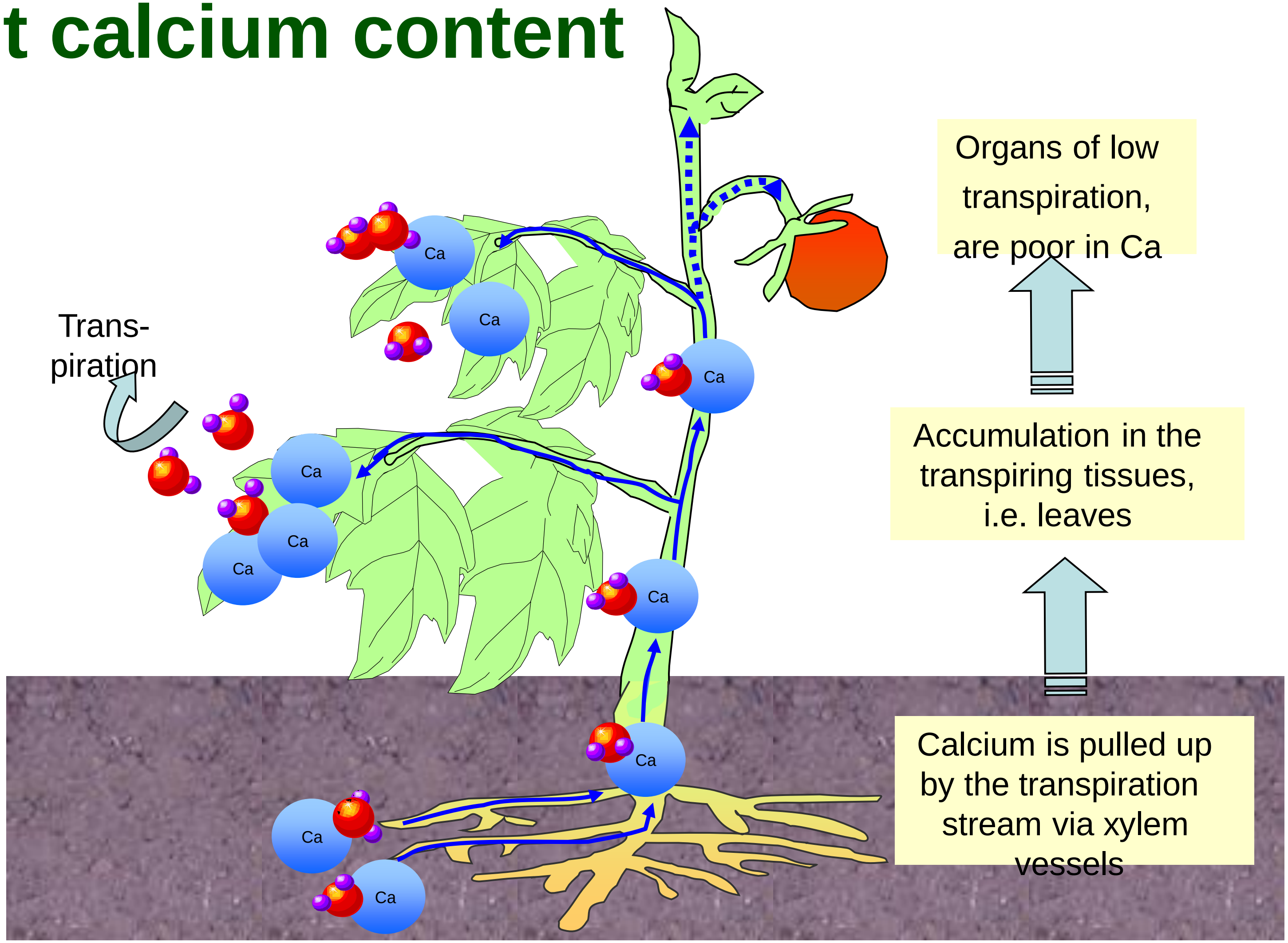
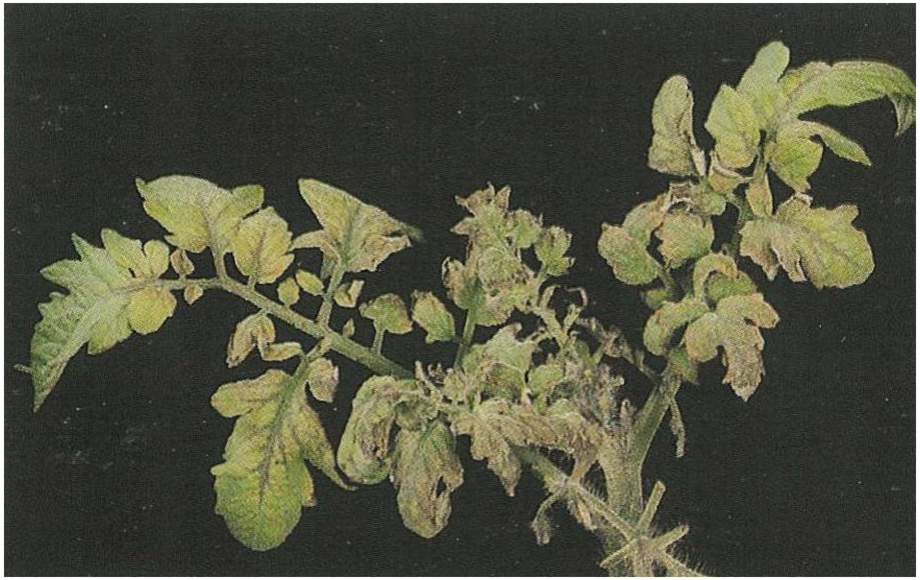
Leaf analysis is NOT a good indication of fruit calcium content



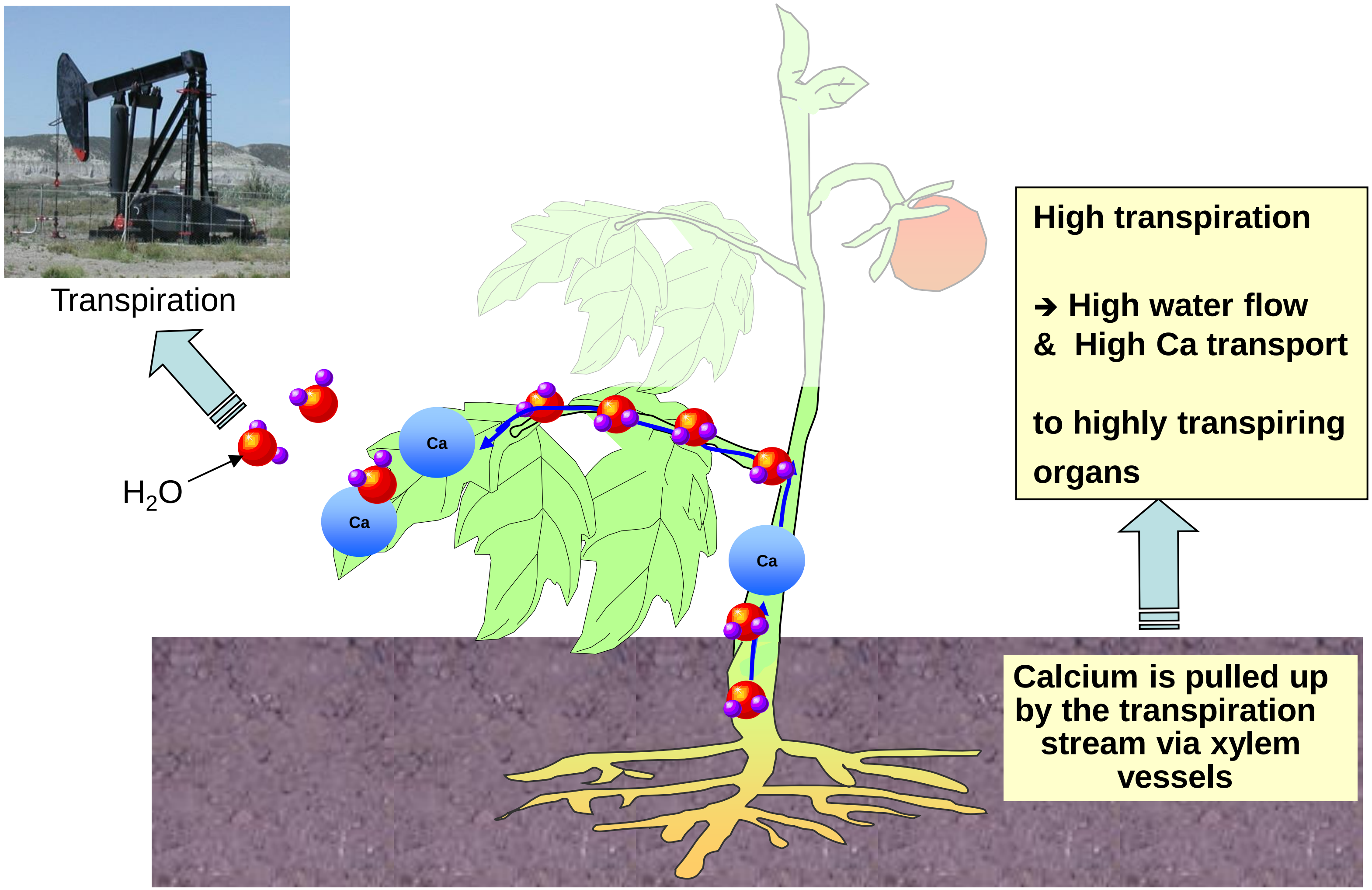
Deficiency symptoms



Calcium deficiency Tomato

Source: PPO, The Netherlands

Ca is transported in the xylem… driven by transpiration



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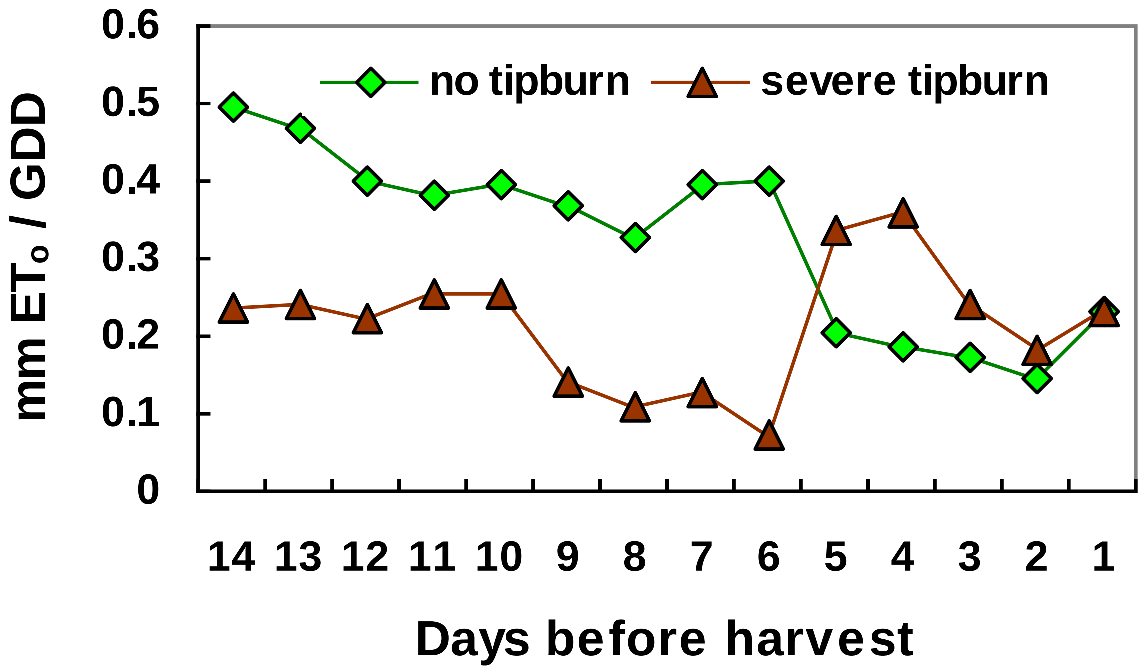
Calcium effects on tipburn of romaine lettuce :

Survey of 15 commercial fields for tipburn severity, and soil and plant Ca

- saturated paste soil Ca
- Ca concentration of inner leaves
- tipburn severity (mean number of affected leaves / plant)

Restricted transpiration limits Ca to expanding tissue :



Already after 5 days of Ca deficiency the crop develops severe deficiency symptoms

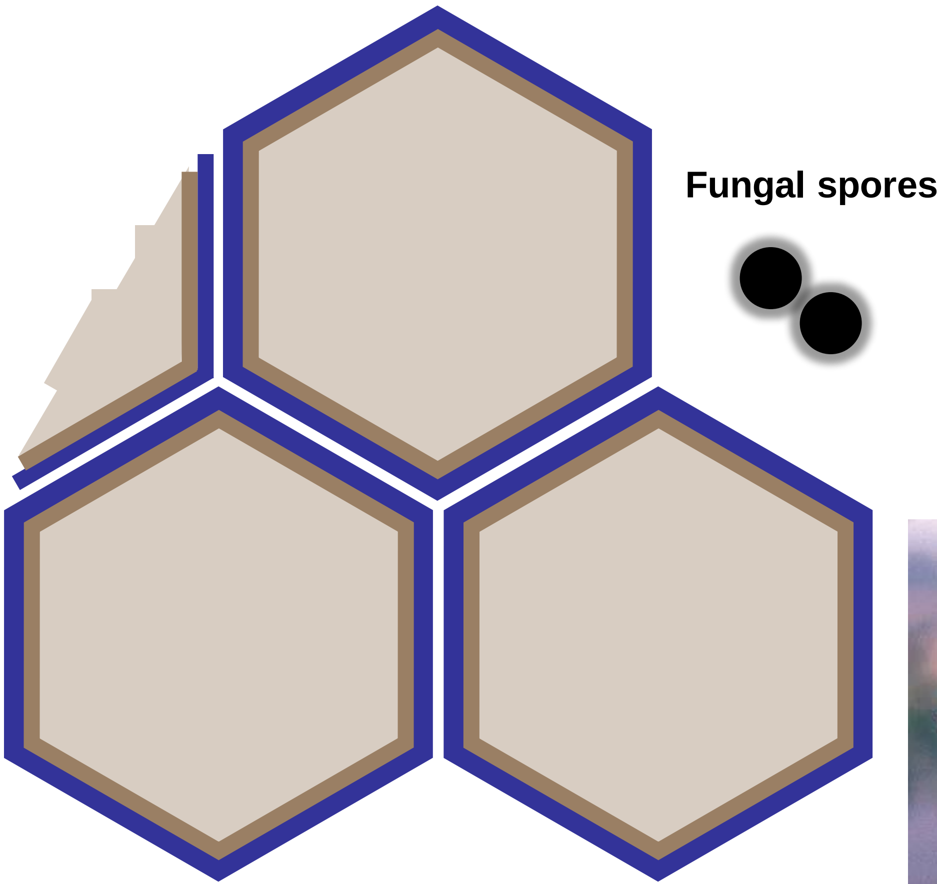
Calcium and defense mechanisms

- Calcium for stronger cell walls and better integrity of cell membranes - mechanical resistance

- Speed up leaf hardening (young leaves become firm in a shorter term, and are therefore less attractive to insects/vectors).

- Reduce the activity of enzymes produced by the fungi or bacteria to penetrate the plant tissue

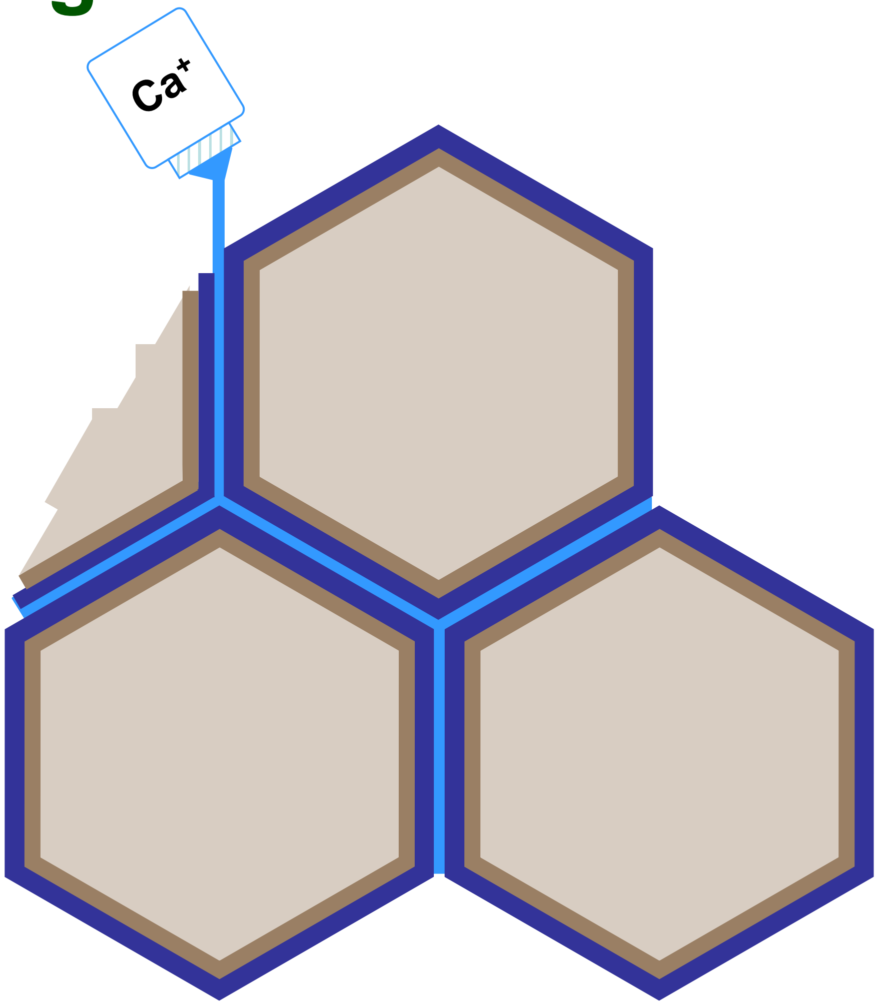
...without the ‘calcium glue’ cells are free to move apart



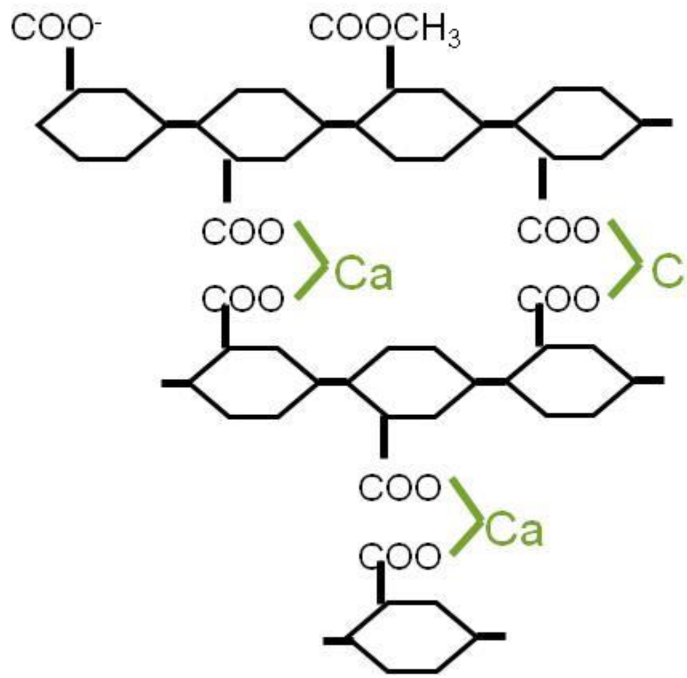
Physiological disorders & splitting of fruit

Susceptibility to attack by diseases

Calcium binds the cells together - like a glue…

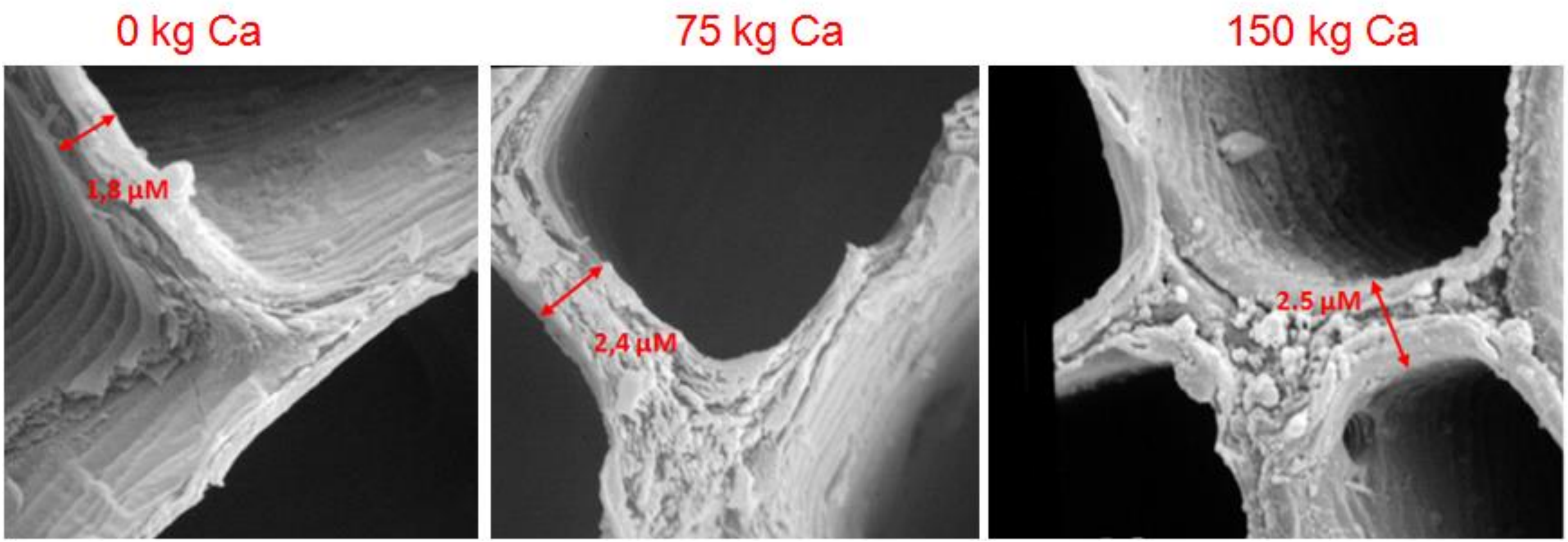


Ca saturates the free COO^- groups of the pectins in the middle lamella



Under the microscope it becomes visible - Stronger cells with calcium

Cell walls of xylem tissue in the fruit peel of banana were stronger with Calcium Nitrate; Costa Rica; 3rd year of trial



REF: Corbana (2008)

Calcium deficiency - apples : bitter pit

(Kwast, Research Centre Hanninghof, Yara)

Calcium deficiency - apples : bitter pit

REF: Yara, webtoprint

Calcium deficiency – cabbage : tip burn

(Harriman, Yara International)

Calcium deficiency – cabbage : tip burn

(Simmes, Research Center Hanninghof, Yara)

Ca deficiency in chinese cabbage, first symptoms are black spots at the leaf margins of the younger leaves inside the head

(Wojcieszek, Yara Poland (top), Kwast, Yara International (below))

Calcium deficiency in cauliflower

Necrotic leaf margins and "claw-like" deformations at the youngest leaves. Finally also the curd dies off.

(Kwast, Research Centre Hanninghof, Yara; Yara Phosyn)

Plants cannot redistribute or “recycle” calcium

- Therefore deficiency symptoms are most pronounced in *young growing tissue….*

REF: Simmes, Research Center Hanninghof, Yara

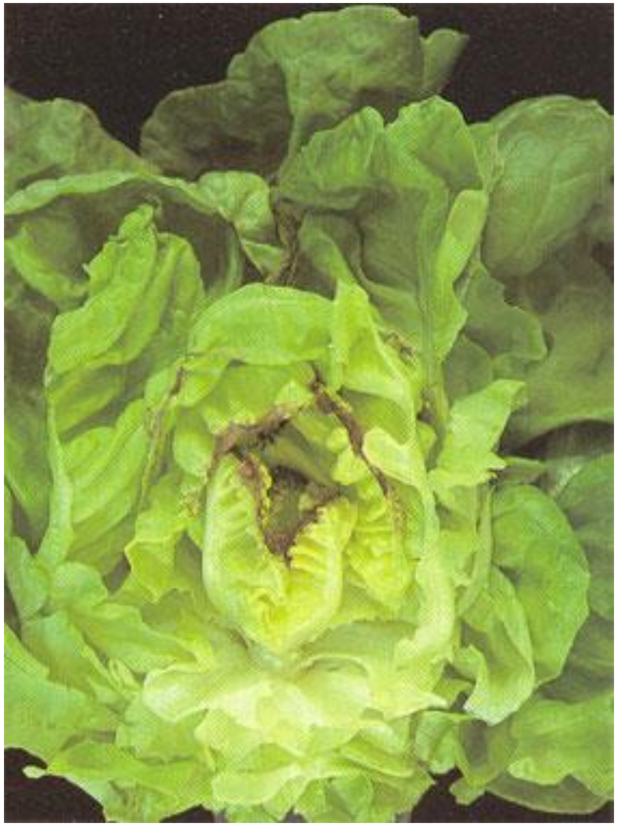
With Ca deficiency – the heart of lettuce finally dies

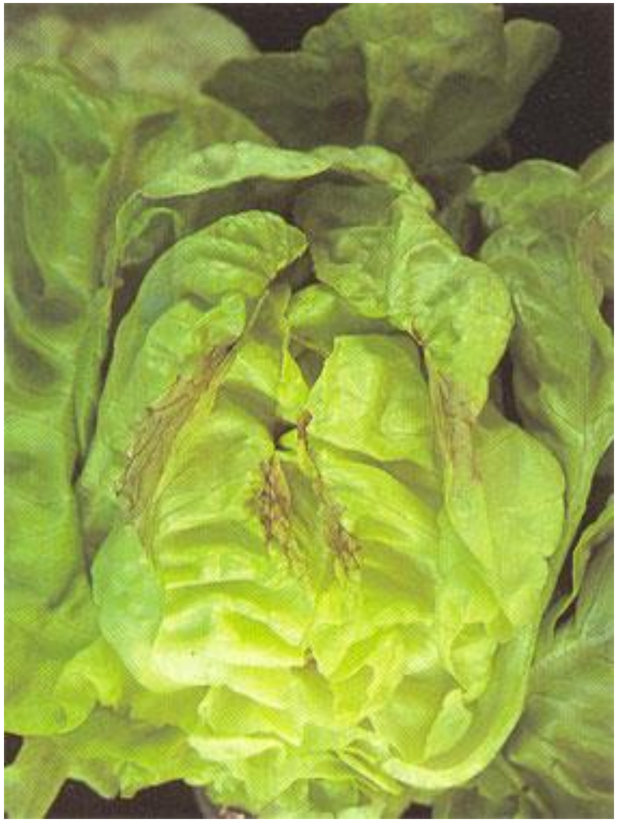
REF: Kwast, Research Center Hanninghof, Yara

Calcium deficiency - cucumber

REF: Yara, webtoprint

Calcium deficiency - lettuce : tip burn





(Bull, Yara International)

Calcium deficiency - lettuce : tip burn

(Kwast, Research Center Hanninghof, Yara)

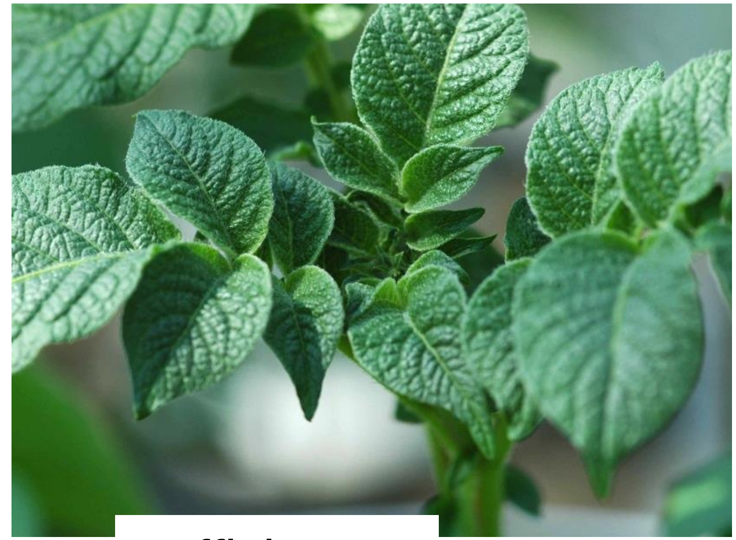
Calcium deficiency - Melon : blossom end rot

REF: Yara, webtoprint

Calcium deficiency – pepper : blossom end rot

(Kwast, Research Center Hanninghof, Yara)

A short term deficiency of Ca (5 days) resulted in Ca deficiency at the shoot tips

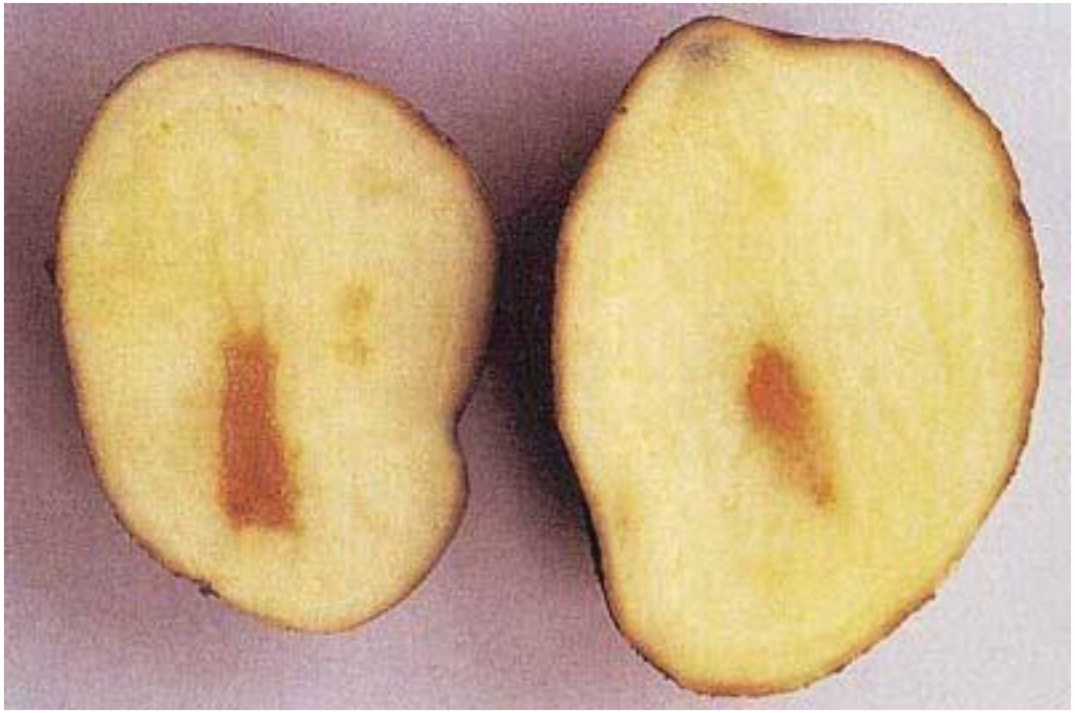


Ca deficient

Sufficient Ca

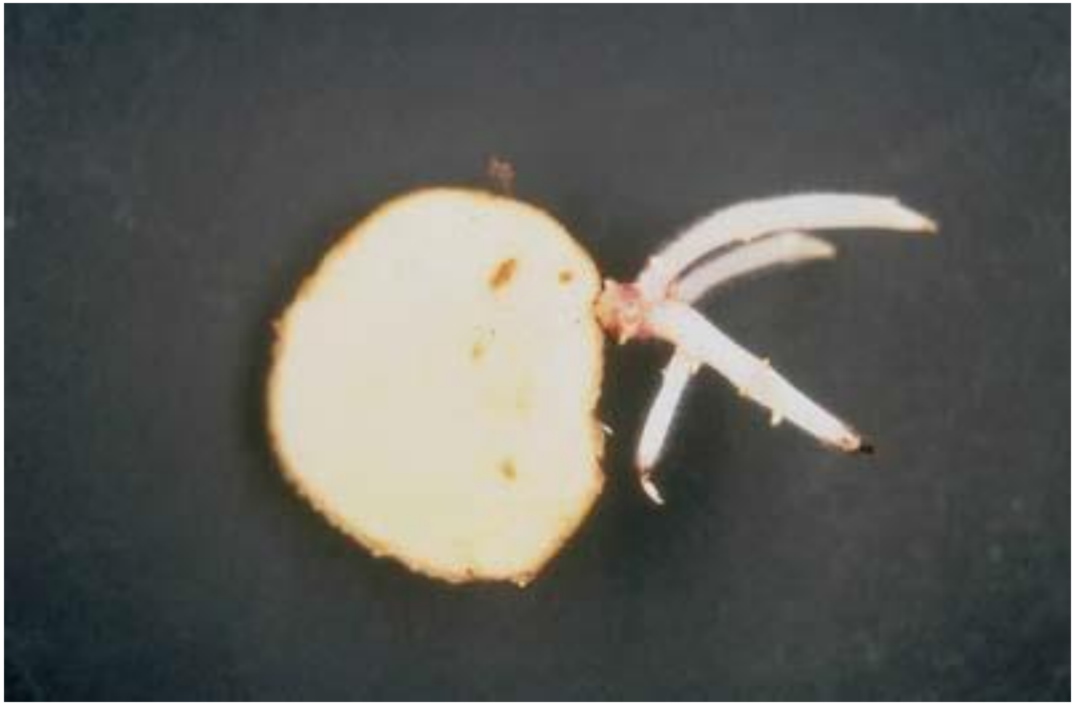
(Goto/Kwast, Research Center Hanninghof, Yara)

Calcium deficiency - potato : internal brown spot



REF: Yara, webtoprint

Calcium deficiency – potato : internal rust spot



REF: Yara, webtoprint

Calcium deficiency - strawberry

- Ca can not be remobilized, therefore the deficiency symptom
  appear on the youngest leaves

(Simmes, Research Center Hanninghof, Yara)

Calcium deficiency - tomato : blossom end rot

REF: Yara, webtoprint

Calcium deficiency - tomato : blossom end rot

(Kwast, Research Center Hanninghof, Yara)

When to apply Ca ?

- In general Ca is continuously needed during the whole growth period.
  - Roots need a continuous Ca supply for growth.
  - Ca uptake follows the growth curve.

- However, there are growth phases in which applying supplemental Ca will benefit the plant, for example:
  - During periods of fast growth to counteract Ca dilution.
  - During early growth to support requirements during cell division.
  - During periods of plant stress, as calcium is important for stress amelioration, periods of low transpiration.

Calcium:

Impact on Soil Physical Properties

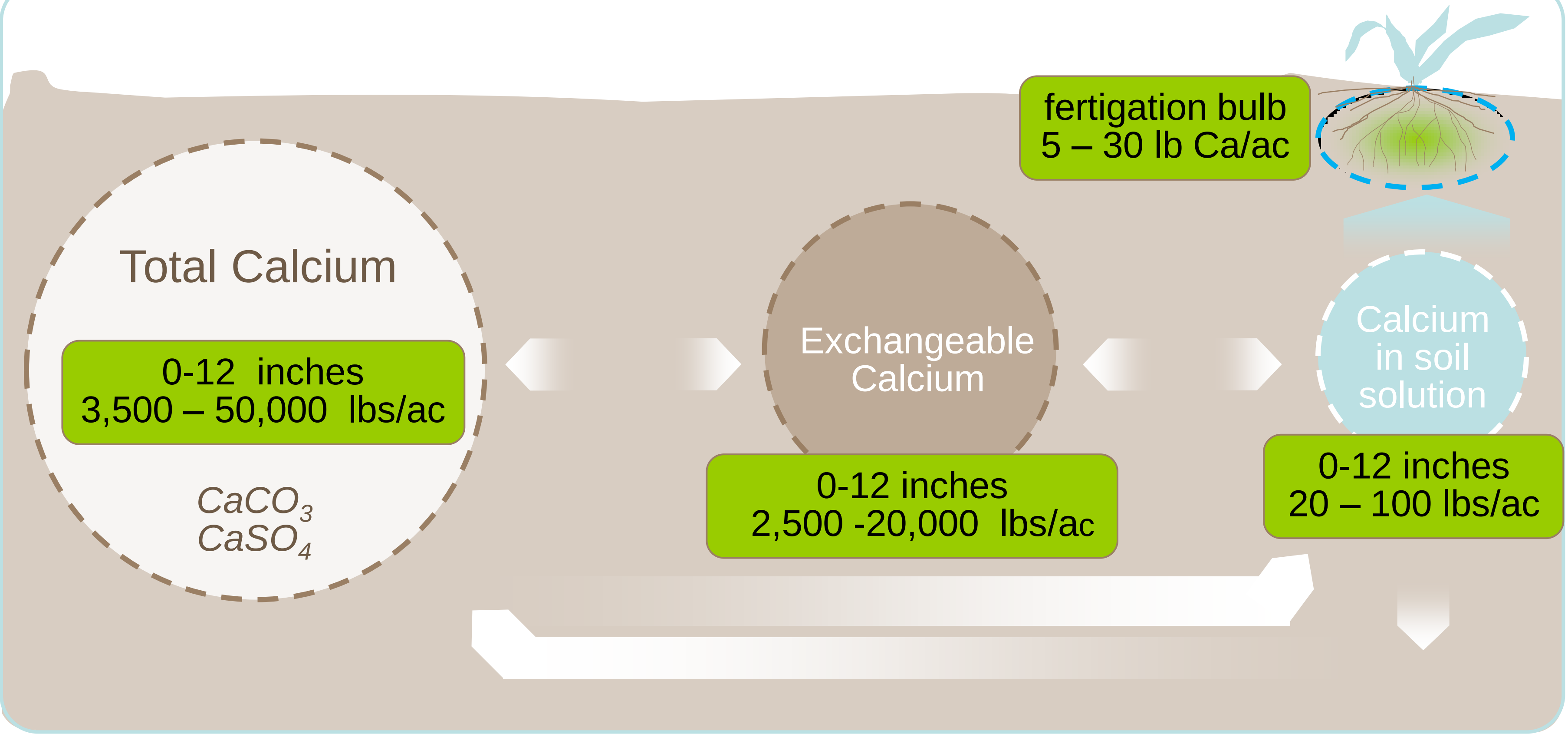
Other Benefits of Gypsum

- **Improve soil properties**
  - **Improve water infiltration**
  - **Control soil erosion and crusting**

- **Reduce contaminates in water runoff.**

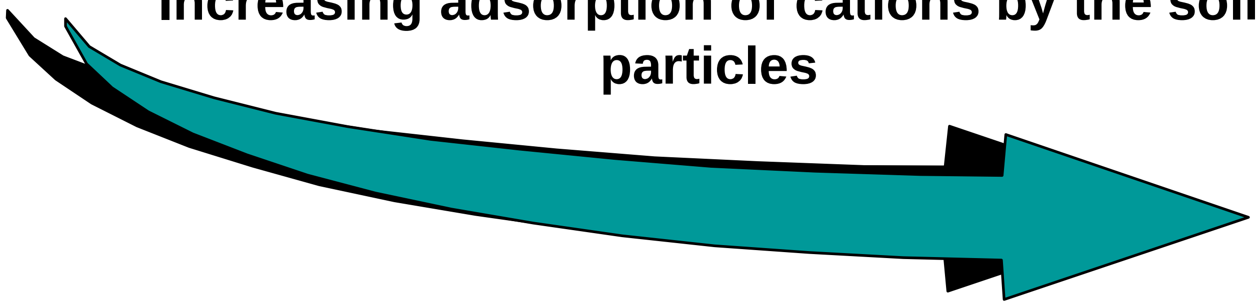
Ca dynamics in the soil

- Example: typical soil



The Ca content in soil solution is relatively low because Ca is preferentially adsorbed at the cation exchange sites of soil

Increasing adsorption of cations by the soil particles



Na^{+} NH_4^{+} H^{+} K^{+} Mg^{2+} Ca^{2+} AL^{3+}

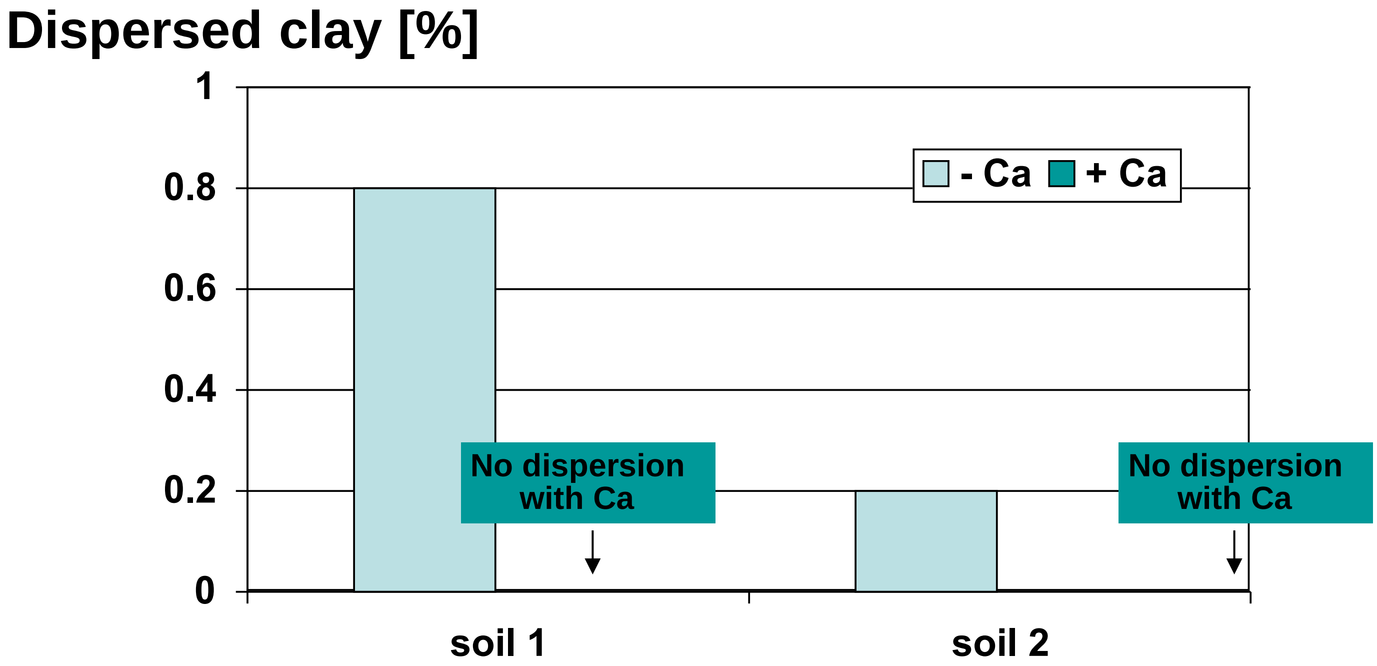
Sodium < Ammonium < Proton<Potassium<Magnesium < **Calcium**<Aluminum

Ca is essential for good soil structure

- Improves soil water infiltration
- Improves soil water movement
- Improves aeration
- Reduces surface crusting

Ca prevents dispersion of clay

…which means reduction of crusting & soil compaction



REF: Greene et al. -1988

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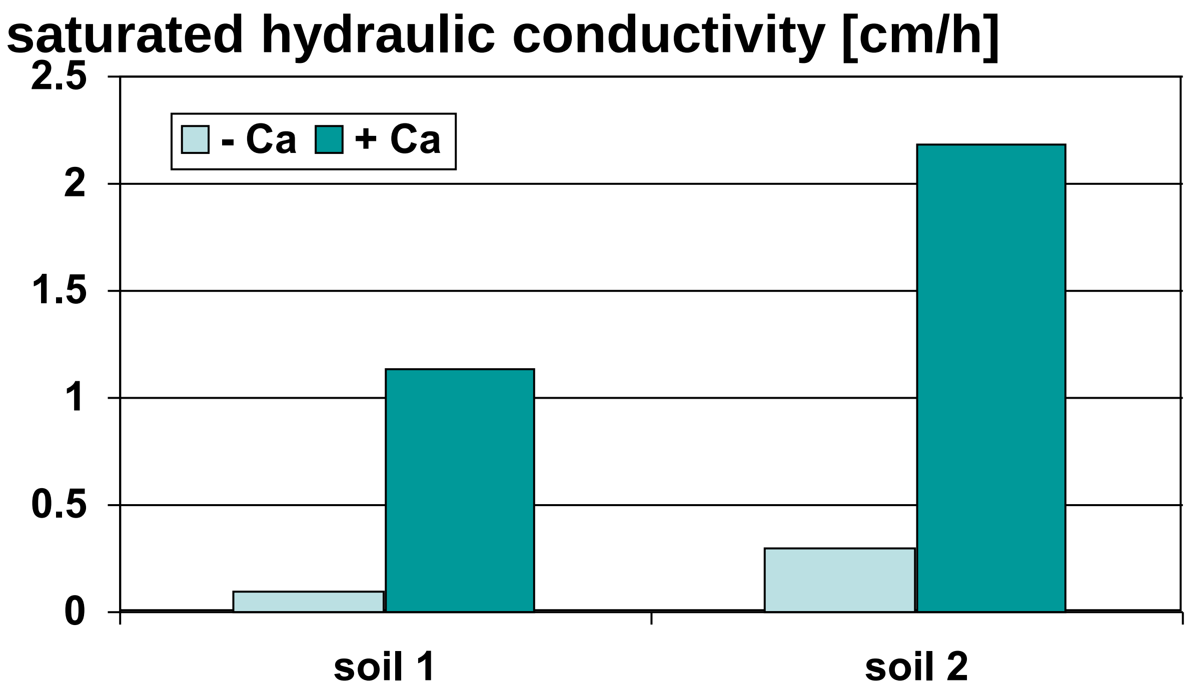
Calcium creates a fine crumb soil texture which improves hydraulic conductivity

…which means higher water infiltration and water mobility



REF: Greene et al. -1988

Gouy-Chapman Double Layer

- Some of the earliest work was done in the early twentieth century by Gouy and Chapman.
  - Gouy, G. 1910. Sur la constitution de la charge électrique à la *surface d’un* electrolyte. Ann. Phys. (Paris) [IV] 9:457-468.
  - Chapman, D.L. 1913. A contribution to the theory of electrocapillarity. Philos. Mag. 25(6):475-481.

Diffuse Double Layer

- **Cations are attracted to… and anions are repelled by negatively charged soil colloids**

- *These interactions are described by Coulomb's law:*

Where F is the force of attraction or repulsion, q and q' are the electrical charges, r is the distance of charge separation, D is the dielectric constant and K is a proportionality constant.

$$F = \frac{qq'}{Dr^2} K$$

Coulomb's law

- **The strength of ion retention or repulsion:**
  - increases with increasing ion charge
  - Increases with increasing colloid charge
  - Increases with decreasing distance between the colloid surface and the source of charge

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The Stern layer

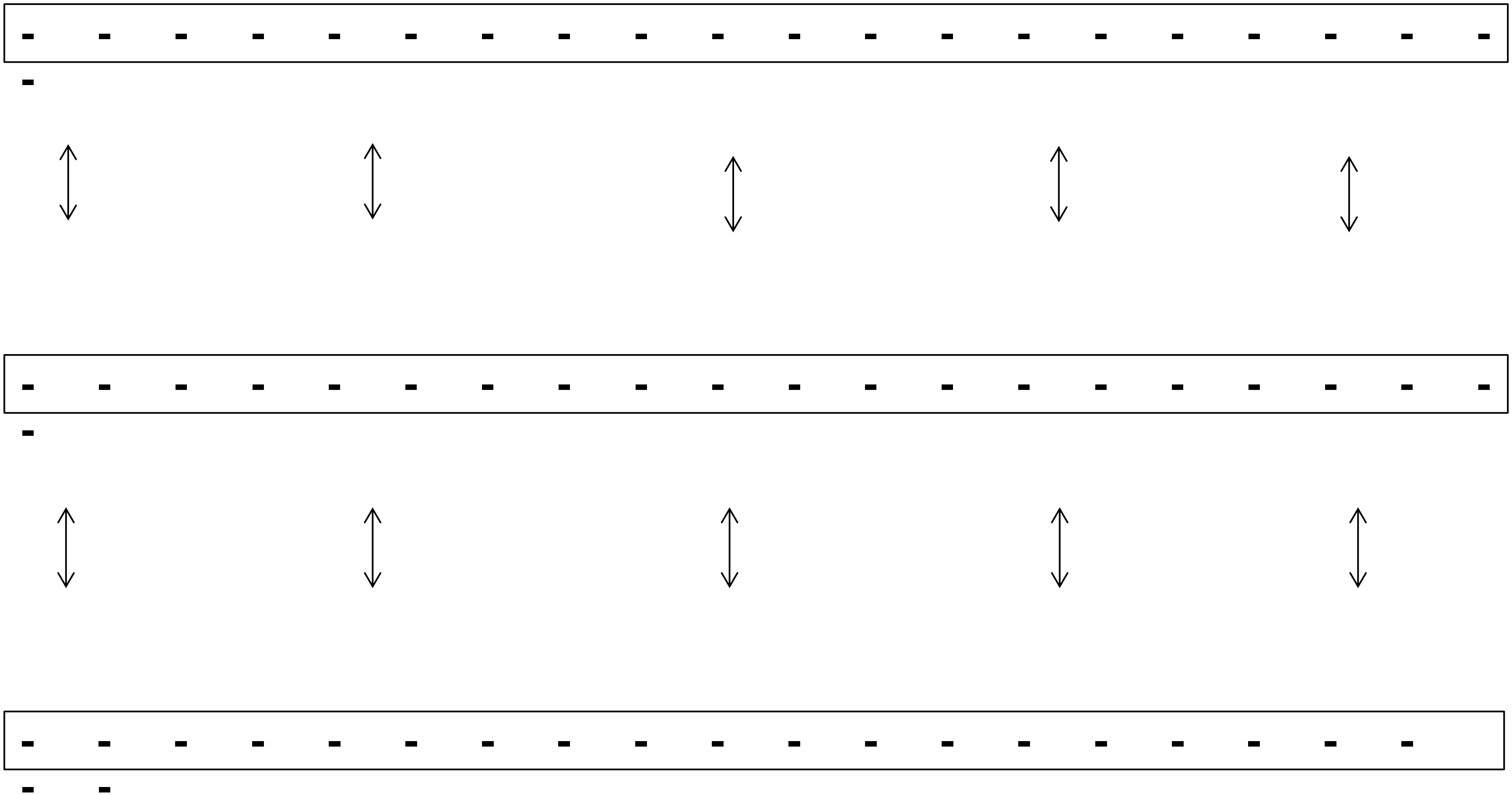
- Stern improved the Gouy-Chapman model by assuming that some ions are tightly held close to the colloid surface.
- Strongly hydrated ions (Na for example) are more tightly held in the Stern layer compared to more loosely hydrated ions that have higher concentrations in the diffuse layer.

See Shainberg and Kemper 1966. SSSAP 30:70-713.

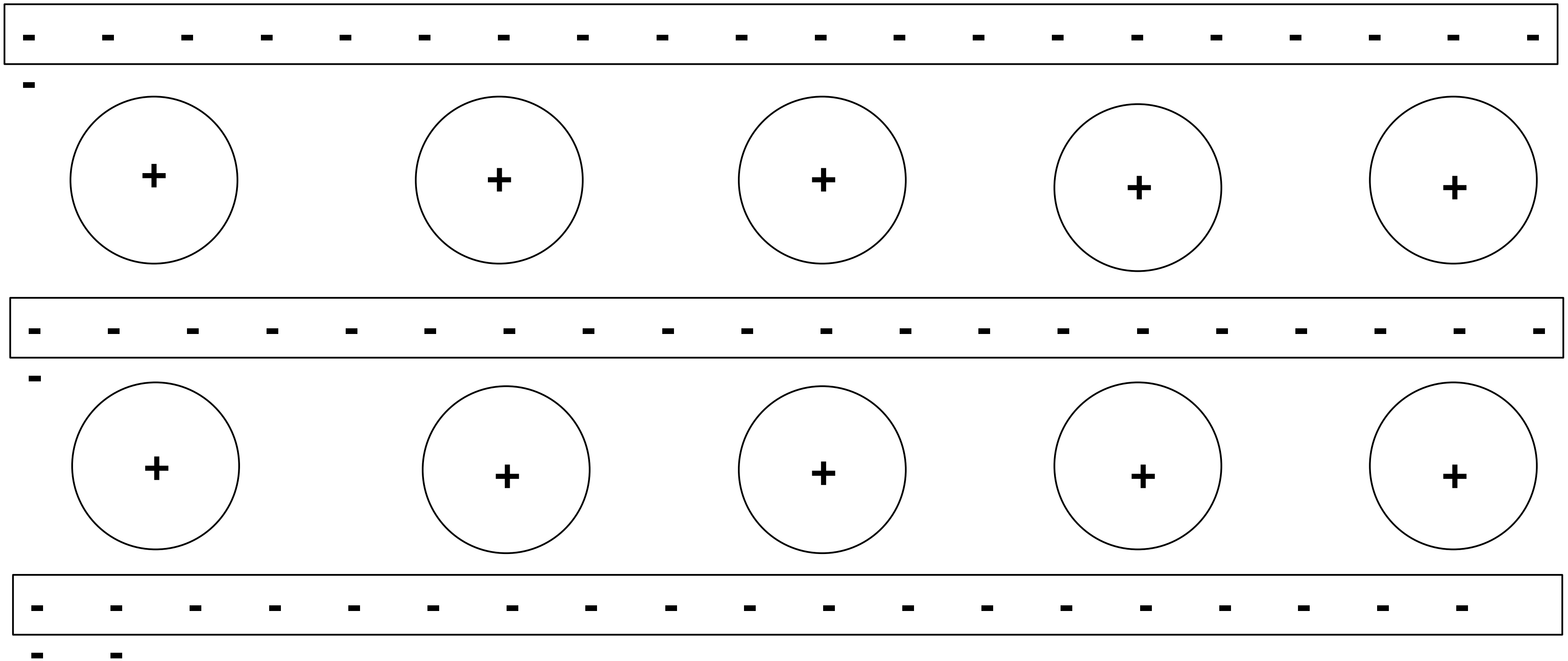
How Ca impacts soil physical properties:

- Clay plates are negatively charged and repel each other
- Cations *‘bridge’ the plates and bind them* together
- The force depends on the ionic charge and hydrated radius
- Higher charge = stronger binding force
- Smaller radius = stronger binding force

Clay platelets repel one another

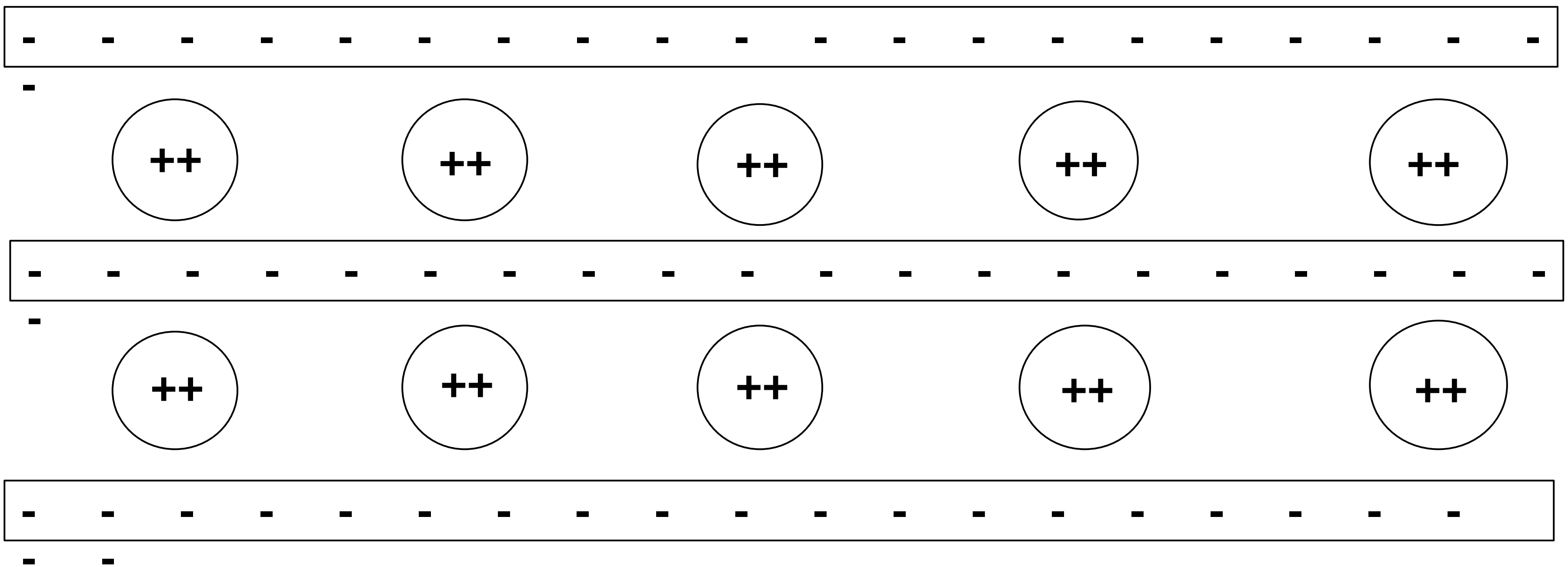


Cations bind clay platelets together



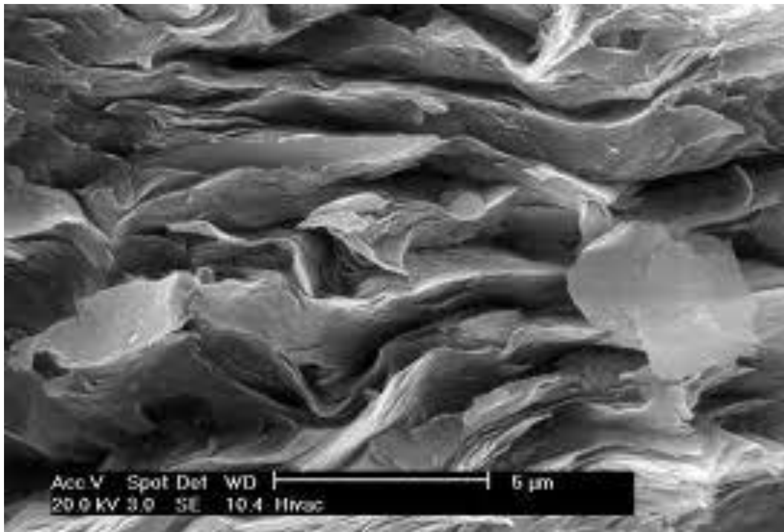
Na^{+} or K^{+}

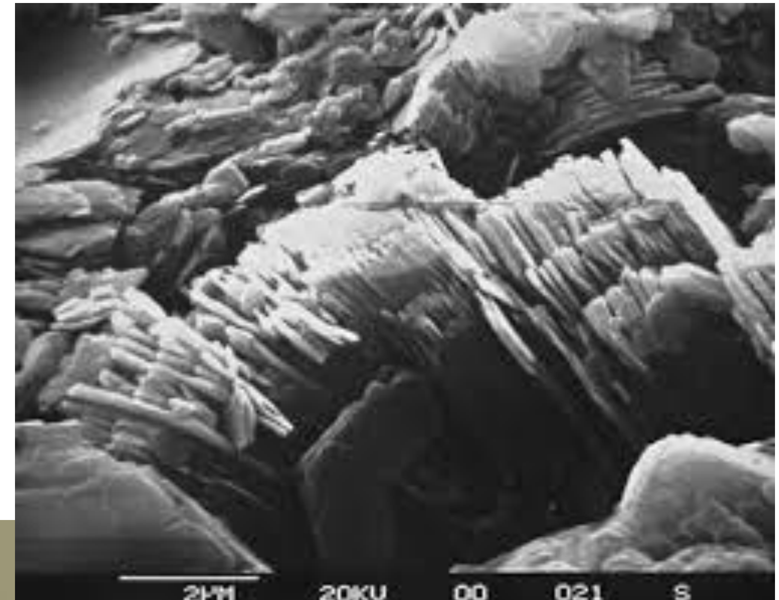
Cations bind clay platelets together

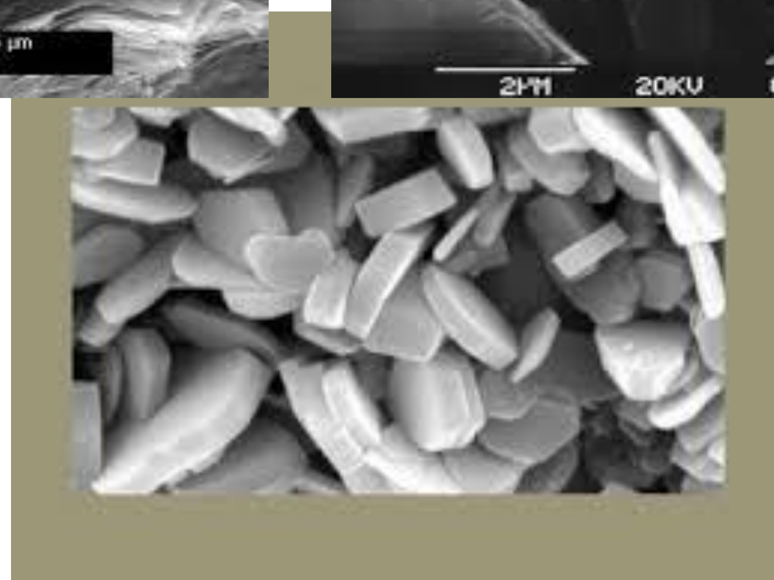


Mg^{2+} or Ca^{2+}

Photomicrographs of clay platelets







Assumptions

- Exchangeable cations exist as point charges.
- Colloid surfaces are planar and infinite in extent.
- Surface charge is distributed uniformly over the entire colloid surface.

Other Assumptions

- Clay particles are rigid flat surfaces.
- Soils are monomineralic.
- Soils contain iron oxihydroxides and organic matter but these are often not considered when discussing clay-ion interactions.
- MOST of these assumptions are incorrect, but the diffuse double layer theory appears to explain the role of sodium in swelling and dispersion.

Cation Comparison

Element	Charge	Ionic radius	Relative flocculating power
		-- nm --	
Na	1	0.79	1
K	1	0.53	1.7
Mg	2	1.08	27
Ca	2	0.96	43

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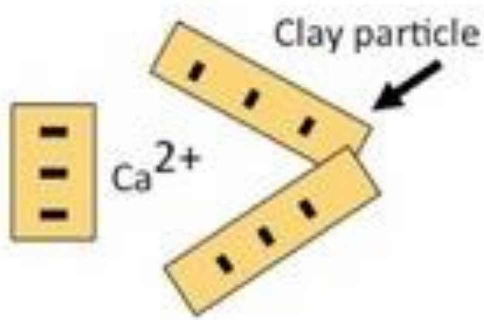
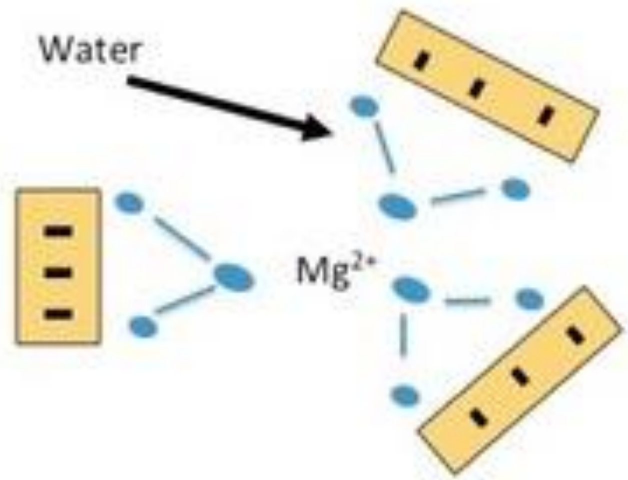
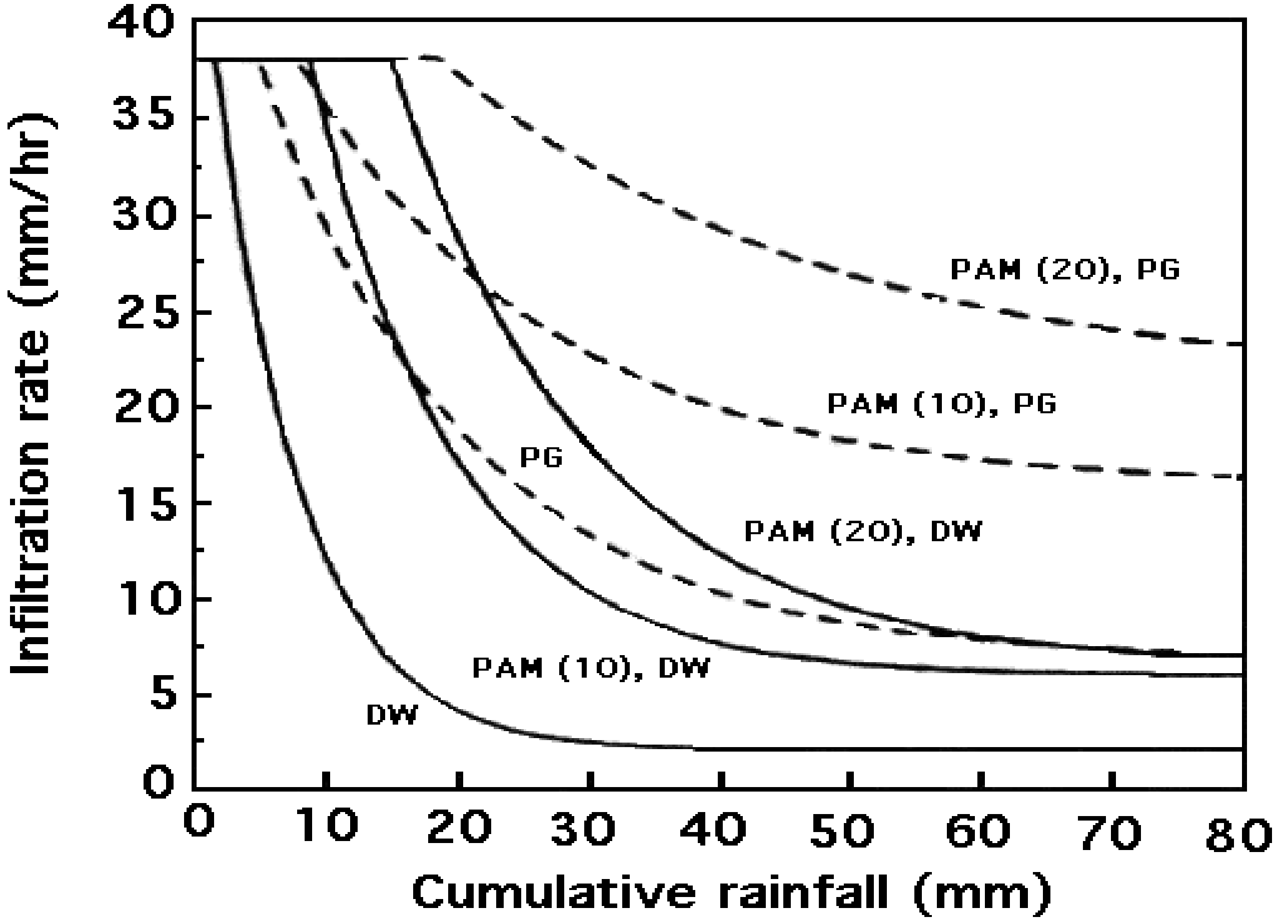
Soil Structure

Flocculated	Dispersed





Influence of Aggregate Stability on Infiltration Rate (Laboratory study)



- PAM is a chemical soil stabilizer
- PG (gypsum)

From: Flanagan DC, L.D. Norton, and I. Shainberg. 1997. Trans. ASAE 40:1549-1554.

Solubility of Ca sources

- Plants take up Ca from the soil solution
- In order to increase the Ca concentration in the soil solution, sources with highly soluble Ca should be used

Ca source	Ca content	Water required to dissolve 1 lb Ca
	--%--	gallons
Calcium nitrate	19	0.6
Calcium chloride	36	1
Calcium sulfate (gypsum)	23	48
Calcium carbonate	40	7,940

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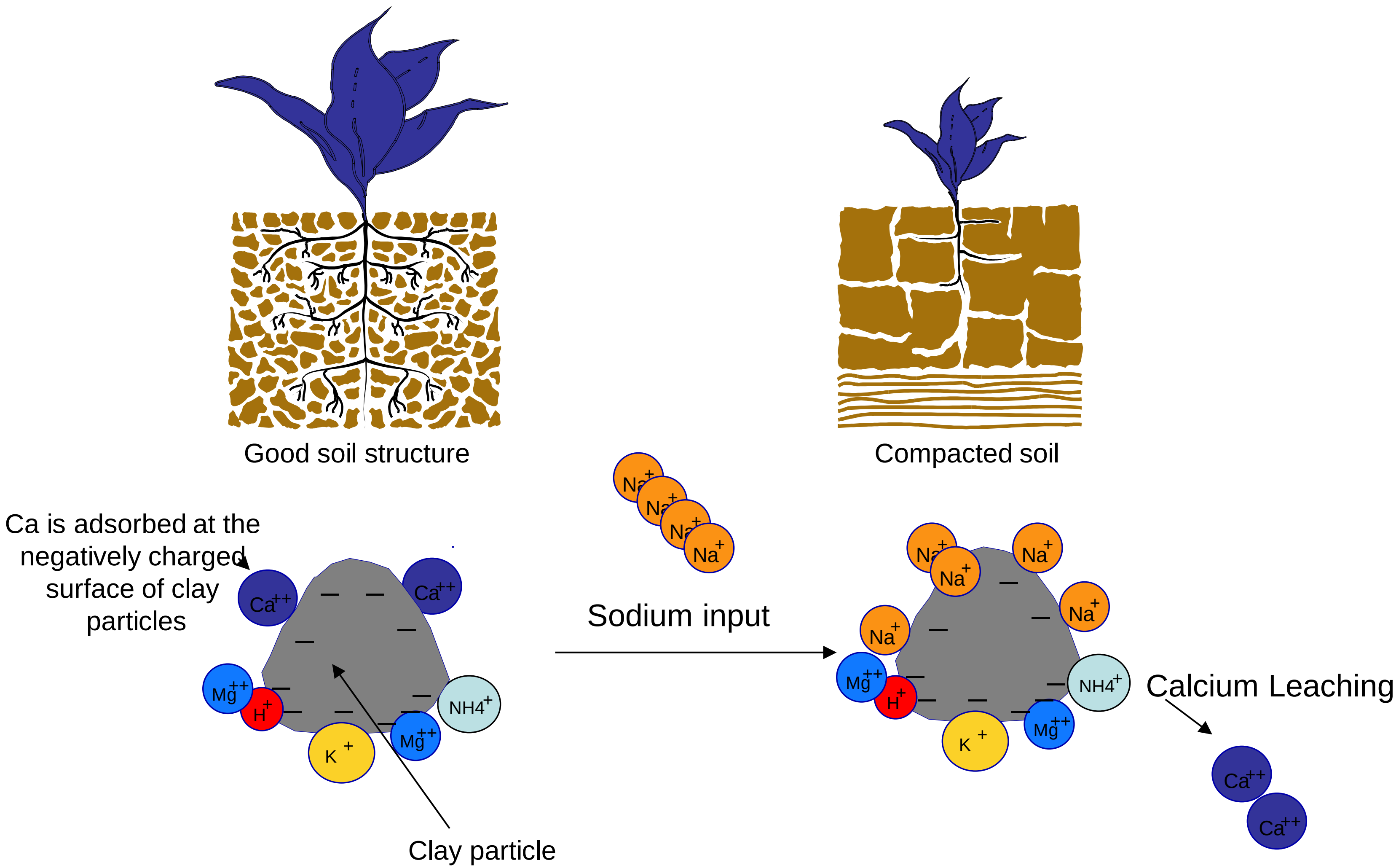
Ca dissolution:

Ca Source	lb dissolved in one acre inch of rain water
	------- lb material -------
$CaCO_3$	3 (if pH allows)
$CaSO_4$	560
Tropicote/CN9	450,000

Ca displacement by Na: soil structure is destroyed



Cation effects on soil

- **Low Ca soils tend to**
  - Become encrusted and
  - Have a poor soil structure.

- High Sodium Adsorption Ratio (SAR)
  - Is a result of an exchange of Ca by Na at the binding sites at the surface of clay minerals.
  - Leads to de-flocculation of clay.

➔ As a consequence, these soils have
  - Low water infiltration (hydraulic conductivity).
  - Poor aeration.

➔ Ca counteracts the sodium effect
  - Helps to keep the soil flocculated.
  - Improves water infiltration and aeration.

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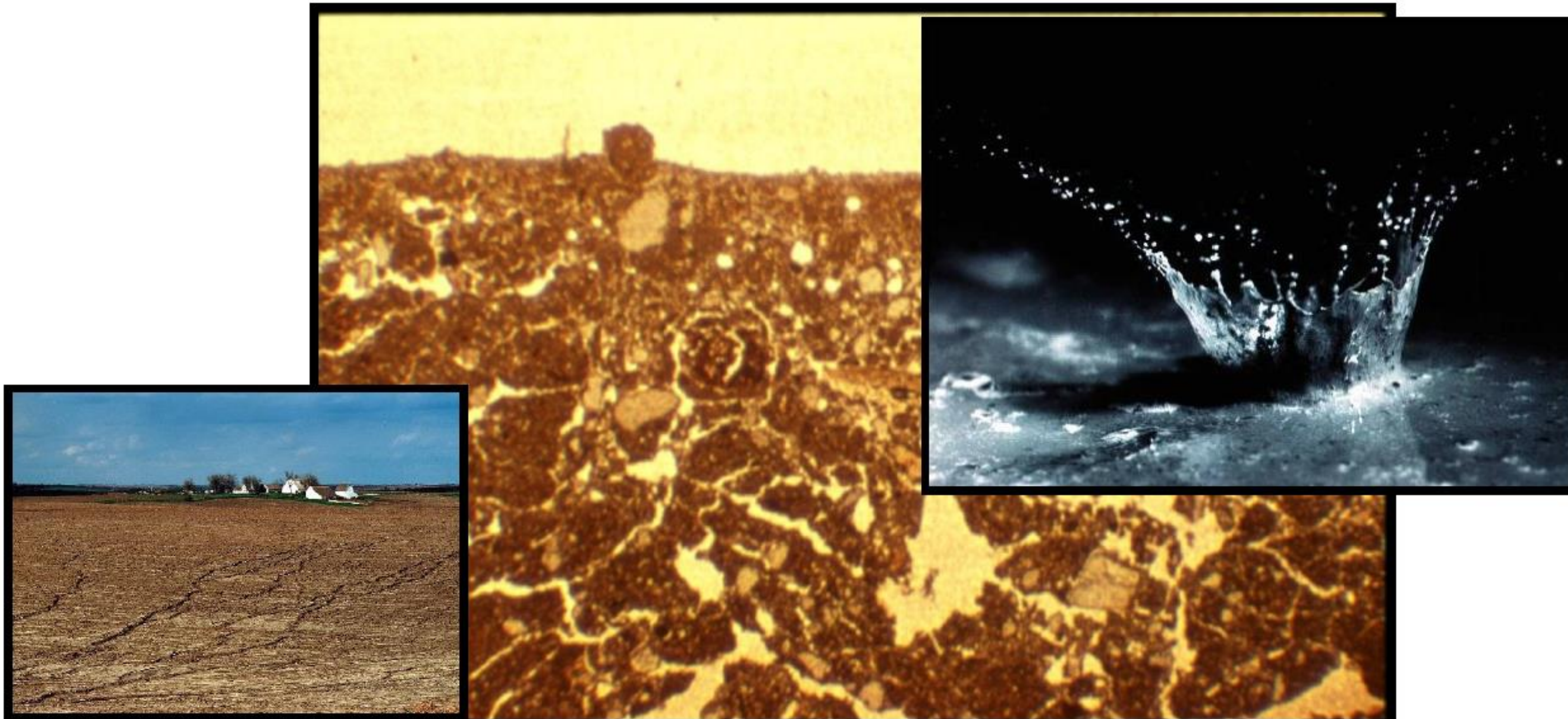
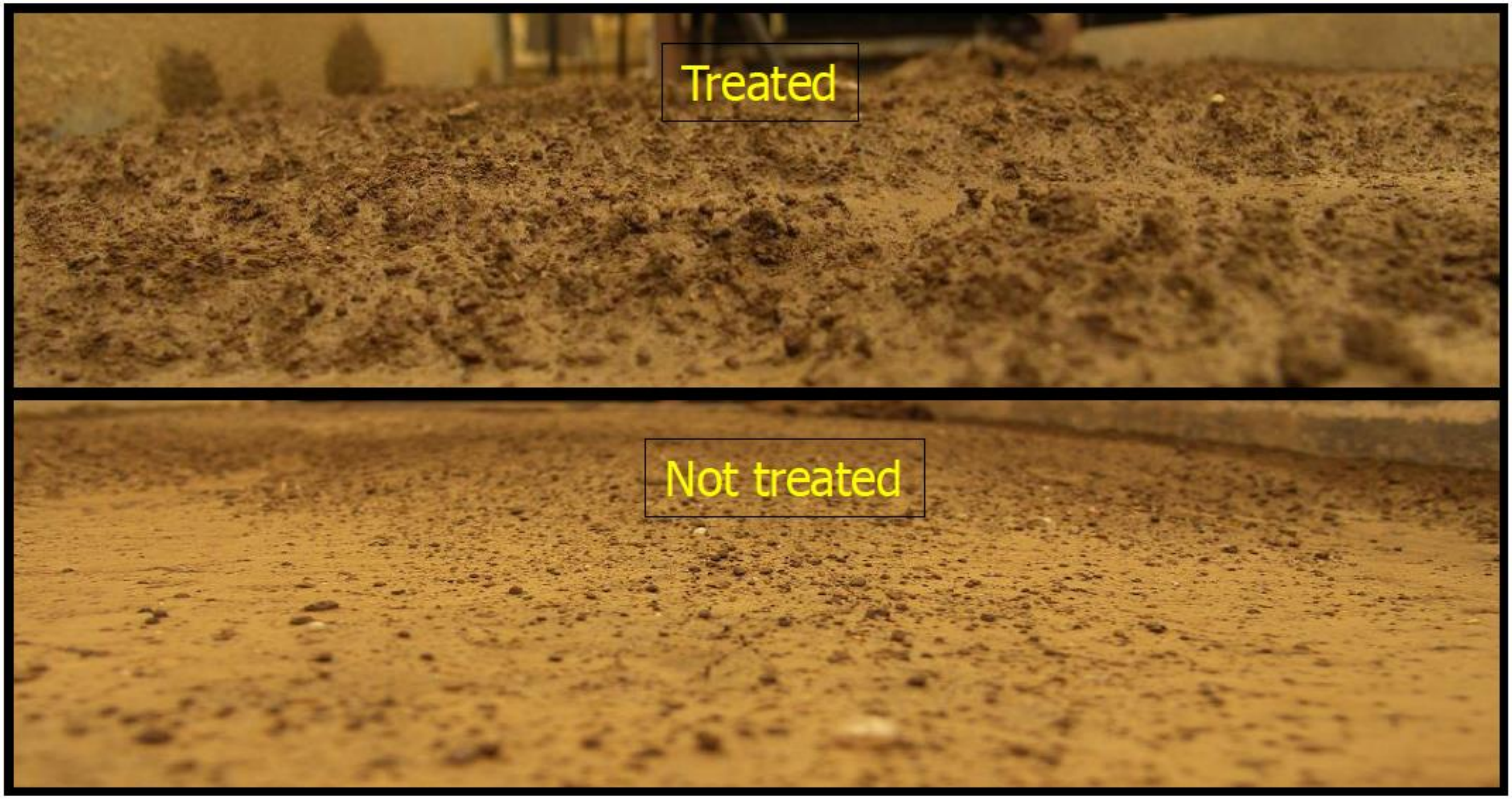
Surface application of gypsiferous products to change the physical or chemical properties of soil.

Photo courtesy of Darrell Norton

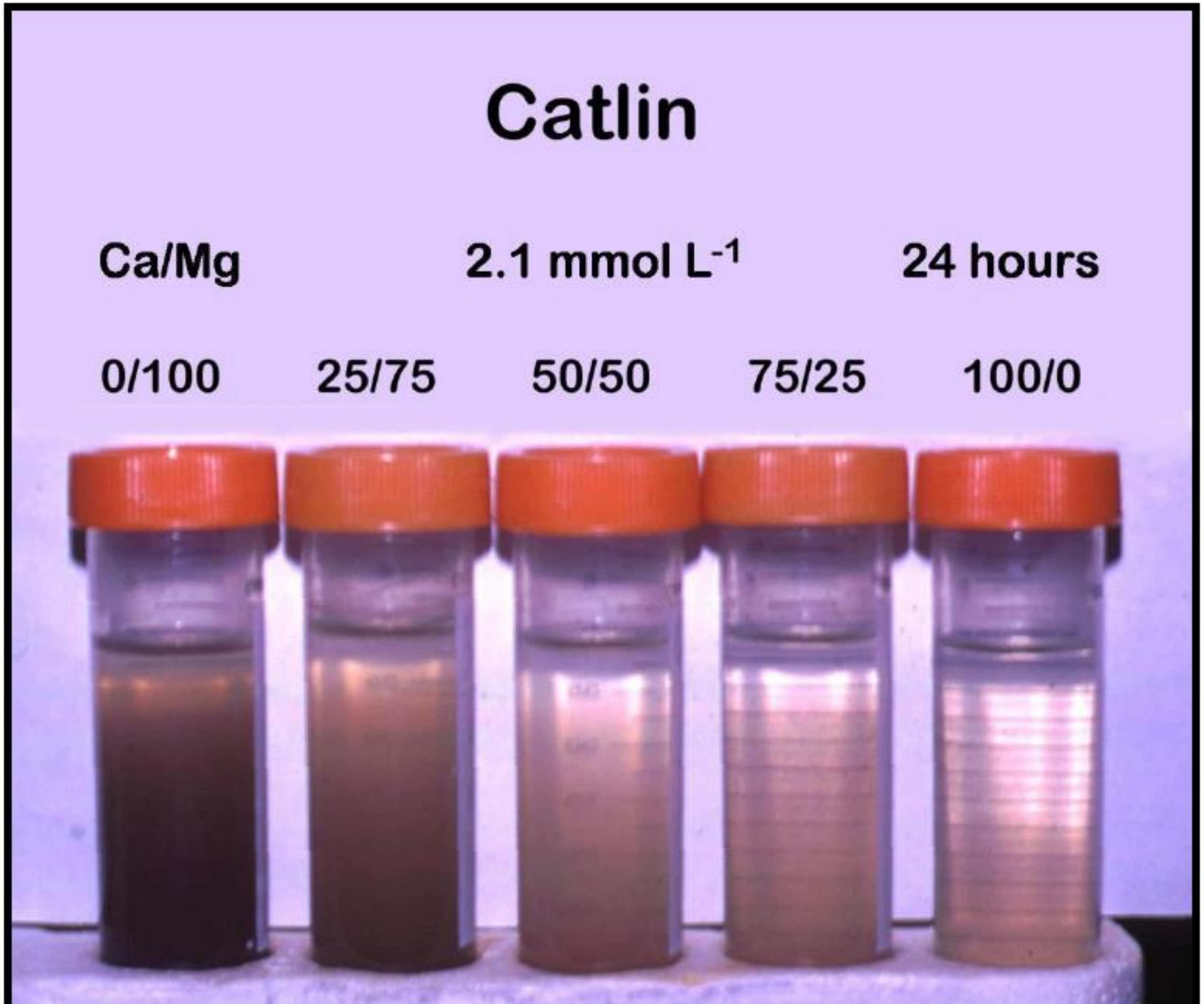
RAINDROP IMPACT AND DISPERSION LEADS TO SURFACE SEALING



AGGREGATE STABILIZATION



CA EFFECT ON DISPERSION/ FLOCCULATION



Improve soil physical/chemical properties to increase infiltration and reduce soil erosion

Additional Criteria:

Apply 1.5 tons/acre of gypsum

Photo courtesy of Darrell Norton

DETACHMENT BY FLOW REDUCED BY GYPSUM+PAM

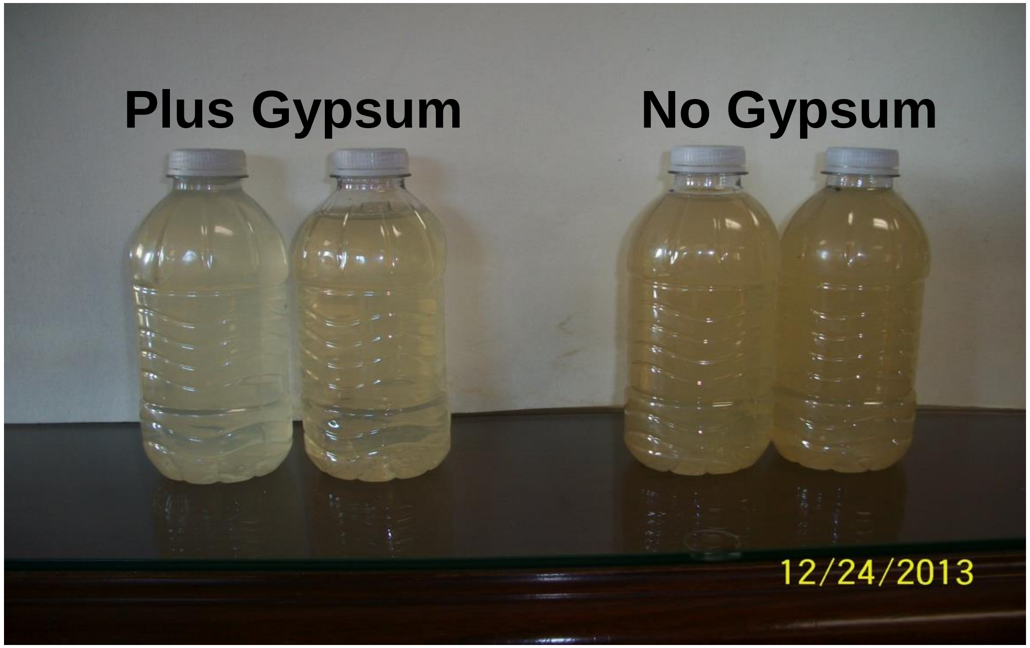
Gypsum Use For Improved Environmental Stewardship

Rolland Wolfrum Hale Farm samples (Hicksville, OH) eight months after 1 T/A gypsum application.

Gypsum Use For Improved Environmental Stewardship

Ken Hahn Farm sample (Antwerp, OH) eight months after 1 T/A gypsum application.

Gypsum Use For Improved Environmental Stewardship



Rolland Wolfrum farm samples 20 months after 1 T/A gypsum application

Gypsum Interaction with Soluble P

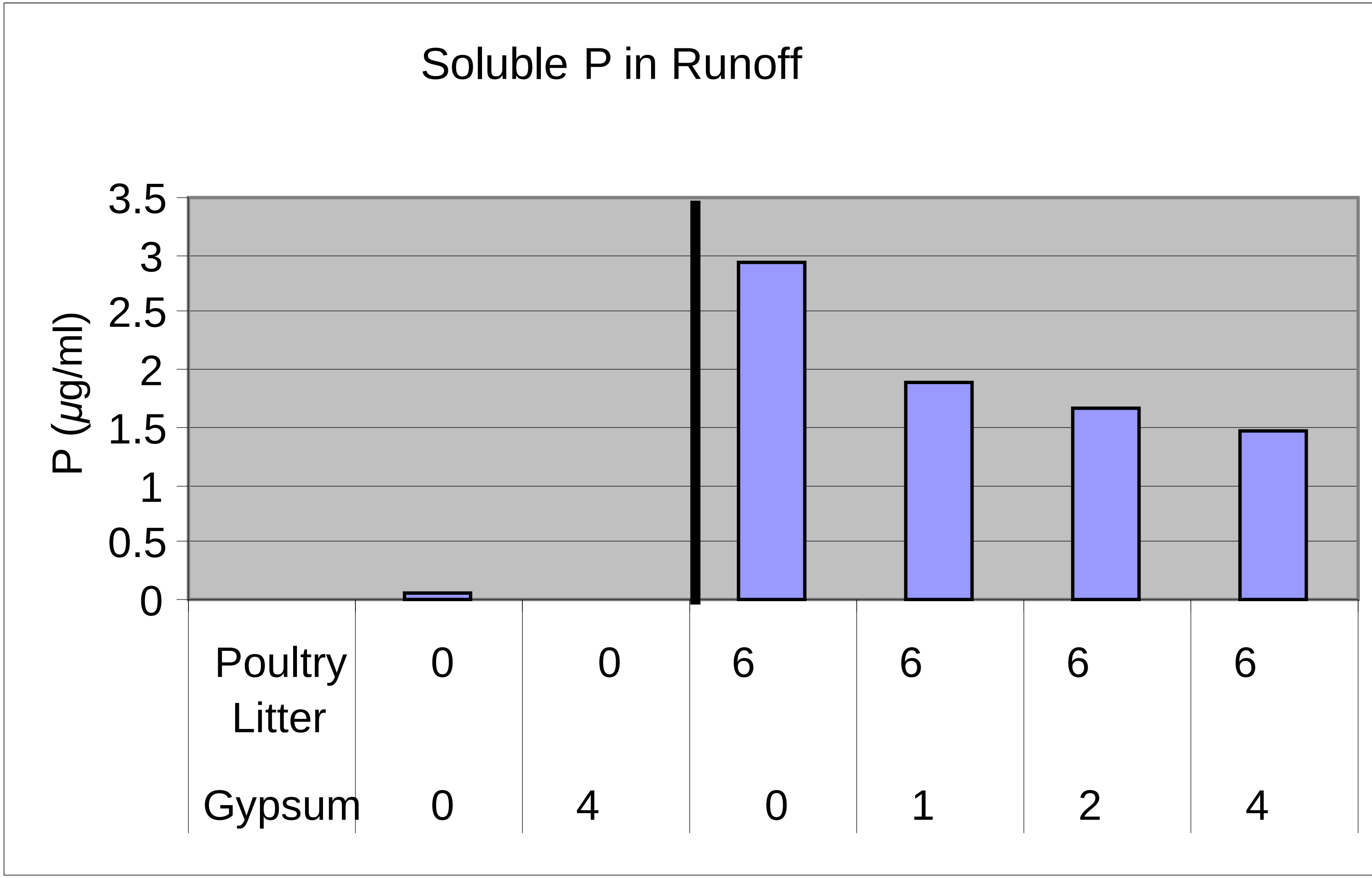
- Formation of an insoluble Ca-phosphate complex

- Insoluble hydroxyapatite and fluorapatite

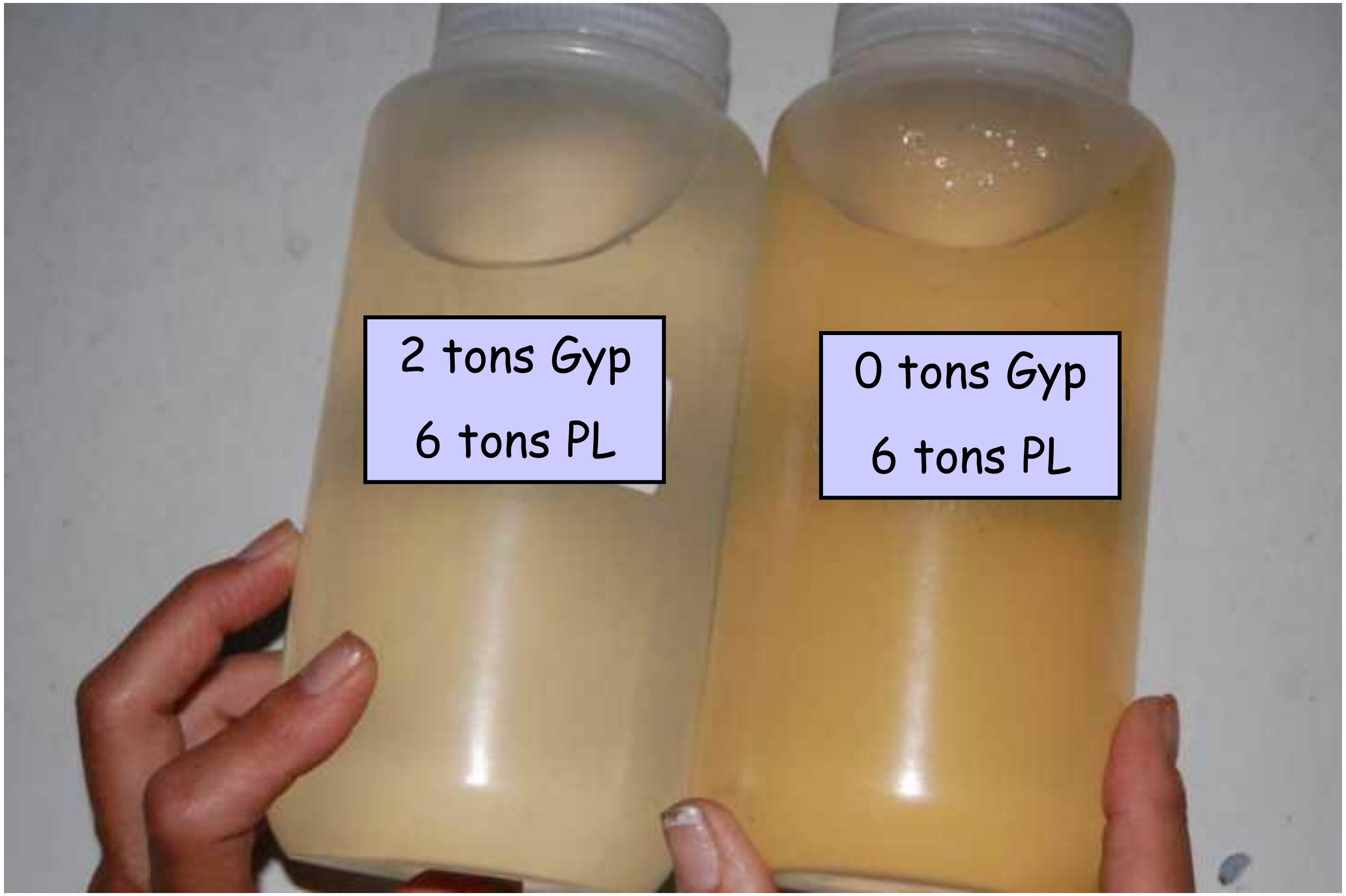
Orthophosphate $\mathbf{PO_4^{3-}} \rightarrow \mathbf{Ca_5(PO_4)_3(OH)}$

$\rightarrow \mathbf{Ca_5(PO_4)_3F}$

Time samples - 0, 10, 20, 30, 40, 50, 60
Cumulative samples
Unfiltered – Total nutrient
Filtered - Dissolved


Soluble P in Runoff
P (µg/ml)
3.5
3
2.5
2
1.5
1
0.5
0
Poultry Litter
0
0
6
6
6
6
Gypsum
0
4
0
1
2
4

Runoff



POLLUTION ATTRIBUTED TO STRATIFICATION OF PHOSPHOROUS FROM REDUCED TILLAGE IN LAKE ERIE

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Gypsum: One contributor to the solution?

There were 55 total sampling events... from tile drains.

Average P reductions for all gypsum-treated areas was 54%.

P reductions in tile drainage water persist at least 20 months after gypsum treatment.

CONDITIONS WHERE GYPSUM USED

*…*gypsiferous products are used to alter the physical and/or chemical characteristics of soil to help achieve one of several specific purposes.

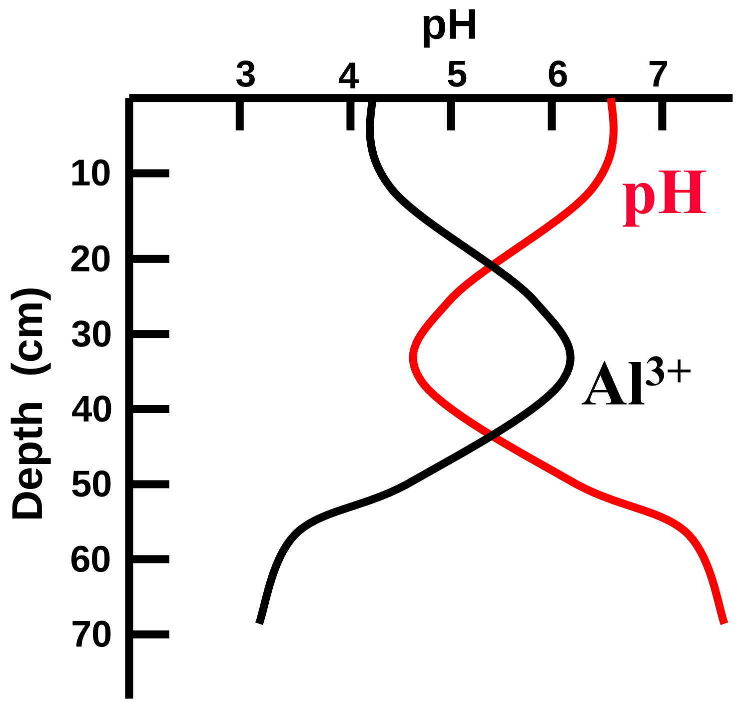
To remediate sodic soils: *Conservation Practice Salinity and Sodic Soil Management (Code 610)*

Photo courtesy of Mike Singer

AGRICULTURAL RESEARCH SERVICE

Gypsum is Not a Liming Agent

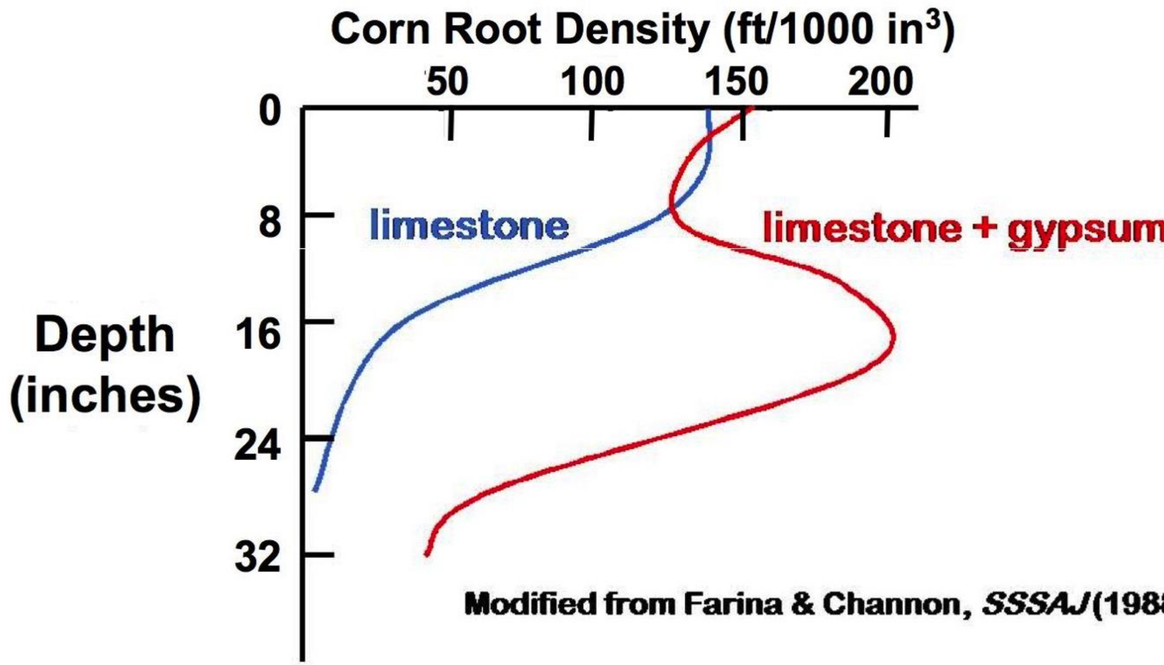
Low pH soils may need both lime and gypsum.



Typical pH profile for a Blount soil in Ohio

Gypsum forms soluble complexes with Al^{3+}

$$CaSO_4 + Al^{3+} \longrightarrow Al(SO_4)^{+} + Ca^{2+}$$



Modified from Farina & Channon, *SSSAJ* (1988)

Purpose: Reduce the potential for pathogen transport

Additional Criteria:

Apply 2 tons of gypsum within 5 days after manure or biosolid application, or prior to the next runoff event after manure application, whichever occurs first.

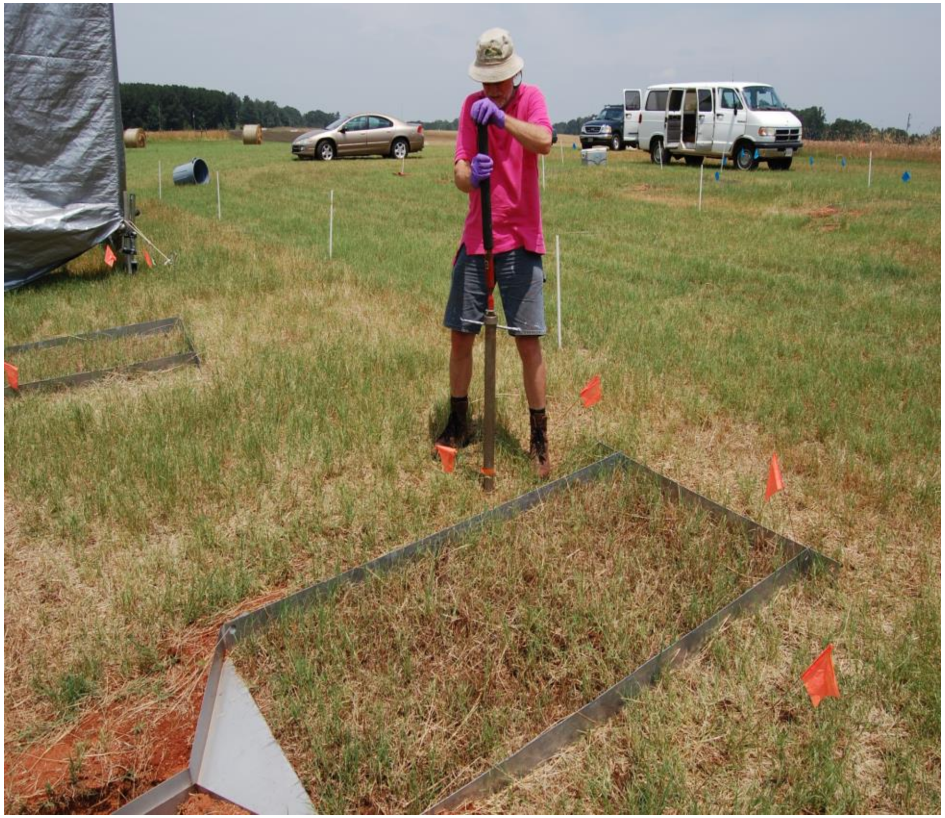
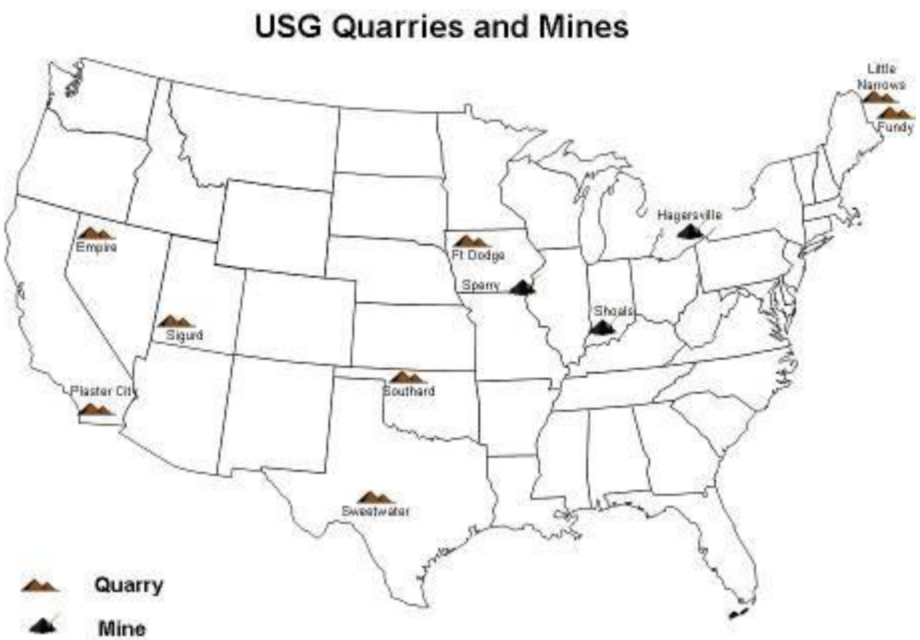


Photo courtesy of Michael Jenkins

SOURCES OF GYPSUM

Economics of Gypsum Use

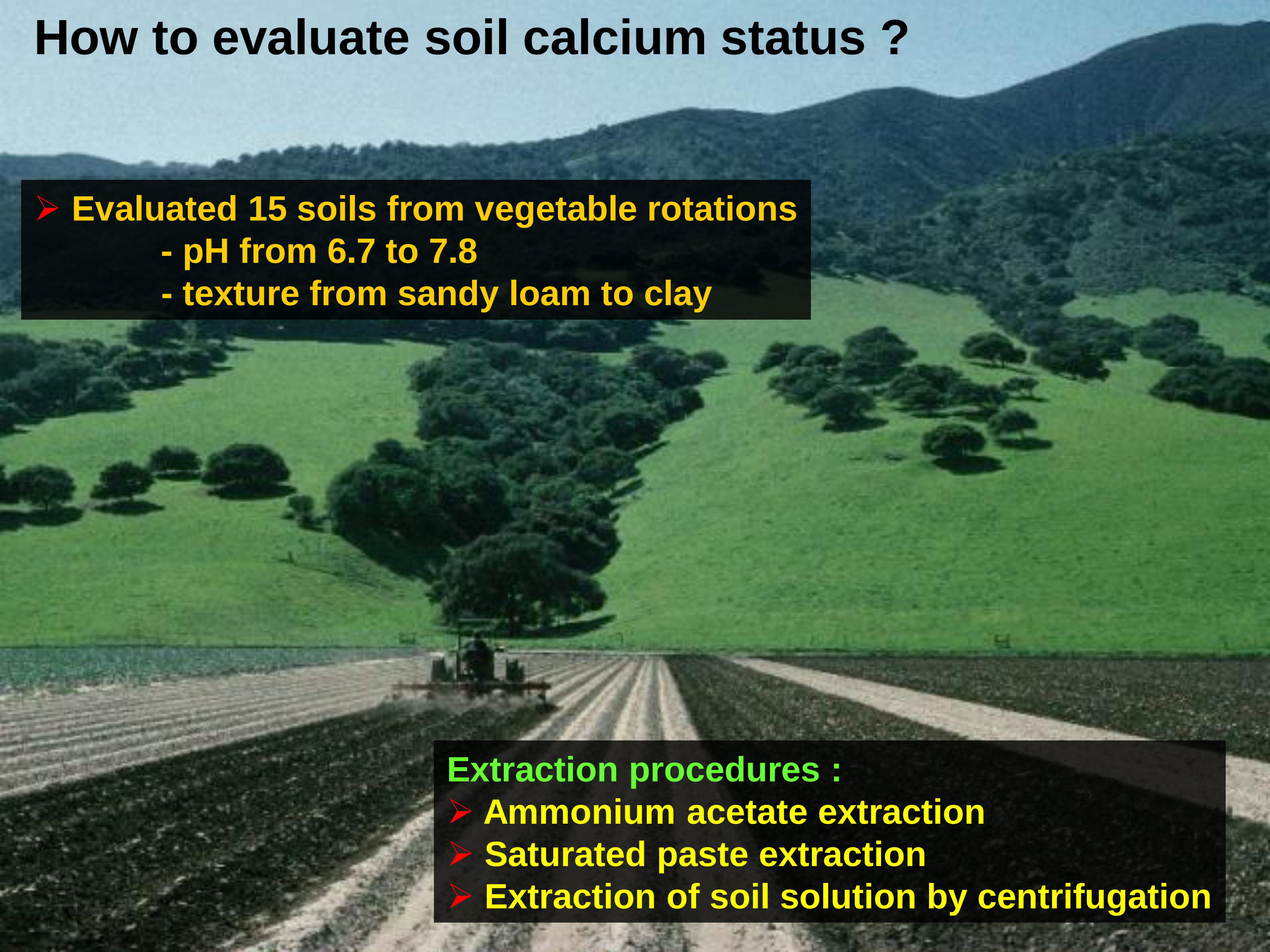
- Historical
  - Bulk gypsum
    - Generally natural gypsum – high cost
      - Proximity to market?
  - “Powder” gypsum
    - Generally fine ground natural gypsum – high cost
  - “Pelletized” Gypsum
    - Pelletized natural gypsum – high cost



Economics of Gypsum Use

- There must always be a return on investment
  + Product cost
  + Transportation cost
  + Handling cost
  + Application cost
  + Equipment depreciation
  + Time
  = Crop Input cost < crop yield/grade gain

How to evaluate soil calcium status ?



- Evaluated 15 soils from vegetable rotations
  - pH from 6.7 to 7.8
  - texture from sandy loam to clay

Extraction procedures :

- Ammonium acetate extraction
- Saturated paste extraction
- Extraction of soil solution by centrifugation

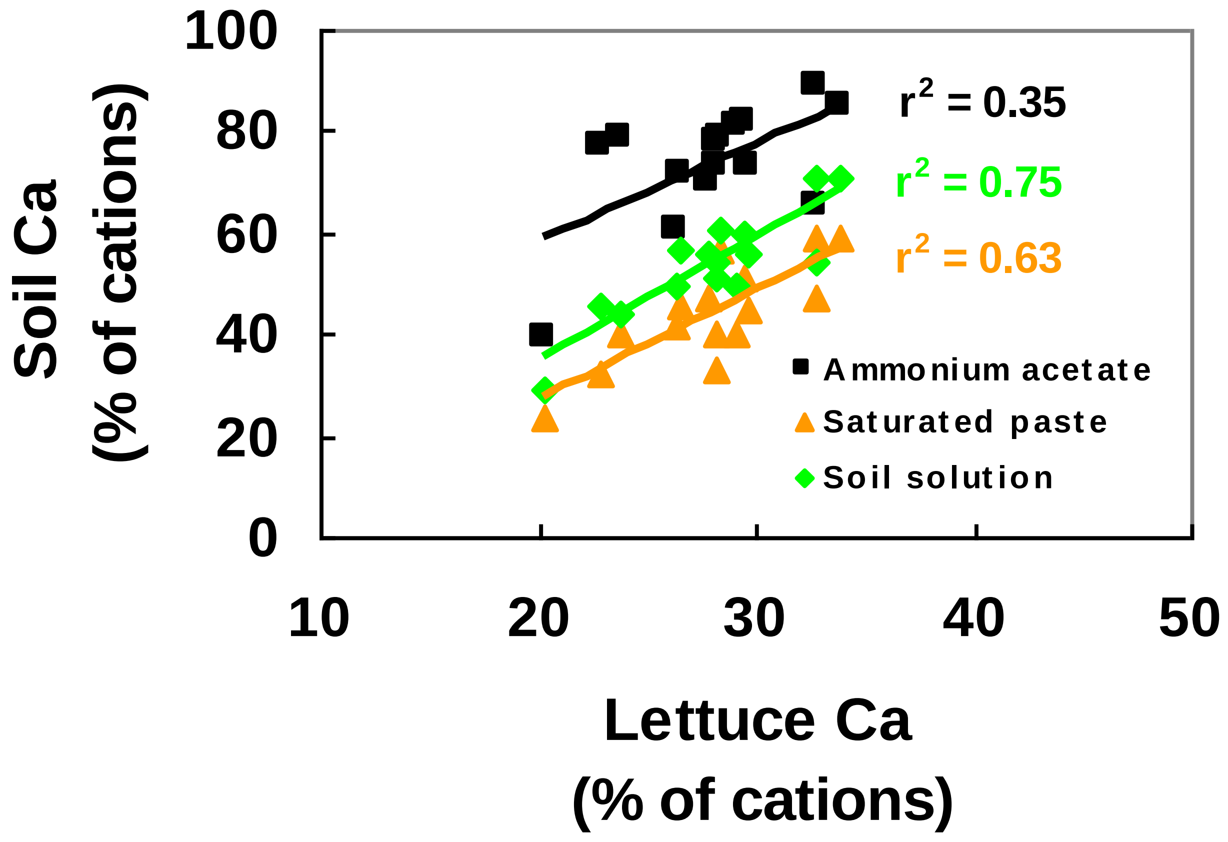

SORVALL LEGEND RT
OPEN
0.00


SARSTEDT
SARSTEDT

What soil test best predicts plant Ca uptake ?

Greenhouse assay :

- **15 field soils**
- **romaine lettuce grown for 6 weeks**
- **whole plant cation uptake determined**


Soil Ca
(% of cations)
100
80
60
40
20
0
10
20
30
40
50
Lettuce Ca
(% of cations)
r² = 0.35
r² = 0.75
r² = 0.63
Ammonium acetate
Saturated paste
Soil solution

How to evaluate soil Ca status ?

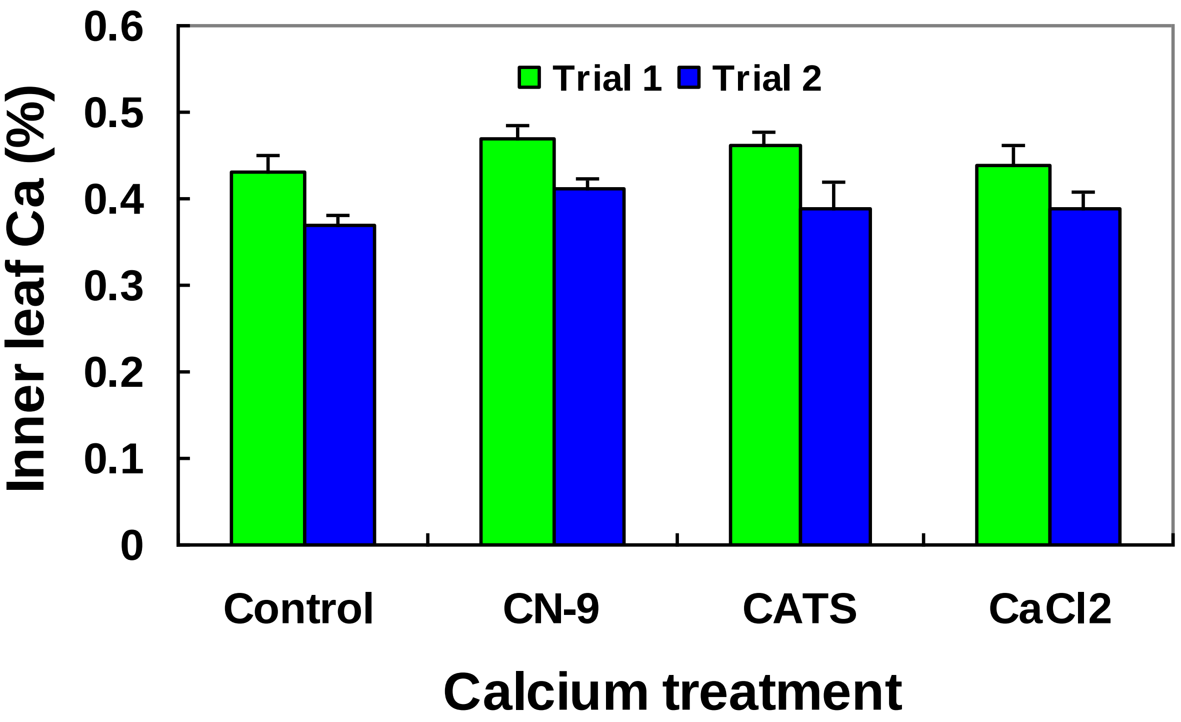
- Soil solution is best measurement, but not practical for routine testing
- Saturated paste extraction is good, but systematically underestimates Ca
  - saturated paste Ca x 5 ≈ soil solution Ca
- Ammonium acetate extraction gives little information about Ca bioavailability

Calcium fertigation trials on romaine :

- Ca fertilizer treatments compared to no Ca control
  - calcium nitrate (CN-9)
  - calcium thiosulfate (CATS)
  - calcium chloride ($CaCl_2$)
- 15 lb Ca/acre fertigated 14 and 7 days preharvest

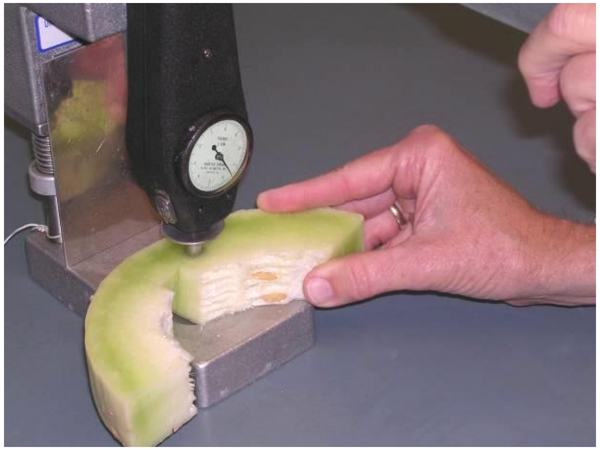
Results :

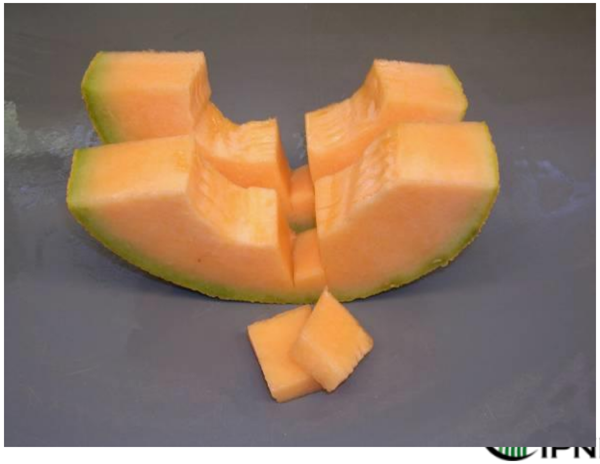
- No Ca effects on yield
- Tipburn incidence low, no Ca treatment effects
- No Ca treatment effects on inner leaf Ca concentration



Melon data :

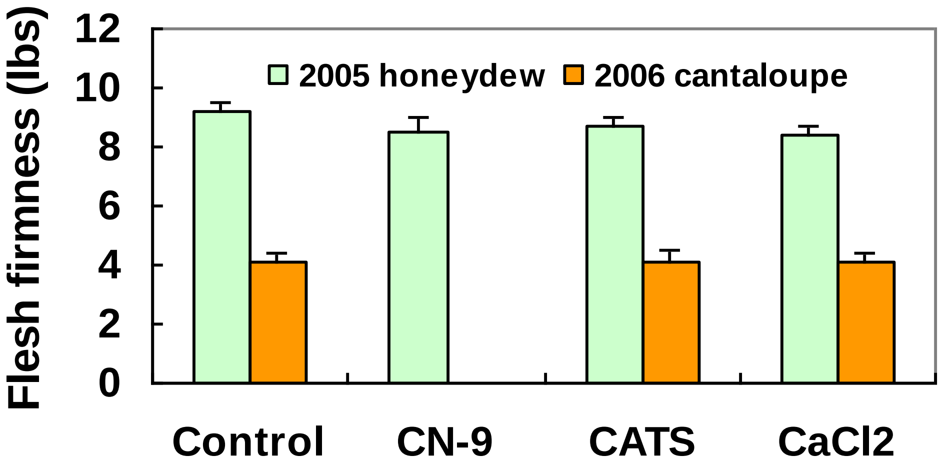
- Yield
- Soluble solids
- Flesh firmness (at harvest and after storage)
- Flesh Ca concentration

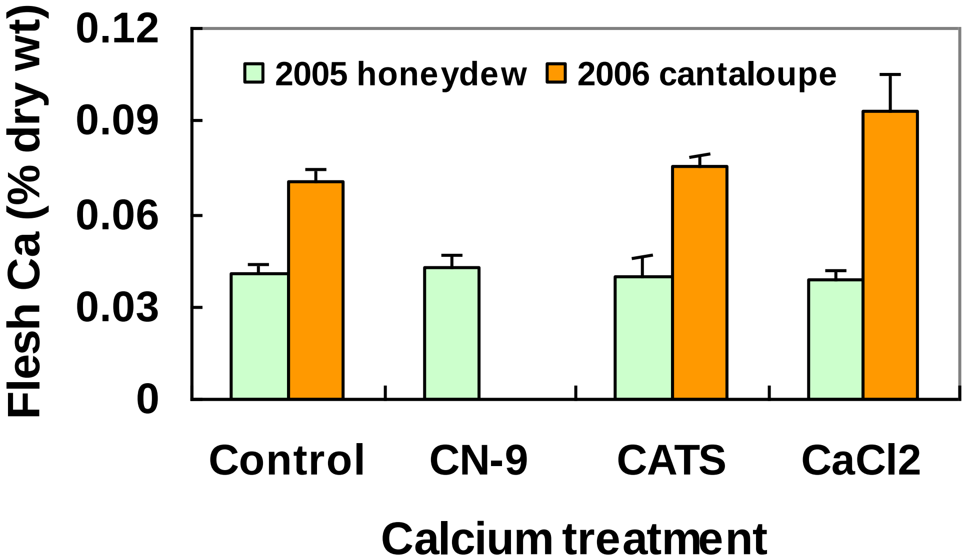




Results :

- ➢ No Ca treatment effects on yield or soluble solids
- ➢ No Ca treatment effects on fruit firmness or Ca concentration





Why such marginal effects from calcium fertigation ?

1) Amount applied is small in comparison to soil solution Ca

Example :

Loam soil with 6 meq Ca/liter in saturated paste extract = 120 PPM Ca

120 PPM Ca x 5 = 600 PPM Ca *in soil solution*

1.5 inches available water = <u>200 lb Ca / acre in soil solution</u>

Fertigation of 15 gal / acre CAN-17 in an application of 0.25 inches of water

15 gal / acre x 1.1 lb Ca / gal = <u>17 lb Ca / acre</u>

17 lb Ca / acre in 0.2 inches of water = 300 PPM Ca

Why such marginal effects from calcium fertigation ?

2) Ca disorders linked to low transpiration difficult to manage with Ca application

Key Points:

- Calcium is key to maintaining good soil structure
  - Well-aggregated clay
  - Good water infiltration
  - Good water percolation
  - Good aeration
- Soil surface characteristics are important
- Calcium should occupy at least 65% of the exchange sites?.... 50%.... 40%

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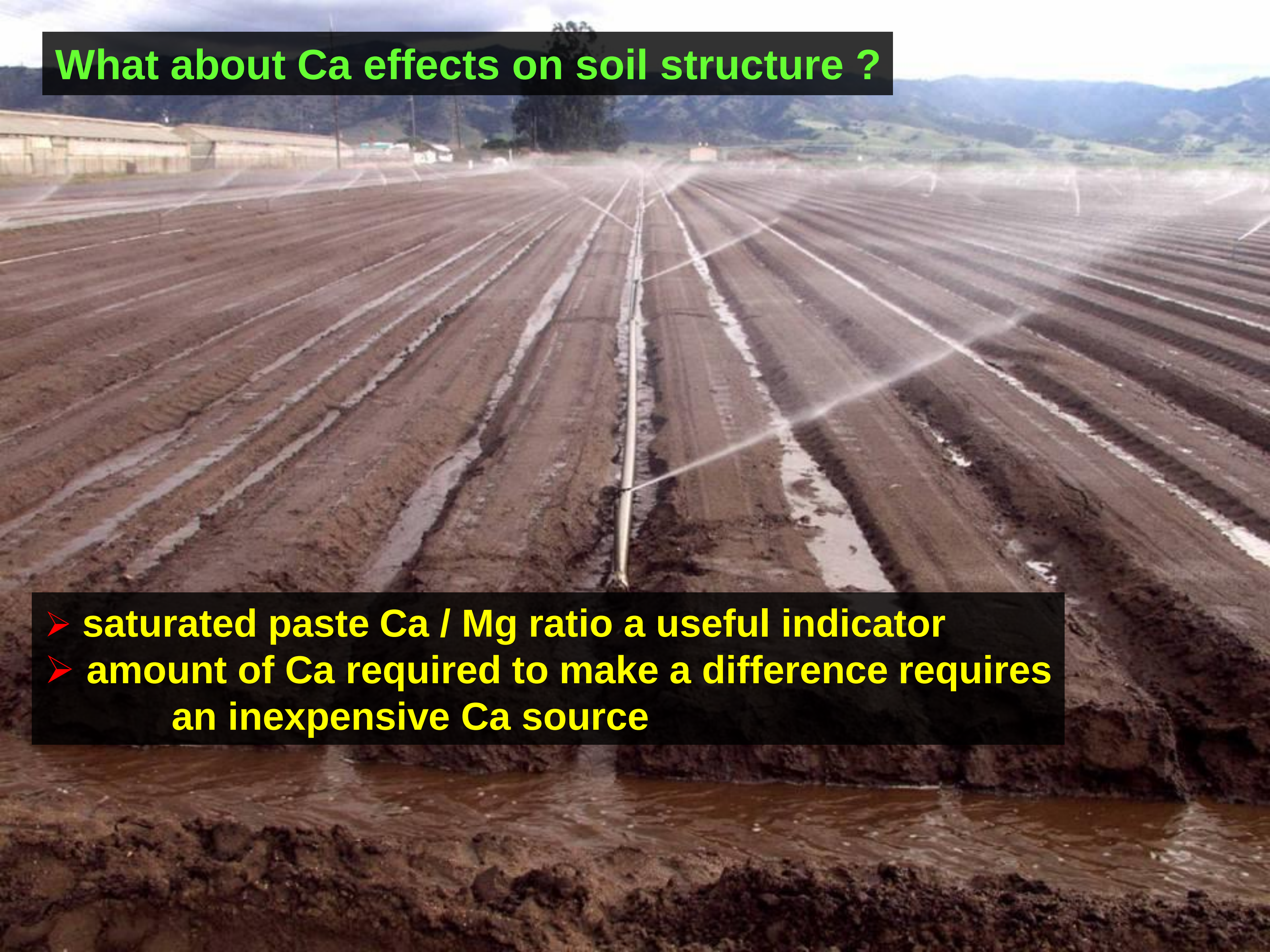
What about Ca effects on soil structure ?



- saturated paste Ca / Mg ratio a useful indicator
- amount of Ca required to make a difference requires an inexpensive Ca source

In summary :

- Saturated paste extract gives useful information on soil Ca status, but ammonium acetate extraction is of marginal value
- Calcium disorders are more often related to low transpirational flow to affected plant parts than to soil Ca limitation in typical California soils
- Fertilizing to overcome soil Ca limitations will be most effective in sandy soils; substantially changing Ca status of high CEC soils requires large Ca applications

Conclusions: Gypsum

- Gypsum is a useful tool for <u>some</u> soil and water environmental problems
- Gypsum <u>may</u> improve infiltration and reduce erosion
- Gypsum <u>may</u> improve soil drainage and improve sodic soils
- Gypsum is a source of calcium and sulfate for plant nutrition
- Gypsum can reduce the loss of soluble phosphate in runoff and tile drains
- Gypsum applications do not have adverse environmental impacts

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Ca availability in the soil

- All Ca is taken up from the soil solution
- Ca in soil solution is in equilibrium with Ca at the *exchange site… need rapid uptake?*

- Ca availability can be limited due to:
  - Precipitation with anions such as $CO_3^{=}$ and $SO_4^{=}$
  - Acid or sandy soils with low Ca content.
  - Salinity limiting Ca uptake.
  - Uneven Ca distribution (e.g. acid subsoils)

- *Soil testing for Ca is useful, but…*

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Thank You

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