Alleviating Soil Acidity through Organic Matter Management

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Introduction

- Most work on topsoil acidity amelioration
  - Mechanical lime incorporation
- Little work on subsoil acidity amelioration
  - Impractical to incorporate lime (cost)
- No-till systems present a challenge
  - Little opportunity for mechanical mixing of lime

Introduction

- Top- and subsoil acidity
  - Excess Al and Mn
  - Deficient Ca
- Root extension and proliferation
  - Require adequate Ca
  - Limited by toxic levels of Al
    - Poor root system
      - Limited water and nutrient uptake
      - Low yields

Approach

- Theoretical analysis of problem
- Experimental verification

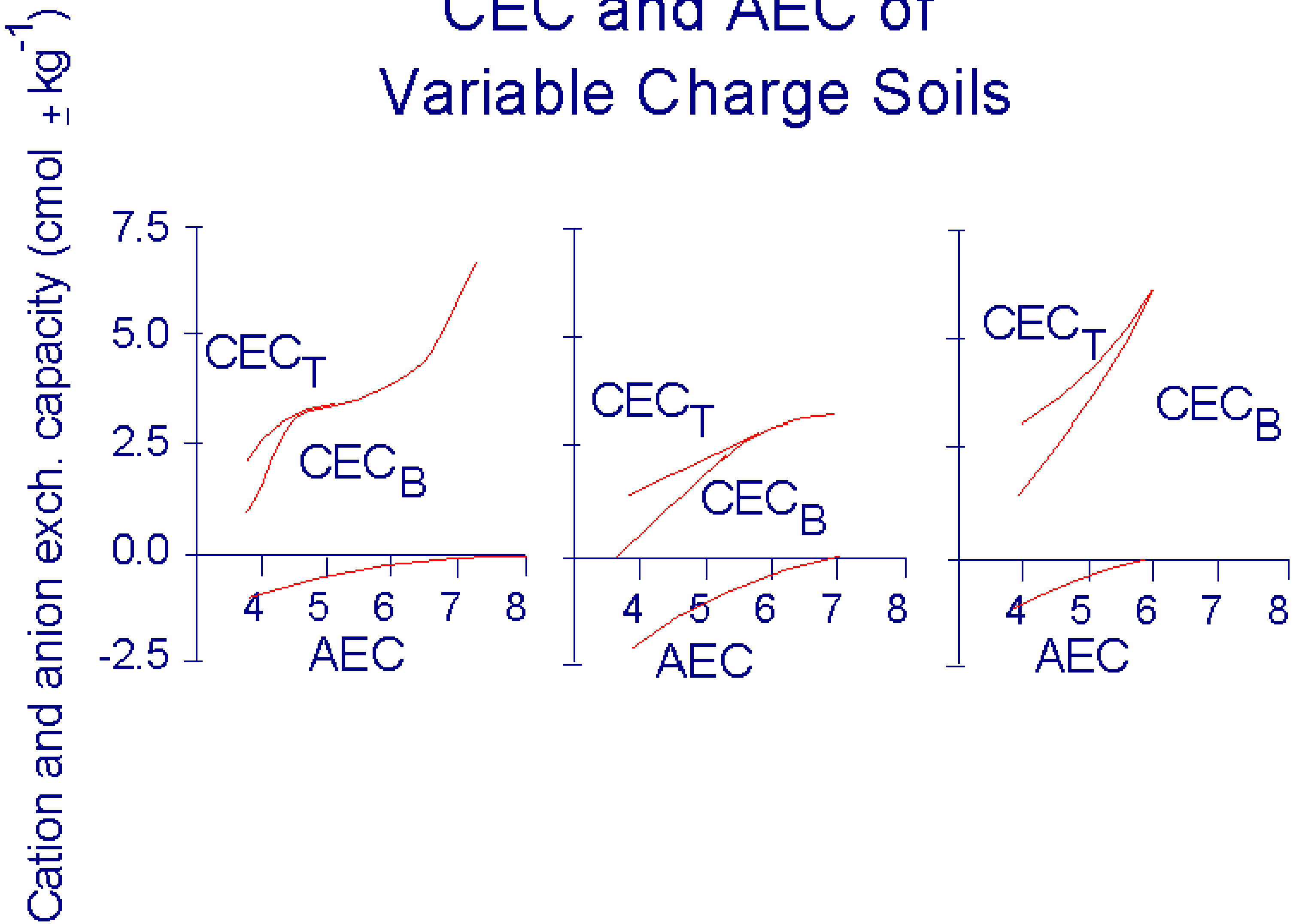
Acidity in Conservation Tillage Systems

- Inability to mix amendments with soil
- Subsoils often already acid
- Ammoniacal fertilizers create acidity
  - Can move down into subsoil
- Acidity problem essential same in top- and subsoil
  - Cannot place lime at site of acidity
- Alternative strategies to move alkalinity into soil without disturbance

Brazilian Situation

- Most conservation tillage on Oxisols and Ultisols
- Variable charge soils
  - Charge depends on pH and salt content
- Acidification causes
  - Reduction in CEC and increase in AEC
  - Lower pH, toxic Al & Mn, deficient Ca

CEC and AEC of Variable Charge Soils



Problem Requiring Solution

- Without disturbance
  - To neutralize soluble Al
  - To increase soluble Ca
- Throughout the profile

Brazilian Situation

- As pH decreases
  - CEC decreases and AEC increases
  - Al saturation increases and base saturation decreases
- Many Cerrado soils near ZPC
  - Limited capacity to hold essential cations
    - Mainly Al and H

Brazilian Situation

- Amelioration to depth involves
  - Neutralization of Al and Mn
  - Restoration of basic cations
- Organic matter builds up under no-till
  - Decreases ZPC
  - Increases CEC and reduces AEC
  - Soil should be more resilient
  - Can maintain pH at lower value?

Variable Charge Soils

- Acidity literature shows
  - Lime does not move down profile
  - Acidity chemistry well known
- Allows formulation of rules to predict lime behavior in profile

Rules for Lime Movement

- For surface applied lime to move
  - Alkalinity (HCO_3^-, OH^-) must move downward
    - Mass flow
- If topsoil is sufficiently acid
  - Al^{3+}, Mn^{2+}, H^+ can also move downward
- At pH 5.2-5.4, mass flow of alkalinity and acidity roughly balance

Rules for Lime Movement

- For alkalinity to move downward
  - Topsoil pH must be > 5.4
  - Above pH 5.4
    - HCO_3^-, OH^- and CO_3^{2-} increase exponentially
- In variable charge soils
  - Alkaline front retarded
    - Alkalinity used up to increase CEC

Processes Involved

- Precipitation of Al^{3+} and Mn^{2+}
- $2\text{Exch-Al}^{3+} + 3Ca(HCO_3)_2 \rightarrow 3\text{Exch-Ca}^{2+} + 2Al(OH)_3 + 6CO_2$
- $\text{Exch-Mn}^{2+} + Ca(HCO_3)_2 \rightarrow \text{Exch-Ca}^{2+} + MnCO_3 + H_2O + CO_2$
- Decrease in AEC
- $\text{Solid-OHH}^{+}Cl^{-} + ½Ca(HCO_3)_2 \rightarrow \text{Solid-OH} + H_2O + CO_2 + ½CaCl_2$
- Increase in CEC
- $\text{Solid-OH} + ½Ca(HCO_3)_2 \rightarrow \text{Solid-O}^{-}½Ca^{2+} + H_2O + CO_2$

Consequently

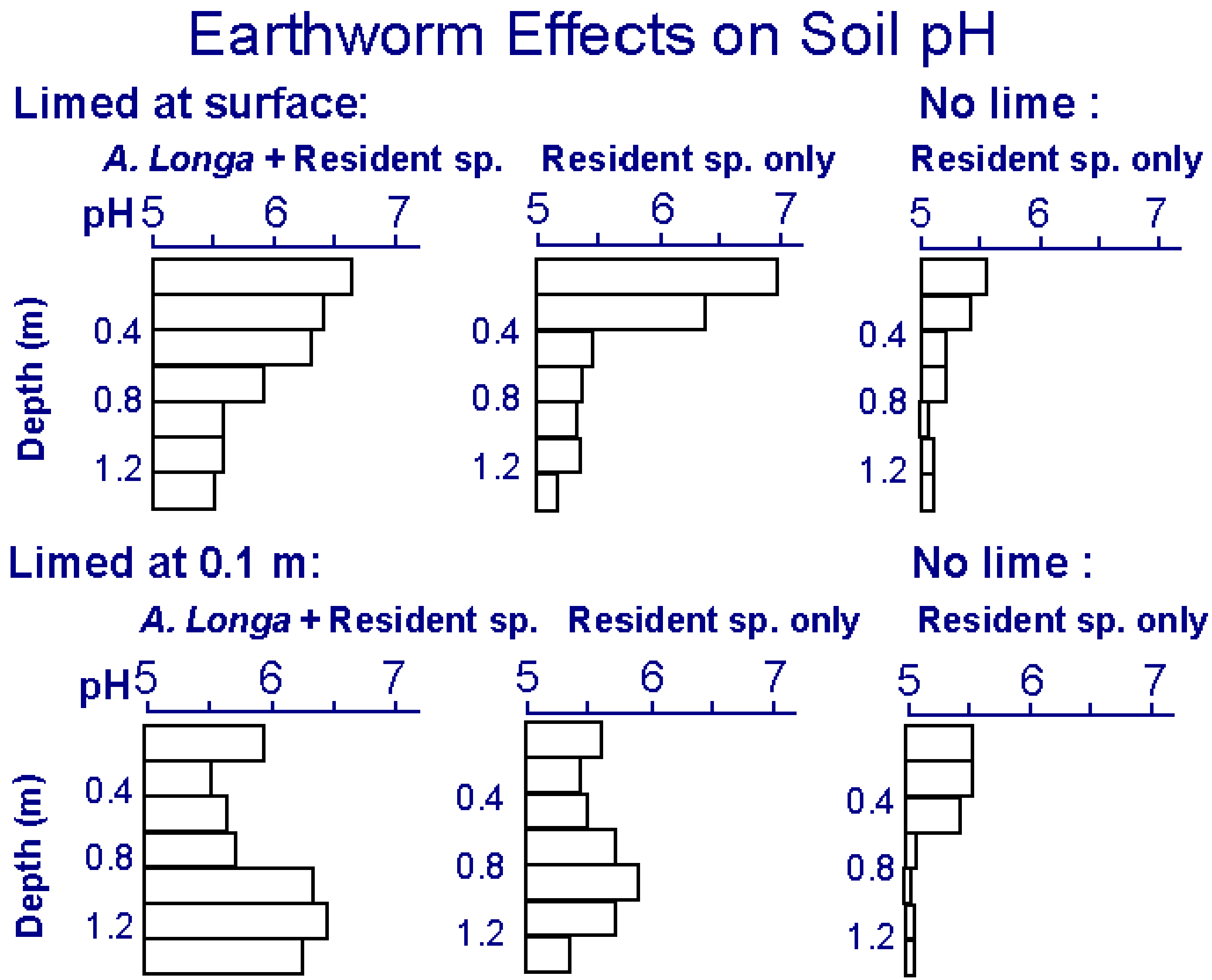
- Lime movement slower in variable than permanent charge soils
- Positively charge sites result in salt ($CaCl_2$) formation
  - $CaCl_2$ moves down freely
  - Reason for often observed rapid downward movement of Ca^{2+} with no change in pH
- No lime movement without other factors

Factors Promoting Lime Movement

- Soil Fauna
- Acid Inputs
- Gypsum
- Organic Compounds

Soil Fauna

- Burrowing animals mix lime with soil
  - Earthworms mix laterally and vertically
  - Ants and termites mix mainly vertically
- Lime better distributed if mix with topsoil
- More soil fauna under conservation than conventional tillage
  - Should be encouraged
  - Avoid pesticides that impact fauna


Earthworm Effects on Soil pH
Limed at surface:
No lime :
A. Longa + Resident sp.
Resident sp. only
Resident sp. only
pH
5
6
7
Depth (m)
0.4
0.8
1.2
Limed at 0.1 m:
No lime :
A. Longa + Resident sp.
Resident sp. only
Resident sp. only

Acid Inputs

- Ammoniacal fertilizers and legumes
  - Appear to be deleterious
  - Benefits under appropriate management
    - Sufficient lime must be present in topsoil
    - Crop must be actively growing
- Alkalinity transferred down
  - Nitrification, lime dissolution, differential uptake of Ca^{2+} and NO_3^-

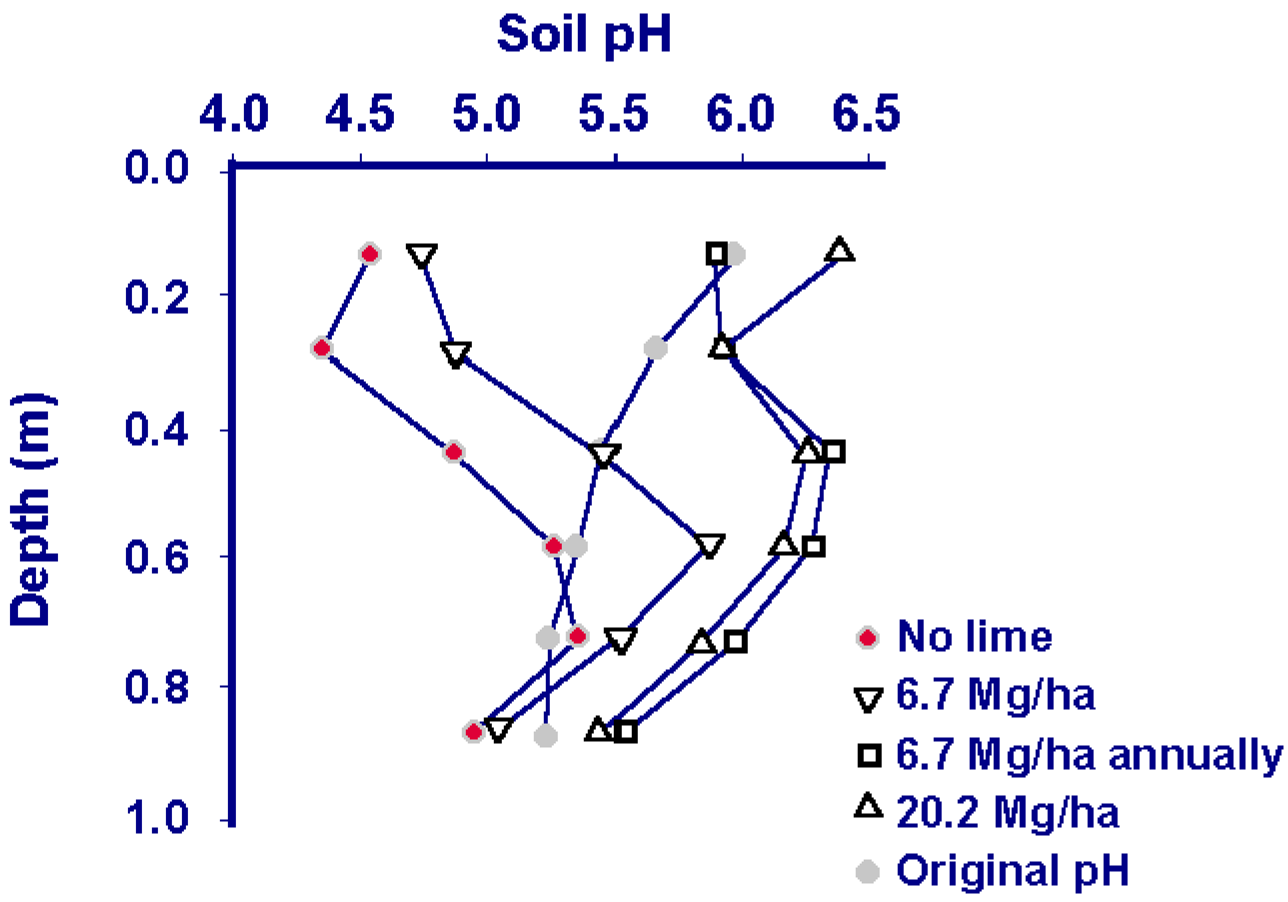
Processes Involved

- Nitrification
  - $NH_4X + 2O_2 \rightarrow HNO_3 + HX + H_2O$
    - where X can be NO_3^-, $\frac{1}{2}SO_4^{2-}$, $H_2PO_4^-$ or HPO_4^{2-}
- Lime Dissolution
  - $CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$
    - $Ca(NO_3)_2$ free to move down

Processes Involved

- Differential Uptake of Ca^{2+} and NO_3^-
  - Roots excrete H^+ to take up Ca^{2+}
  - Roots excrete OH^- to take up NO_3^-
  - Roots take up more NO_3^- than Ca^{2+}
- Root$\rightarrow$$4OH^-$ Root$\leftarrow$$4NO_3^-$
  - $+ 2Ca(NO_3)_2 \rightarrow + Ca(OH)_2 + 2H_2O$
- Root$\rightarrow$$2H^+$ Root$\leftarrow$$Ca^{2+}$
- Lime [$Ca(OH)_2$] produced at point of uptake

Effect of N and Lime on Subsoil pH



Gypsum

- Surface applied gypsum ameliorates subsoil acidity
  - Enhances soluble Ca^{2+} and reduces toxic Al^{3+}
  - Allows better root profileration
  - Allows better exploitation of subsoil water
  - Translates into increased yields

Processes Involved

- Ion Pairing
  - $Al^{3+} + CaSO_4 \rightarrow AlSO_4^{+} + Ca^{2+}$
- Self-liming Effect
  - $2OH\text{-}[Fe,Al]\text{-}OH + CaSO_4 \rightarrow (HO\text{-}[Fe,Al]\text{-}SO_4^{-})2Ca^{2+}$
  - $Al^{3+} + Ca(OH)_2 \rightarrow Al(OH)_3 + Ca^{2+}$
- Formation of Basic Aluminum Sulfates
  - $3Al^{3+} + K^{+} + CaSO_4 + 3H_2O \rightarrow KAl_3(OH)_6(SO_4)_2 + 3H^{+} + Ca^{2+}$
  - $KAl_3(OH)_6(SO_4)_2$ in soluble in pH range 4-5

Organic Compounds

- Literature shows that
  - Short chain carboxylic acids detoxify Al^{3+}
    - Depends on relative positions of OH/COOH groups
  - Root growth related to monomeric Al and not total Al in solution
  - Lime + EDTA neutralized subsoil Al but lime alone does not
  - Manure + lime neutralize subsoil Al
- Organic compounds transfer alkalinity

Movement of Organic Compounds

- Al complexation
  - OM complexes and detoxifies Al
  - Al-OM complexes can move downward
- Organic matter as lime
  - Neutralizing value $\propto$ basic cation & N content
    - pH and basic cation content is linear
    - N content generates acidity
  - Quality of OM is important
- Ligand exchange

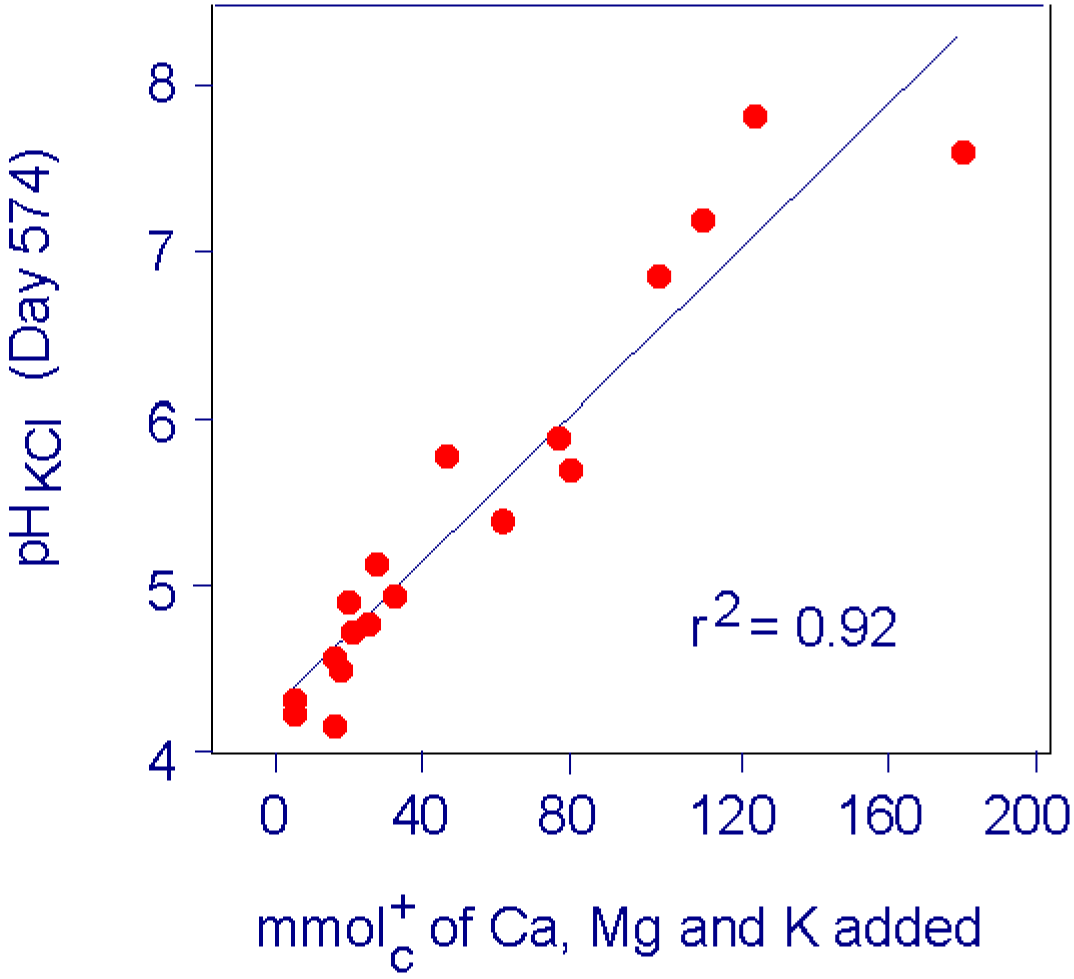
Processes Involved

- Al Complexation
  - $Al^{3+} + 3KOOC\text{-}R \rightarrow Al(OOC\text{-}R)_3 + 3K^+$
- Organic matter as lime
  - $Ca(OOC)_2 + \frac{1}{2}O_2 \rightarrow CaCO_3 + CO_2$
  - $Ca(OOC)_2 + heat \rightarrow CaO + CO_2$
  - $CaO + CO_2 \rightarrow CaCO_3$
  - $Ca(C_6H_{11}O_7)_2.H_2O + 11O_2 \rightarrow CaCO_3 + 11CO_2 + 12H_2O$
- Ligand exchange
  - $2[Fe,Al]\text{-}OH + Ca(OOC)_2C_2H_4 \rightarrow Ca(OH)_2 + [Fe,Al]_2(OOC)_2C_2H_4$

Leaves (200 t/ha) and pH of Cecil Soil (pH 4.0)

Material	N content	Ca+Mg+K	Final pH
Cotton	26.9	2944	7.60
Peach	19.7	1859	7.12
Alfalfa	32.4	1653	6.84
Maize	10.0	958	5.44
Wheat	4.6	344	4.85

Basic Cation Effect on Soil pH



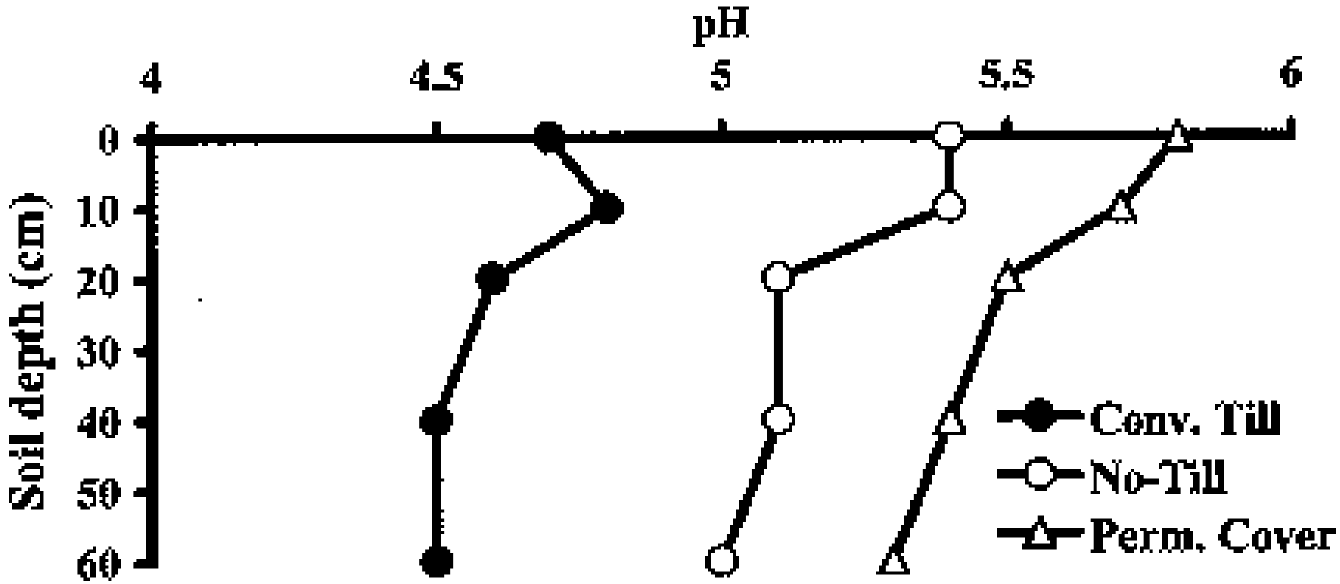
Leaves and pH of Brazilian Soils (pH 4.0, 4.6, 4.4)

Material	Ca+Mg+K	Average pH		
		LV soil	LR soil	LE soil
Radish	84.7	6.5	6.7	5.7
Soya	40.8	6.0	5.8	4.9
Wheat	5.4	4.3	5.2	4.3

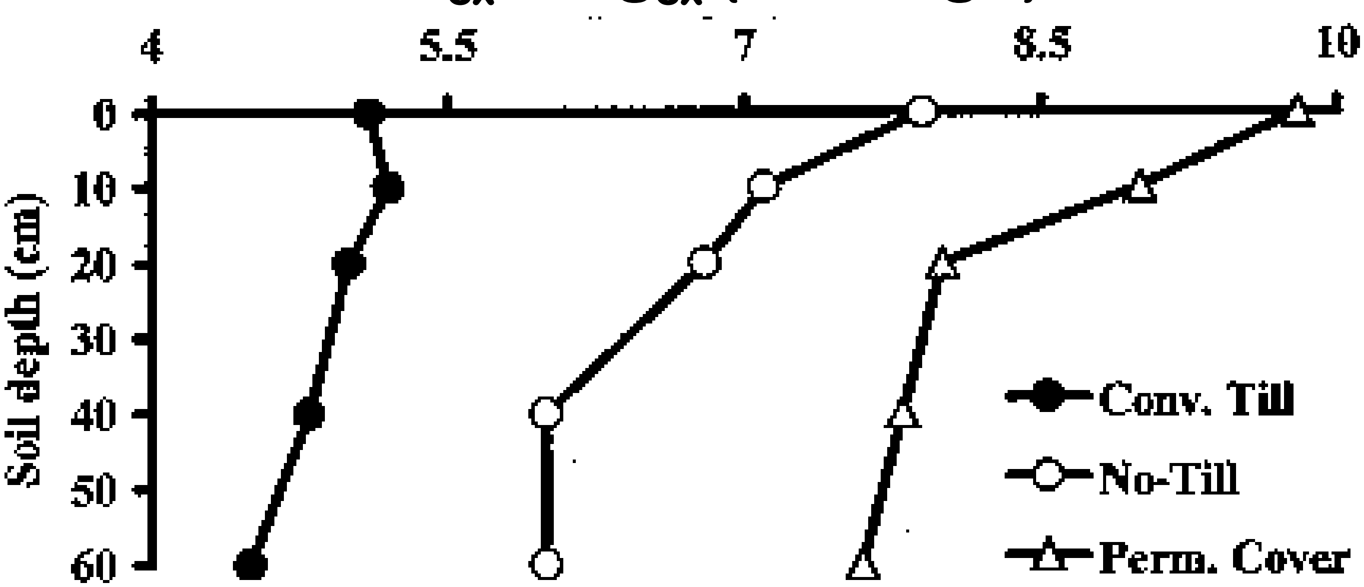
Soluble cations and carbon

Treat	Total C	Σ Tot Cat.	Sol. C	Σ Sol Cat.
	$mmol_c$/kg		$mmol_c$/L	
4% Radish	18.0	84.7	2.97	58.8
4% Soy	20.1	40.8	1.11	23.6
4% Wheat	22.5	5.4	0.29	3.0

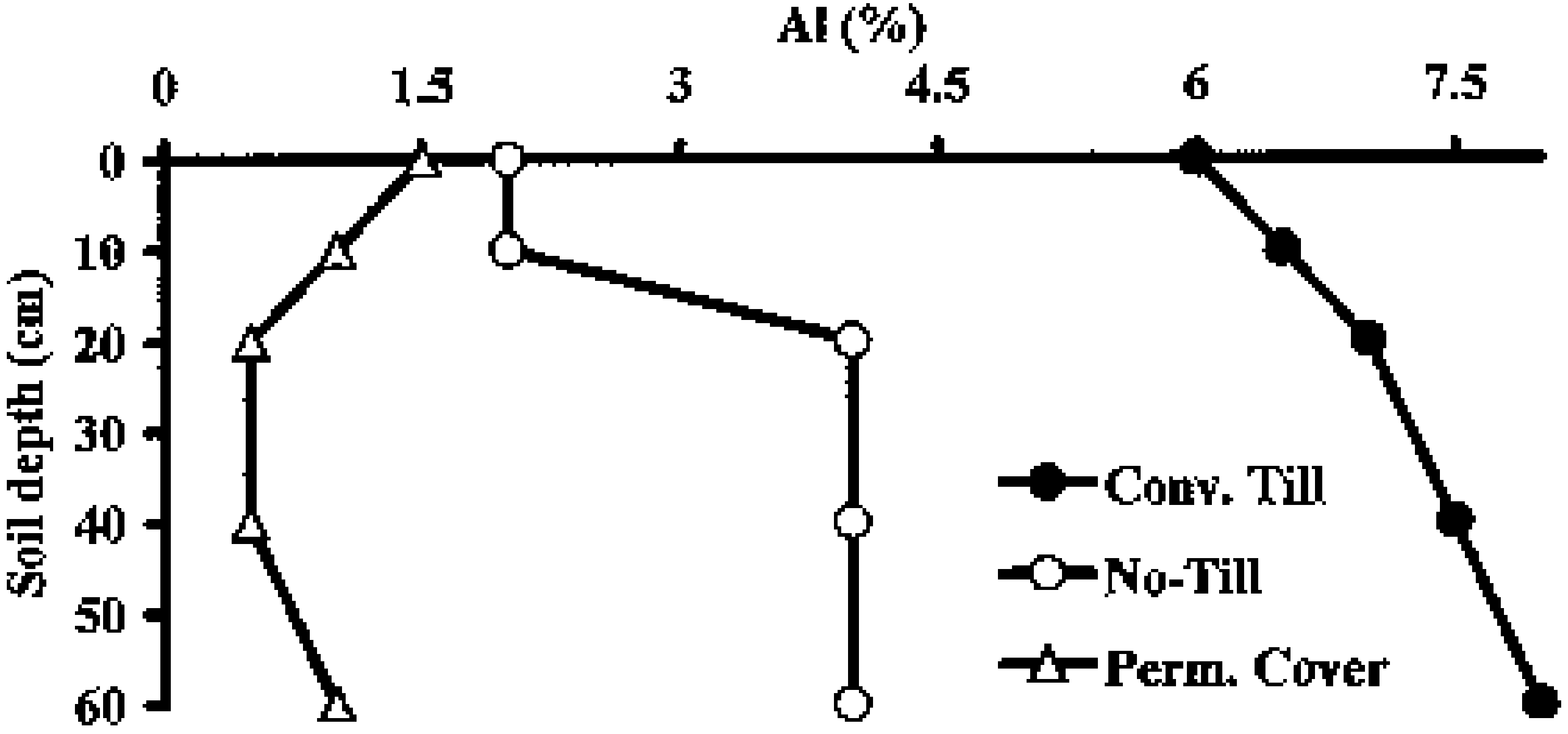
Brazilian Results



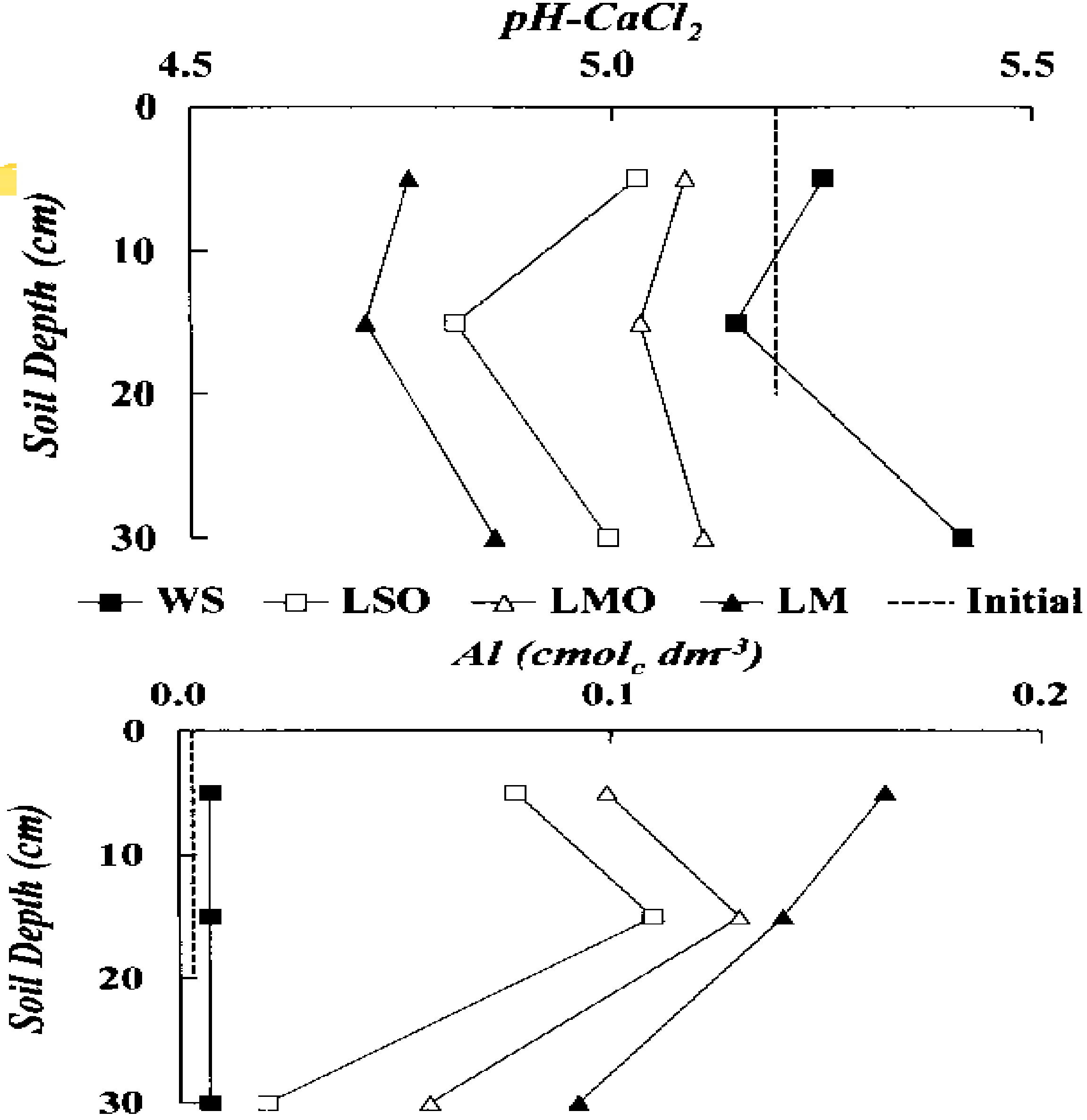
$Ca_{ex} + Mg_{ex}$ (cmol kg^{-1})



Brazilian Results

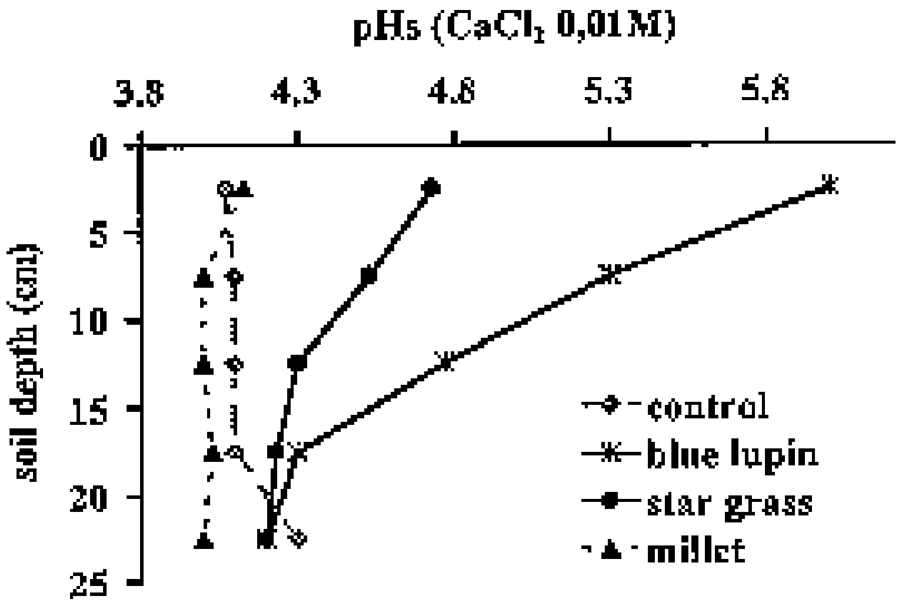


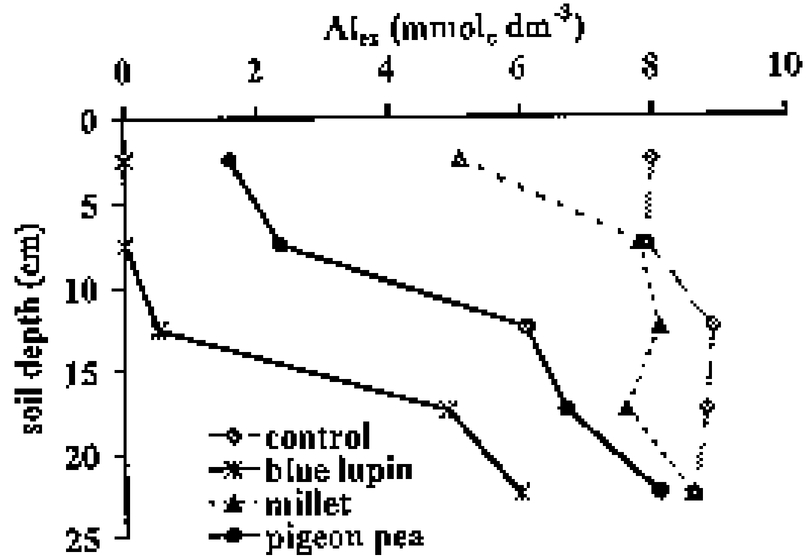
Brazilian Results



W: wheat; **S**: soybean; **L**: blue lupin; **O**: black oat; **M**: maize

Brazilian Results





Conclusions

- Profile acidity can be reduced by
  - Soil fauna incorporating lime and OM
  - Differential uptake of Ca and NO_3 by roots
  - Leaching of gypsum
  - Leaching of bases with OM
- Brazilian results confirm last three mechanisms

Conclusions

- Reduced tillage systems
  - Promote accumulation of OM
  - Protect soil surface
  - Provide soluble OM to carry bases into subsoil
- Quality of residue is of prime importance
  - Cotton, tobacco, radish, lupin, soybean> wheat, millet, oats, rice, maize