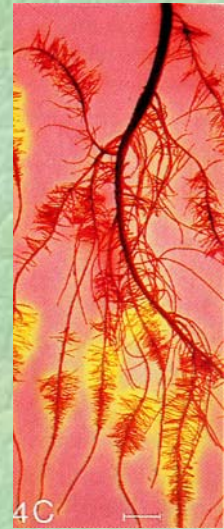


Enhancement of rhizosphere acidification (yellow) of cucumber roots due to net H⁺ extrusion in low iron environments at pH 6 (Marschner et al. 1986)



Soil pH and Lime Requirement

Martha Rosemeyer

Ecological Agriculture

February 2, 2006

Outline

- Basic Chemistry
- Cation Exchange Capacity
- What is soil acidity?
- Why soils are acid
 - natural causes
 - human causes
- Effects of pH on soil nutrient availability
- Changing soil pH
 - managing soil alkalinity
 - managing soil acidity
 - lime Requirement

Basic chemistry

- Atom- smallest representative sample of the element, composed of protons, neutrons and electrons
- Molecule- an assembly of two or more atoms tightly bound together
- Ion- charged particle formed by the gaining or loss of electron(s)
 - Cation has + charge
 - Anion has - charge

Periodic table of the elements

H ¹																	He ²
Li ³	Be ⁴											B ⁵	C ⁶	N ⁷	O ⁸	F ⁹	Ne ¹⁰
Na ¹¹	Mg ¹²											Al ¹³	Si ¹⁴	P ¹⁵	S ¹⁶	Cl ¹⁷	Ar ¹⁸
K ¹⁹	Ca ²⁰	Sc ²¹	Ti ²²	V ²³	Cr ²⁴	Mn ²⁵	Fe ²⁶	Co ²⁷	Ni ²⁸	Cu ²⁹	Zn ³⁰	Ga ³¹	Ge ³²	As ³³	Se ³⁴	Br ³⁵	Kr ³⁶
Rb ³⁷	Sr ³⁸	Y ³⁹	Zr ⁴⁰	Nb ⁴¹	Mo ⁴²	Tc ⁴³	Ru ⁴⁴	Rh ⁴⁵	Pd ⁴⁶	Ag ⁴⁷	Cd ⁴⁸	In ⁴⁹	Sn ⁵⁰	Sb ⁵¹	Te ⁵²	I ⁵³	Xe ⁵⁴
Cs ⁵⁵	Ba ⁵⁶	La ⁵⁷	Hf ⁷²	Ta ⁷³	W ⁷⁴	Re ⁷⁵	Os ⁷⁶	Ir ⁷⁷	Pt ⁷⁸	Au ⁷⁹	Hg ⁸⁰	Tl ⁸¹	Pb ⁸²	Bi ⁸³	Po ⁸⁴	At ⁸⁵	Rn ⁸⁶
Fr ⁸⁷	Ra ⁸⁸	Ac ⁸⁹	Rf ¹⁰⁴	Db ¹⁰⁵	Sg ¹⁰⁶	Bh ¹⁰⁷	Hs ¹⁰⁸	Mt ¹⁰⁹	Uun ¹¹⁰								

Ce ⁵⁸	Pr ⁵⁹	Nd ⁶⁰	Pm ⁶¹	Sm ⁶²	Eu ⁶³	Gd ⁶⁴	Tb ⁶⁵	Dy ⁶⁶	Ho ⁶⁷	Er ⁶⁸	Tm ⁶⁹	Yb ⁷⁰	Lu ⁷¹
Th ⁹⁰	Pa ⁹¹	U ⁹²	Np ⁹³	Pu ⁹⁴	Am ⁹⁵	Cm ⁹⁶	Bk ⁹⁷	Cf ⁹⁸	Es ⁹⁹	Fm ¹⁰⁰	Md ¹⁰¹	No ¹⁰²	Lr ¹⁰³

TABLE 8.6 Selected Cations and Anions Commonly Adsorbed to Soil Colloids and Important in Plant Nutrition and Environmental Quality

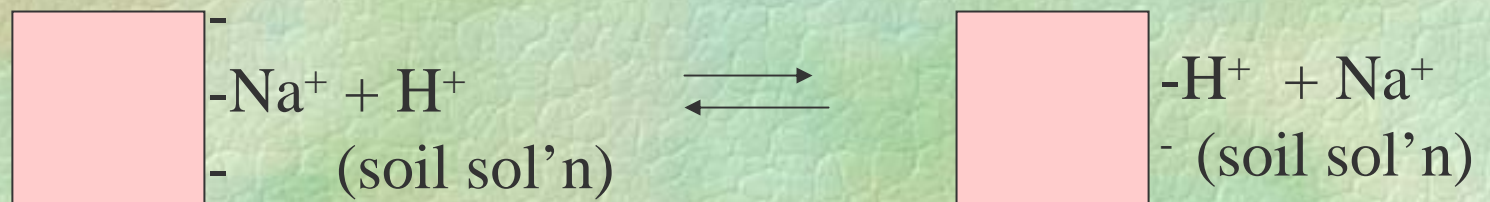
The listed ions form inner- and/or outer-sphere complexes with soil colloids. Ions marked by an asterisk () are among those that predominate in most soil solutions. Many other ions may be important in certain situations.*

<i>Cation</i>	<i>Formula</i>	<i>Comments</i>	<i>Anion</i>	<i>Formula</i>	<i>Comments</i>
Ammonium	NH ₄ ⁺	Plant nutrient	Arsenate	AsO ₄ ³⁻	Toxic to animals
Aluminum	Al ³⁺ etc. ^a	Toxic to many plants	Borate	B(OH) ₄ ⁻	Plant nutrient, can be toxic
Calcium*	Ca ²⁺	Plant nutrient	Bicarbonate	HCO ₃ ⁻	Toxic in high-pH soils
Cadmium	Cd ²⁺	Toxic pollutant	Carbonate*	CO ₃ ²⁻	Forms weak acid
Cesium	Cs ⁺	Radioactive contaminant	Chromate	CrO ₄ ²⁻	Toxic pollutant
Copper	Cu ²⁺	Plant nutrient, toxic pollutant	Chloride*	Cl ⁻	Plant nutrient, toxic in large amounts
Hydrogen*	H ⁺	Causes acidity	Fluoride	Fl ⁻	Toxic, natural and pollutant
Iron	Fe ²⁺	Plant nutrient	Hydroxyl*	OH ⁻	Alkalinity factor
Lead	Pb ²⁺	Toxic to animals, plants	Nitrate*	NO ₃ ⁻	Plant nutrient, pollutant in water
Magnesium*	Mg ²⁺	Plant nutrient	Molybdate	MoO ₄ ²⁻	Plant nutrient, can be toxic
Manganese	Mn ²⁺	Plant nutrient	Phosphate	HPO ₄ ²⁻	Plant nutrient, water pollutant
Nickel	Ni ²⁺	Plant nutrient, toxic pollutant	Selenate	SeO ₄ ²⁻	Animal nutrient and toxic pollutant
Potassium*	K ⁺	Plant nutrient	Selenite	SeO ₃ ²⁻	Animal nutrient and toxic pollutant
Sodium*	Na ⁺	Used by animals, some plants, can damage soil	Silicate*	SiO ₄ ⁴⁻	Mineral weathering product, used by plants
Strontium	Sr ²⁺	Radioactive contaminant	Sulfate*	SO ₄ ²⁻	Plant nutrient
Zinc	Zn ²⁺	Plant nutrient, toxic pollutant			

^a Important aluminum cations include Al³⁺, AlOH²⁺, and Al(OH)₂⁺.

Cation Exchange Capacity

- Sum total of the cations that a soil can adsorb in an exchangeable form (meaning that they can easily come off the particle and become available for a plant)



Soil particle

Soil particle

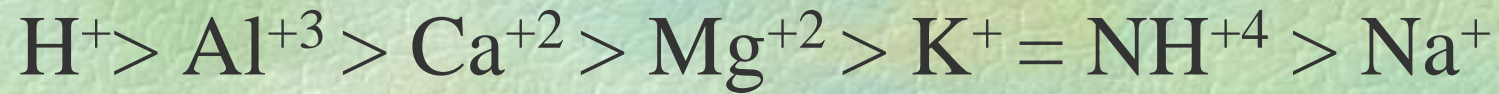
- Measured in cmol_c/kg or $\text{me}/100\text{g}$
- Organic matter is highest, then less weathered clays

CEC of various colloids in soil

Material	cec in cmol_c/kg
■ Organic matter	200-400
■ Allophanic clay (volcanic)	200
■ Vermiculite (clay)	100-150
■ Montmorillinite (clay)	60-100
■ Kaolinite (clay)	2-16
■ Hydroxide clays (Al, Fe)	<2

Cox and Atkins 1979

Cations are adsorbed differently
to soil colloids



Soil acidity is a *Master Variable*

- Affects nearly all soil properties-- chemical, biological and physical
- Controls plant nutrient availability
- Controls soil biotic community composition
- Affects vegetation type: trees, shrubs, grasses, forbs, crop plants

pH

- An acid is a molecule that gives up a proton (H^+)
- A base is a molecule that gives up a OH^-
- pH scale quantifies acidity, 1-14 with 7 = pure water
- Lower pH means more acid, higher more basic

pH Scale

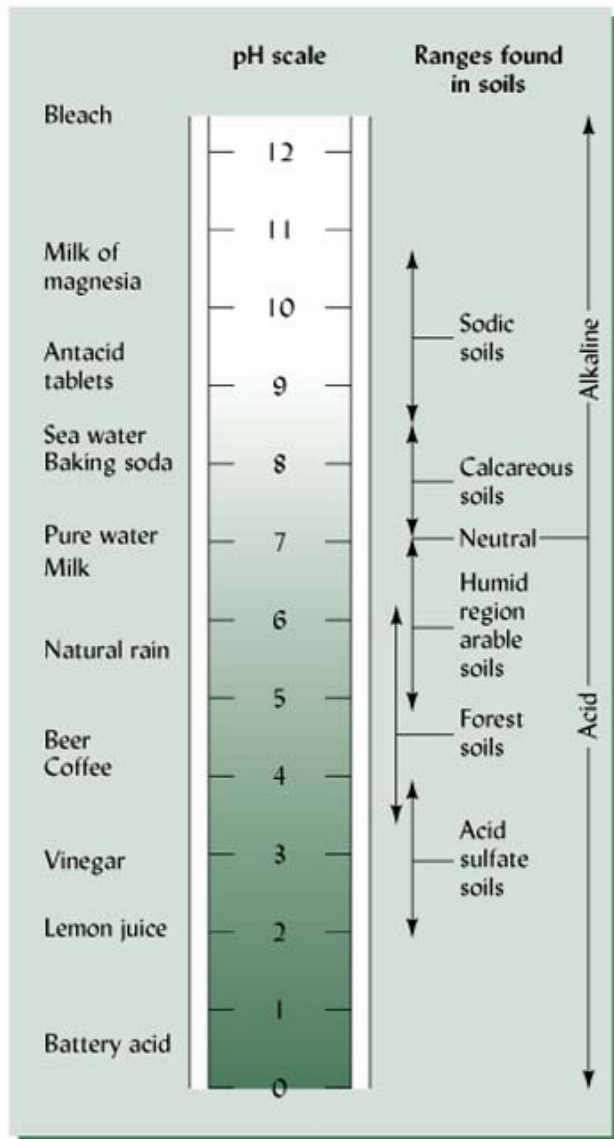


Fig 9.2

Why do soils become acid?

Greater production of H^+ than consumption (p367)

Production:

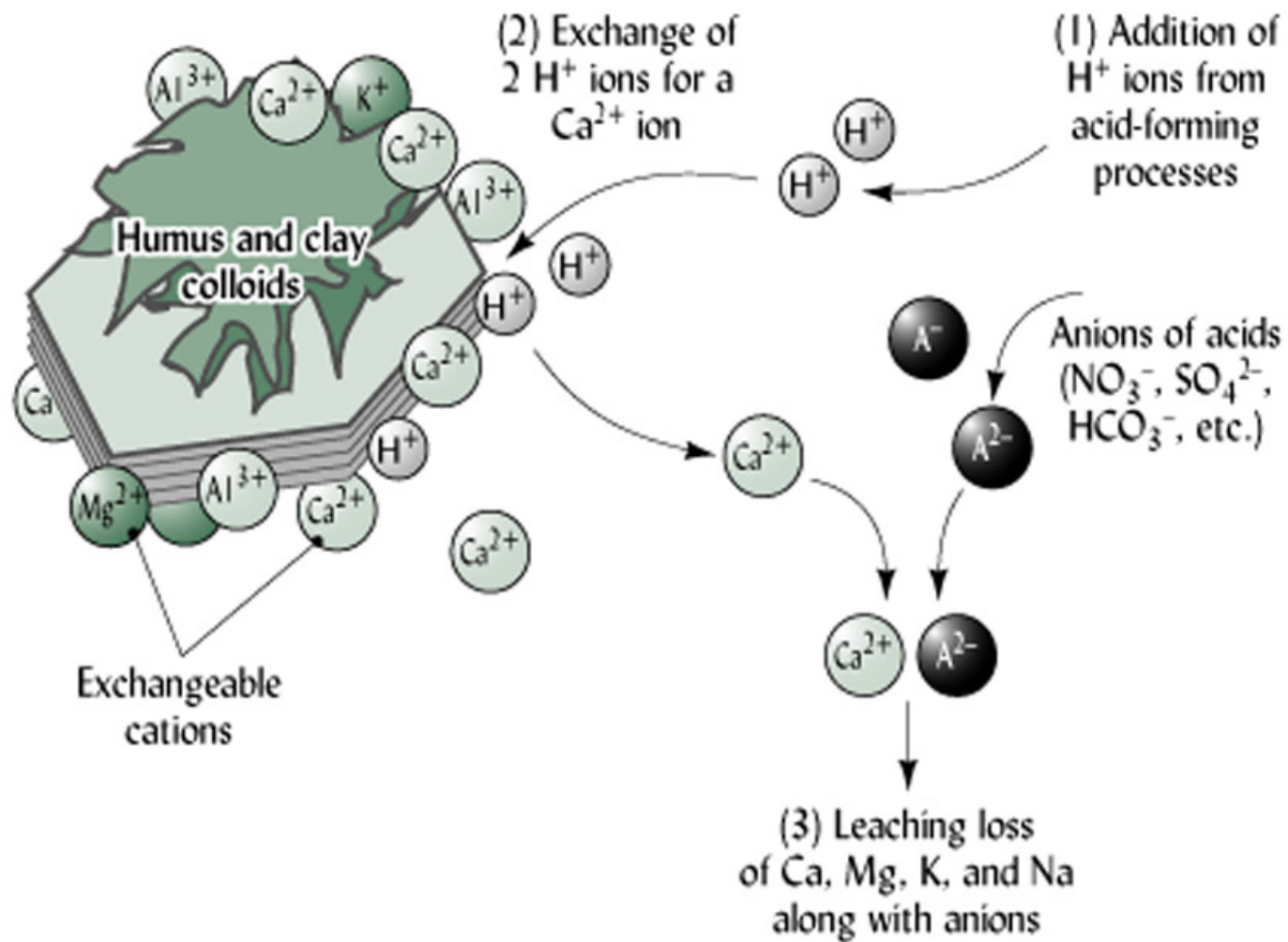
- Production of carbonic acid from CO_2 (page 364)
- Weathering- rainfall leaches Ca^{+2} , Mg^{+2} , K^+
 - leaves H^+ to occupy sites on soil colloids decreasing pH
- Cations taken up by plants in normal plant growth
 - H^+ secreted to maintain charge balance
 - May be exported out of agricultural system
- Conifer residue

Consumption is due to reaction with bicarbonates or carbonates or anion uptake by plants where bicarbonate is released (page 367)

Components of soil acidity

- Hydrogen ions H^+
 - measured by $pH = -\log [H^+]$
 - 10^{-2} of H^+ = pH of 2
 - log scale
- Aluminum ions Al^{+3}
 - releases H^+ in reaction with water
 - Highly toxic— most deleterious effects due to Al^{+3} , causes root stunting, Al blocks Ca uptake sites

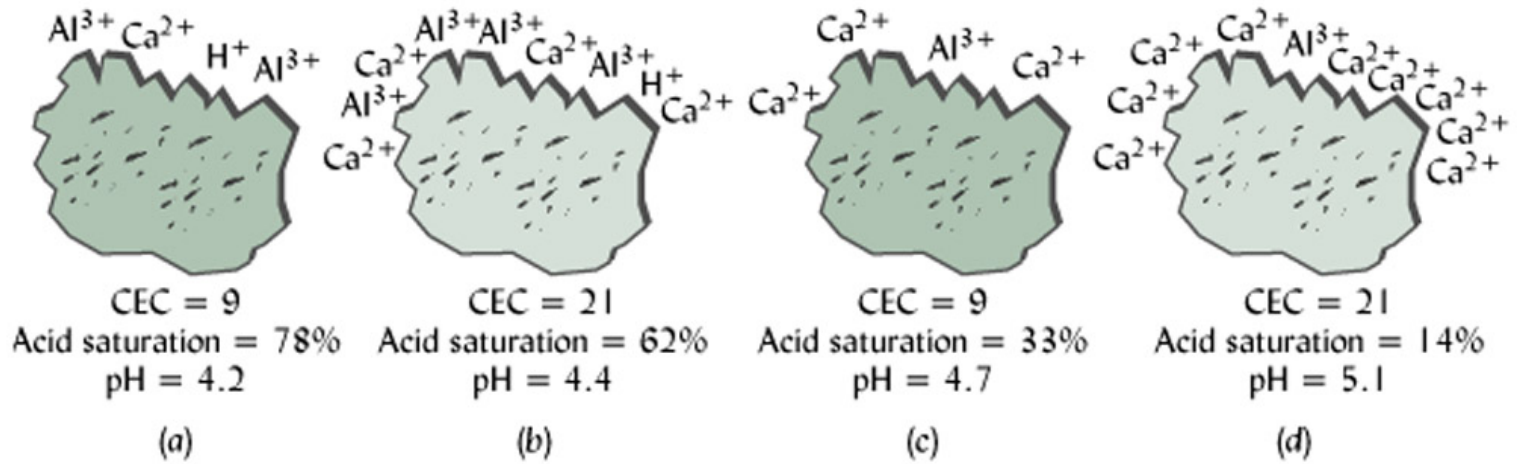
Figure 9.3



Percent Nonacid or “Base” saturation

- Some of cation exchange sites are filled with base forming cations (Ca^{+2} Mg^{+2} K^{+} NH^{+4} Na^{+}) and some with acid forming cations (H^{+} and Al^{+3})
- You want about 80% nonacid bases ideally or Al^{+3} will dominate the soil
- Fig 9.6

Figure 9.6



Conifers have acid residues

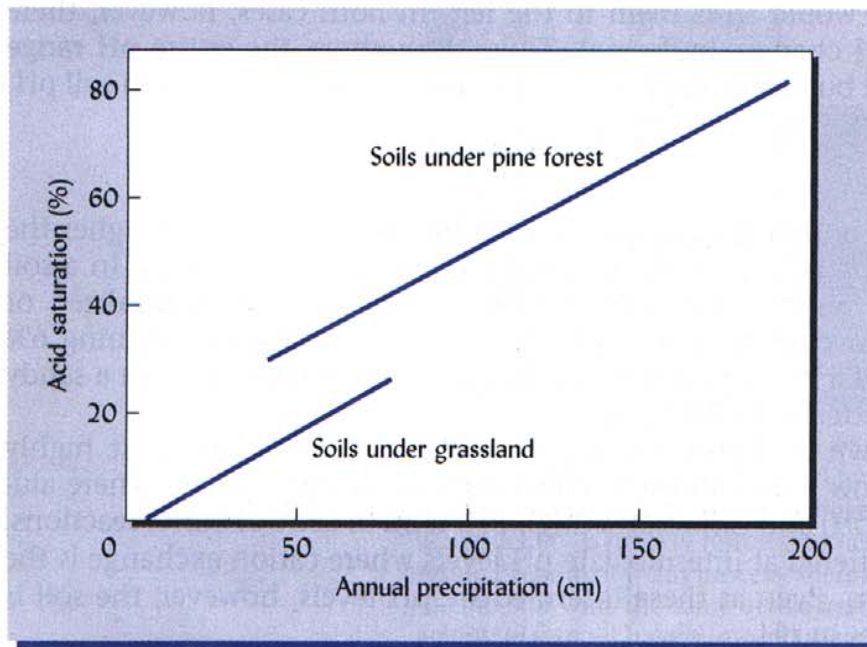


FIGURE 9.7 Effect of annual precipitation on the percent acid saturation of untilled California soils under grassland and pine forests. Note that the degree of acidity goes up as the precipitation increases. Also note that the forest produced a higher degree of soil acidity than did the grassland. [From Jenny, et al. (1968)]

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.

Human-caused acidity

- Chemical fertilizer use
- Tillage and mulches
 - Turn in or mulch with fresh material or cover crops
- Acid rain

Both no-tillage and N application decrease pH

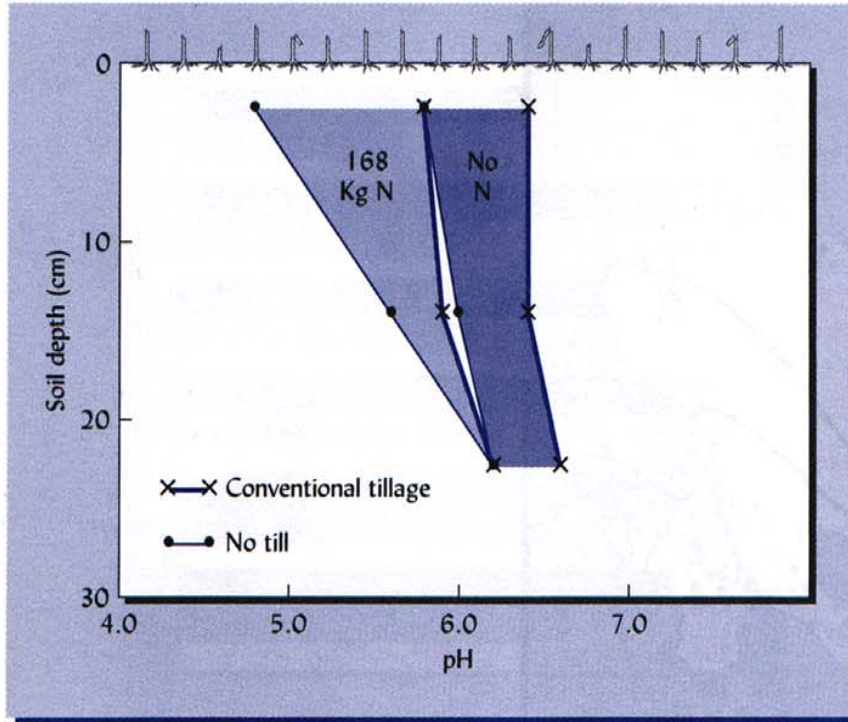


FIGURE 9.8 The effects of 10 years of two tillage practices (conventional and no-till) with and without nitrogen fertilizer on the pH of an Alfisol in a Kentucky corn field. The no-till plots were consistently lower in pH than those that were conventionally tilled. This difference was accentuated on the nitrogen-treated plots, especially in the upper few centimeters of soil. The differences were likely due primarily to the formation of organic acids from residue decay in the no-till plots, and to inorganic acids (e.g., HNO_3) formed from the surface-applied nitrogen fertilizers. [Drawn from data in Blevins, et al. (1983); used with permission of Elsevier Science Publishing Company]

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.

Acid rain from cars, biomass burning and industry forms nitric and sulfuric acids

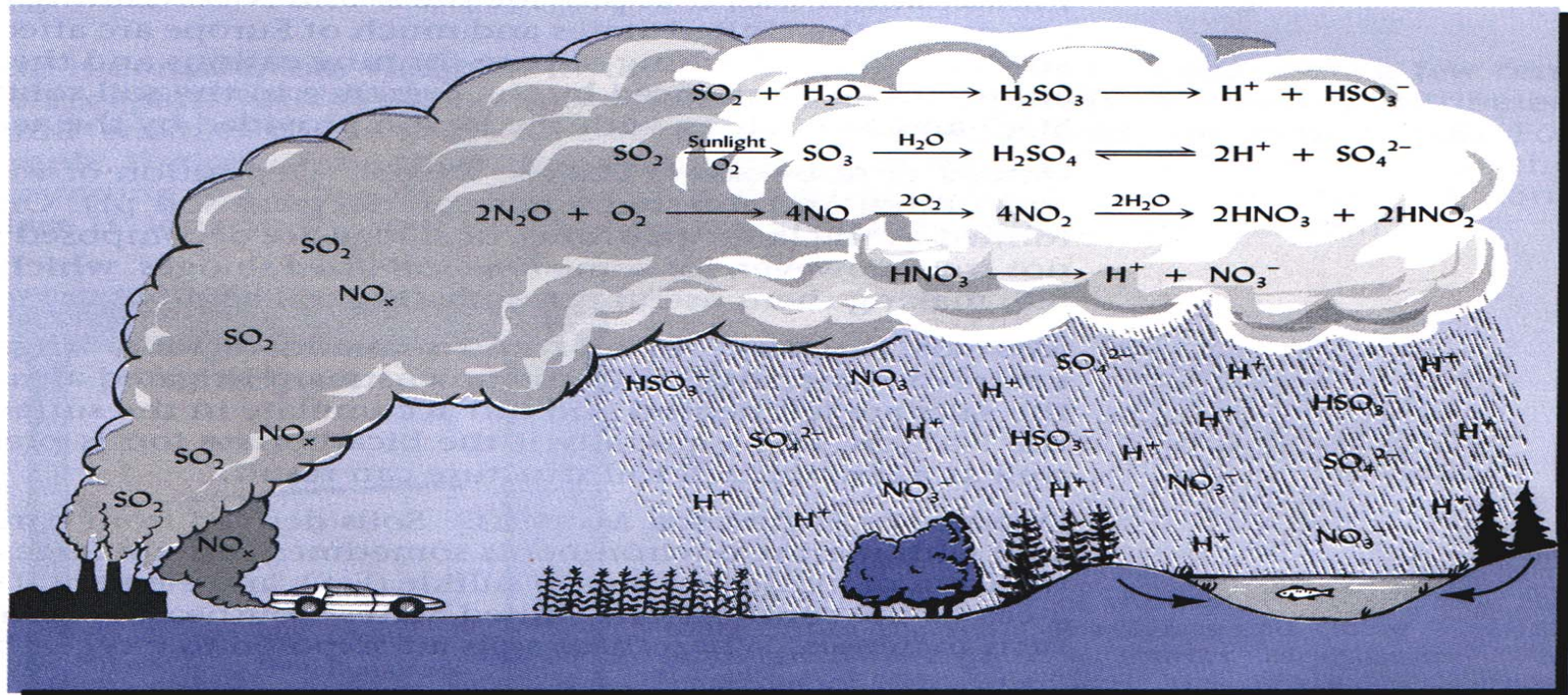


FIGURE 9.9 Illustration of the formation of nitrogen and sulfur oxides from the combustion of fuel in sulfide ore processing and from motor vehicles. The further oxidation of these gases and their reaction with water to form sulfuric acid and nitric acid are shown. These help acidify rainwater, which falls on the soil as acid rain. NO_x indicates a mixture of nitrogen oxides, primarily N_2O and NO . [Modified from National Research Council (1983)]

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.

Acid precipitation in the US

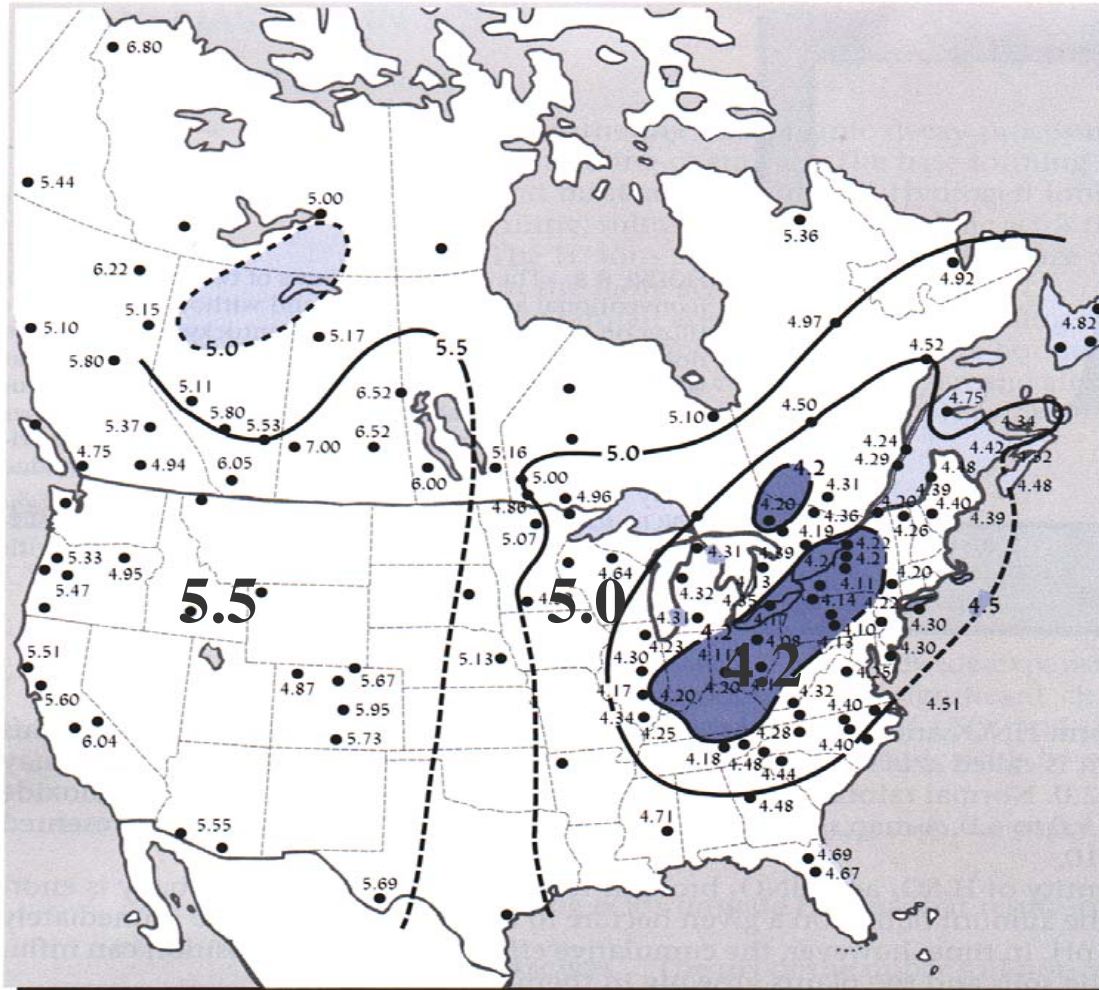
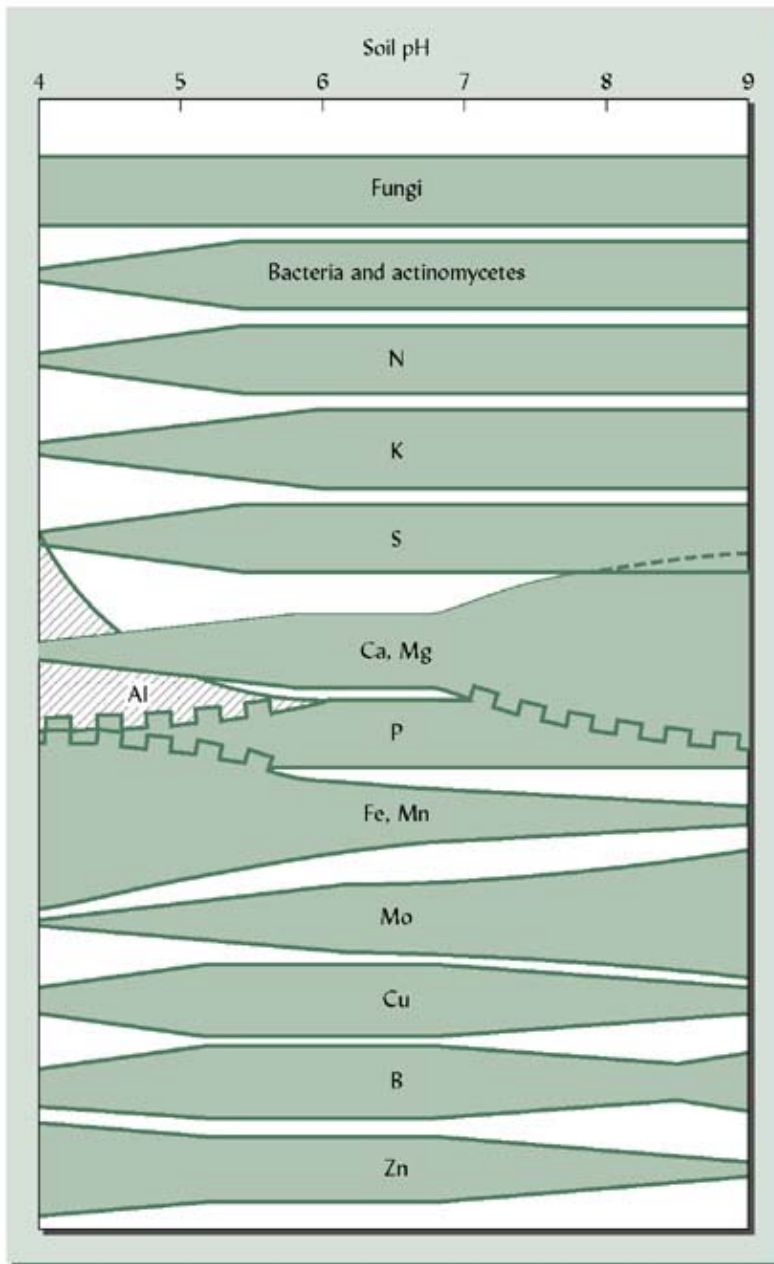


FIGURE 9.10 Annual mean value of pH in precipitation weighted by the amount of precipitation in the United States and Canada for 1980. [From U.S./Canada Work Group No. 2 (1982)]

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.

Outline

- What is soil acidity?
- Why soils get acid
 - natural causes
 - human causes
- **Effects of pH on soil nutrient availability**
- Managing soil pH
 - managing soil alkalinity
 - managing soil acidity
 - lime requirement



Relationship between pH and soil nutrient Availability (Figure 9.22)

FIGURE 9.13 Relationships existing in mineral soils between pH on the one hand and the activity of microorganisms and the availability of plant nutrients on the other. The wide portions of the bands indicate the zones of greatest microbial activity and the most ready availability of nutrients. Note the hatched area showing that low pH greatly increases the solubility of aluminum, a nonnutrient element which is often toxic to many plants in very acid soils. When the correlations as a whole are taken into consideration, a pH range of about 5.5 to 7.0 seems to best promote the availability of plant nutrients. In short, if soil pH is suitably adjusted for phosphorus, the other plant nutrients, if present in adequate amounts, will be satisfactorily available in most cases.

Rainforest

Desert

Managing soil alkalinity in desert areas- decrease pH

- Add fresh (not composted) organic matter
 - form organic and inorganic acids
- Iron Sulfate - FeSO_4 or elemental sulfur
 - Iron needed by plants in desert
 - Sulfate forms sulfuric acid
 - Don't use Ironite- many heavy metals

Managing soil acidity- increase pH

- Burn
- Bone meal?
- Wood ashes (CaO , MgO)
- Add limestone- calcium carbonate (CaCO_3) or dolomitic limestone ($\text{CaCO}_3 + \text{CaMg}(\text{CO}_3)_2$)
- Hydrated lime ($\text{Ca}(\text{OH})_2 + \text{Mg}(\text{OH})_2$)
- Burned lime ($\text{CaO} + \text{MgO}$)

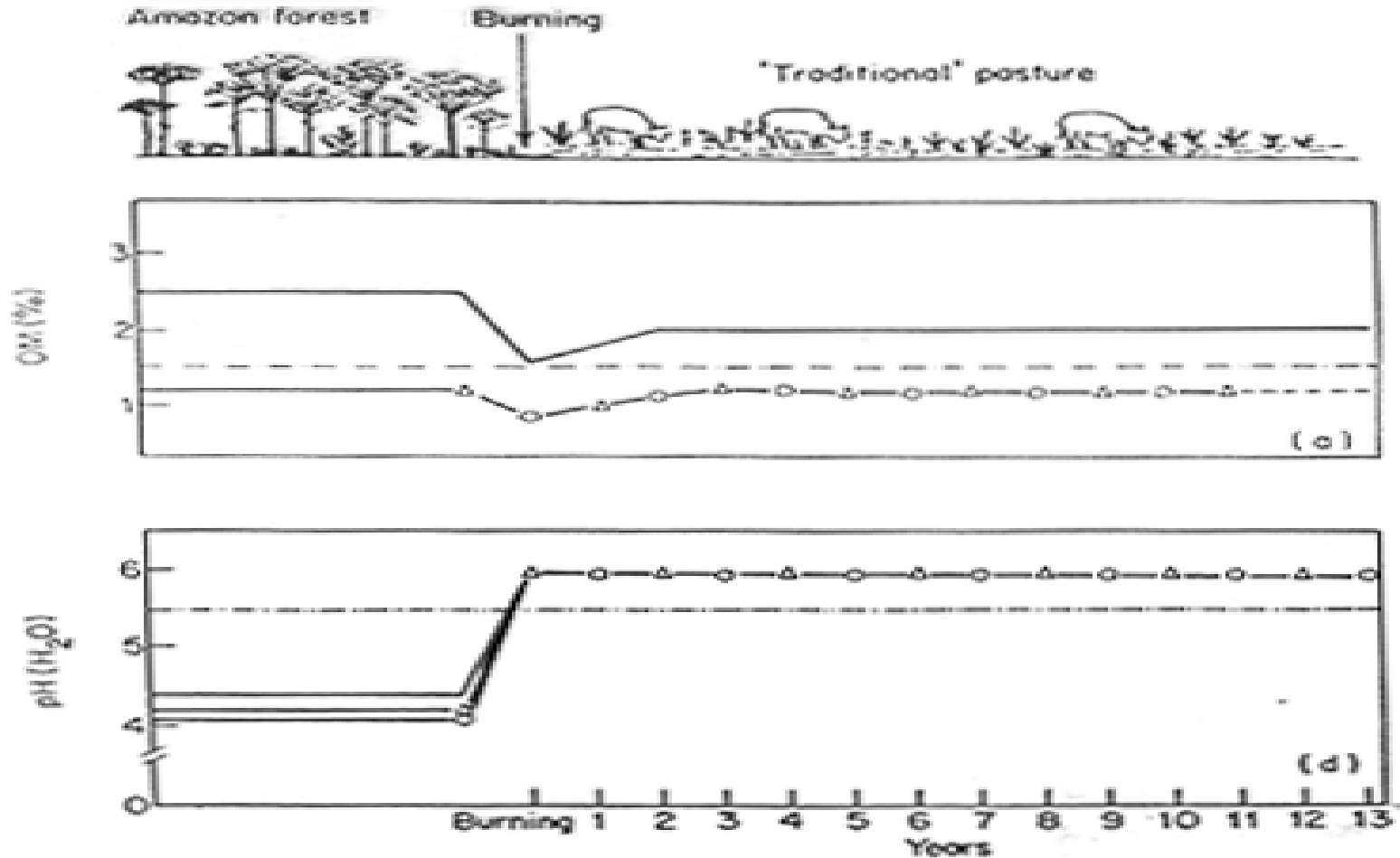
TABLE 9.4 Common Liming Materials: Their Composition and Use

The two limestones are by far the most commonly used. Use of the other materials is largely dependent on the need for fast reaction, cost, and local availability. The relative amounts needed of the different materials can be judged by comparing the respective CaCO₃ equivalent values.

<i>Common name of liming material</i>	<i>Chemical formula (of pure materials)</i>	<i>% CaCO₃ equivalent</i>	<i>Comments on manufacture and use</i>
Calcitic limestone	CaCO ₃	100	Natural rock ground to a fine powder. Low solubility; may be stored outdoors uncovered. Noncaustic, slow to react.
Dolomitic limestone	CaMg(CO ₃) ₂	95–108	Natural rock ground to a fine powder; somewhat slower reacting than calcitic limestone. Supplies Mg to plants.
Burned lime (oxide of lime)	CaO (+ MgO) ^a	178	Caustic, difficult to handle, fast acting, can burn foliage, expensive. Made by heating limestone. Protect from moisture.
Hydrated lime (hydroxide of lime)	Ca(OH) ₂ (+ Mg(OH) ₂) ^a	134	Even more caustic and more difficult to handle than CaO. Fast acting, can burn foliage, expensive. Made by slaking hot CaO with water. Protect from moisture.
Basic slag	CaSiO ₃	70	By-product of pig-iron industry. Must be finely ground. Also contains 1–7%P.
Marl	CaCO ₃	40–70	Usually mined from shallow coastal beds, dried, and ground before use. May be mixed with soil or peat.
Wood ashes	CaO, MgO, K ₂ O, K(OH), etc.	40	Caustic, largely water-soluble, must be protected from water.
Misc. lime-containing by-products	Usually CaCO ₃ with various impurities	20–100	Variable composition; test for toxic impurities.

^a If made from dolomitic limestone.

Burning increases pH



Why does liming work?

Liming with Ca CO_3 has 2 effects

- Ca^{+2} displaces H^+ from soil colloids
- CO_3^{-2} takes up H^+ to form HCO_3^-
(bicarbonate)

Lime requirement depends on:

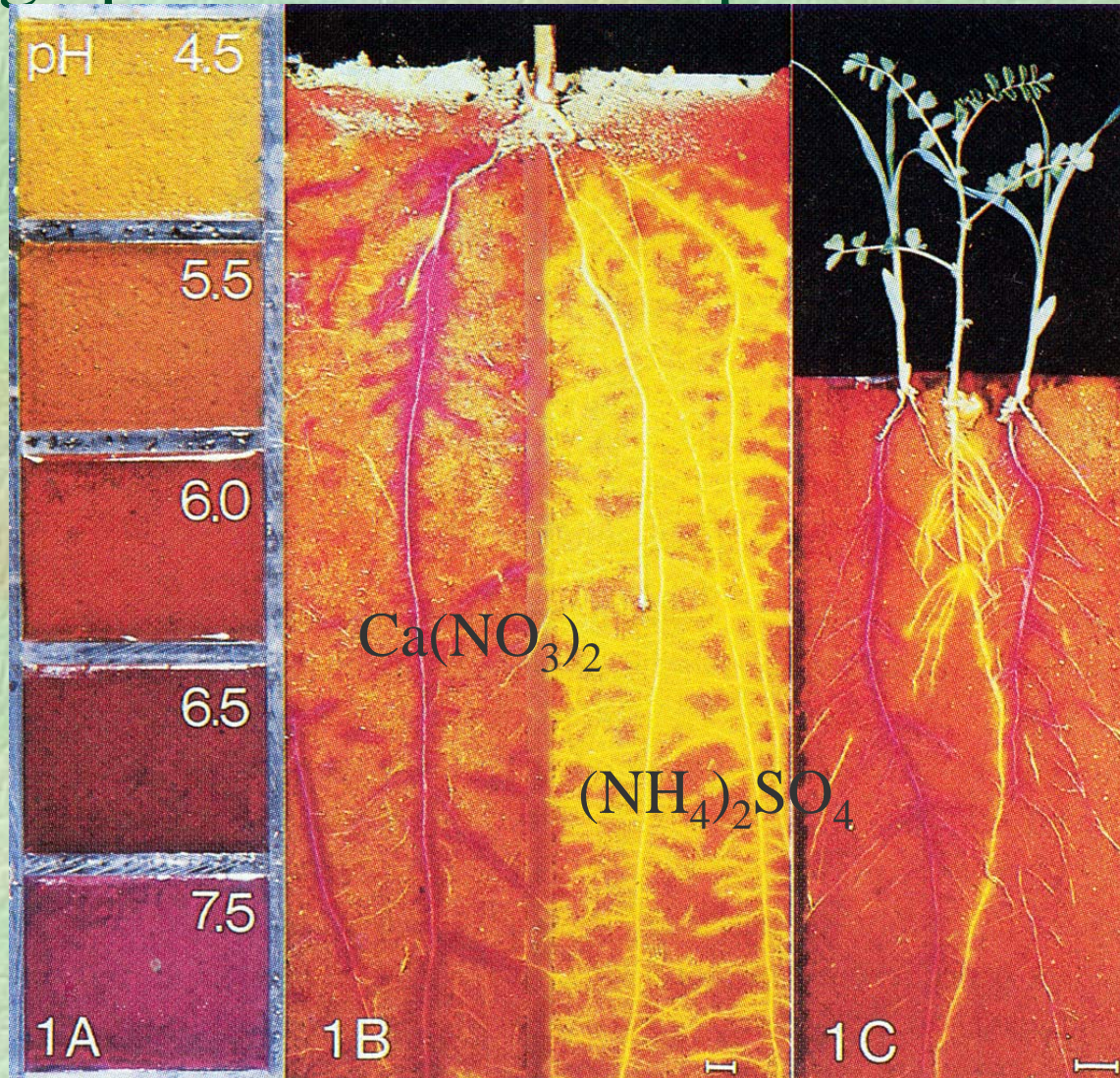
- pH change required
- Buffering capacity of soil
- Chemical composition of lime
- Fineness of particles of lime

Plant species'
tolerance of
soil pH
Manage by
changing
spp

		Soil pH			
		4	5	6	7+
Herbaceous plants	Trees and shrubs	Strongly acid and very strongly acid soils	Range of moderately acid soils	Slightly acid and slightly alkaline soils	
Alfalfa Sweet clover Asparagus Buffalo grass Wheatgrass (tall)	Walnut Alder Eucalyptus Arborvitae			■	
Garden beets Sugar beets Cauliflower Lettuce Cantaloupe	Currant Ash Beech Maple Poplar Tulip tree		■		
Spinach Red clovers Peas Cabbage Kentucky blue grass White clovers Carrots	Philibert Juniper Myrtle Elm Apricot		■		
Cotton Timothy Barley Wheat Fescue (tall and meadow) Corn Soybeans Oats Alsike clover Crimson clover Rice Bermuda grass Tomatoes Vetches Millet Cowpeas Lespedeza Tobacco Rye Buckwheat	Birch Dogwood Fir Magnolia Oaks Cedar Hemlock (Canadian) Cypress Flowering cherry Laurel Andromeda Willow oak Pine oak Red spruce Honey locust		■		
Red top Potatoes Bent grass (except creeping) Fescue (red and sheep's) Western wheatgrass	American holly Aspen White spruce White Scotch pines Loblolly pine Black locust	■			
Poverty grass Eastern gamagrass Love grass, weeping Redtop grass Cassava Napier grass	Autumn olive Blueberries Cranberries Azalea (native) Rhododendron (native) Tea Hemlock (NC) Blackjack oak Sumac Birch Coffee	■			

FIGURE 9.14 Relation of higher plants to the physiological conditions presented by mineral soils of different reactions. Note that the correlations are very broad and are based on pH ranges. The fertility level will have much to do with the actual relationship in any specific case. Such a chart is of great value in deciding whether or not to apply chemicals such as lime or sulfur to change the soil pH.

Different root systems have different rhizosphere pH, and change pH with nutrient uptake



Sorghum
and chickpea
with $\text{Ca}(\text{NO}_3)_2$

Marschner et al.
1986

Split root of corn with two sources of N in pH 6 soil

pH buffering capacity of soil

- Buffer is the tendency of the soil to resist changes in pH-- due to exchange and residual acidity
 - analogy with the coffee dispenser
- Active acidity is small part of total acidity
 - In the soil solution
- Salt-replaceable empirically determined by replacing with K^+ or Ca^{++}
 - H^+ and Al^{+3} adsorbed to soil colloids
- Residual acidity is greater part (100x active)
 - Associated with H and Al bound to clays
- Tested by pH with SMP buffer (in lab today) (Shoemaker, McLean and Pratt 1961)

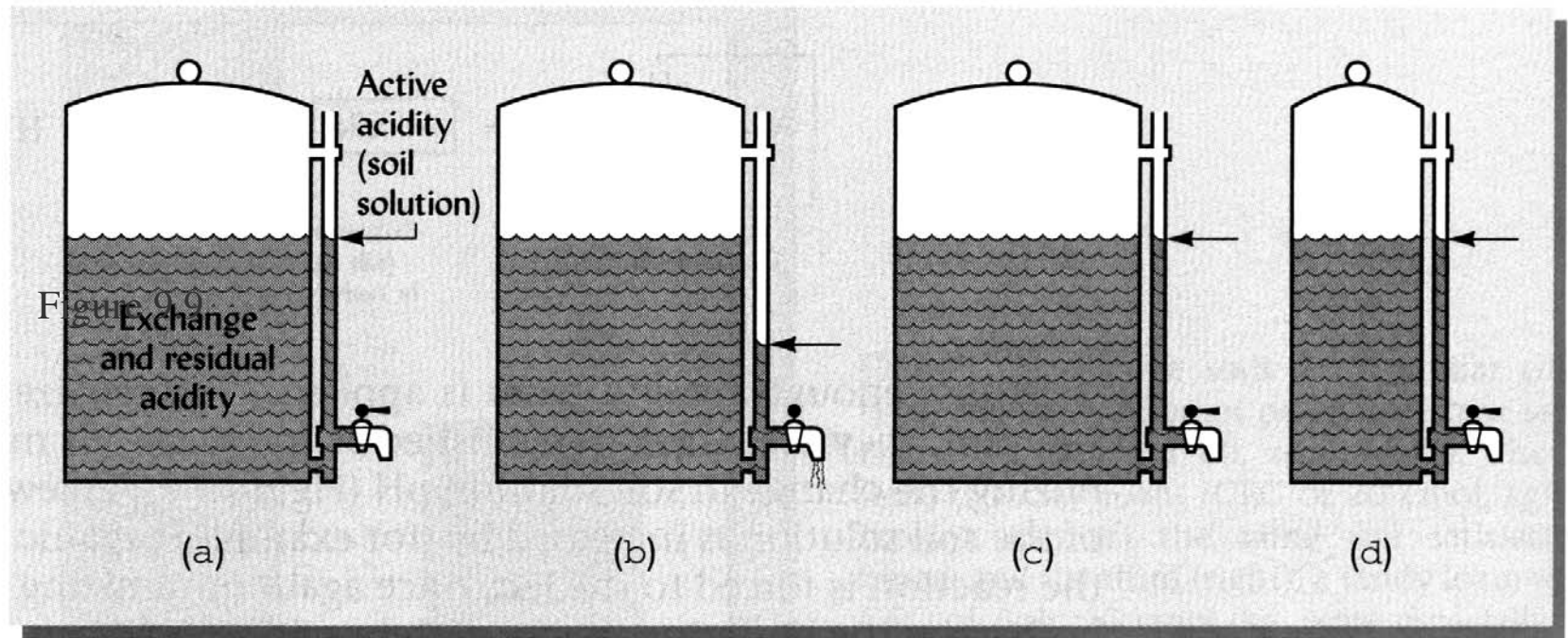
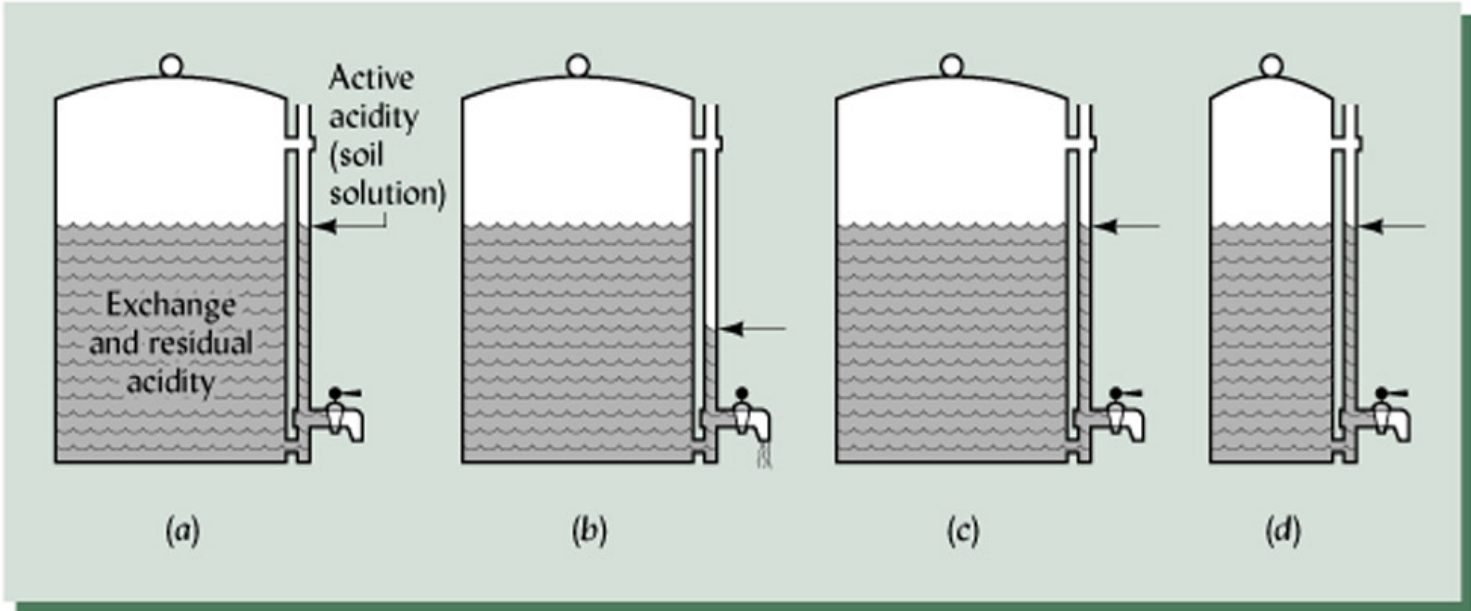


FIGURE 9.7 The buffering action of a soil can be likened to that of a coffee dispenser. (a) The active acidity, which is represented by the coffee in the indicator tube on the outside of the urn, is small in quantity. (b) When hydrogen ions are removed, this active acidity falls rapidly. (c) The active acidity is quickly restored to near the original level by movement from the exchange and residual acidity. By this process, there is considerable resistance to the change of active acidity. A second soil with the same active acidity (pH) level but a much smaller exchange and residual acidity (d) would have a lower buffering capacity.

Brady, N.C. and R.R. Weil. 1999. *The Nature and Properties of Soils*. 12th ed. Prentice Hall, New Jersey.

Figure 9.9



Type of buffering capacity changes with pH

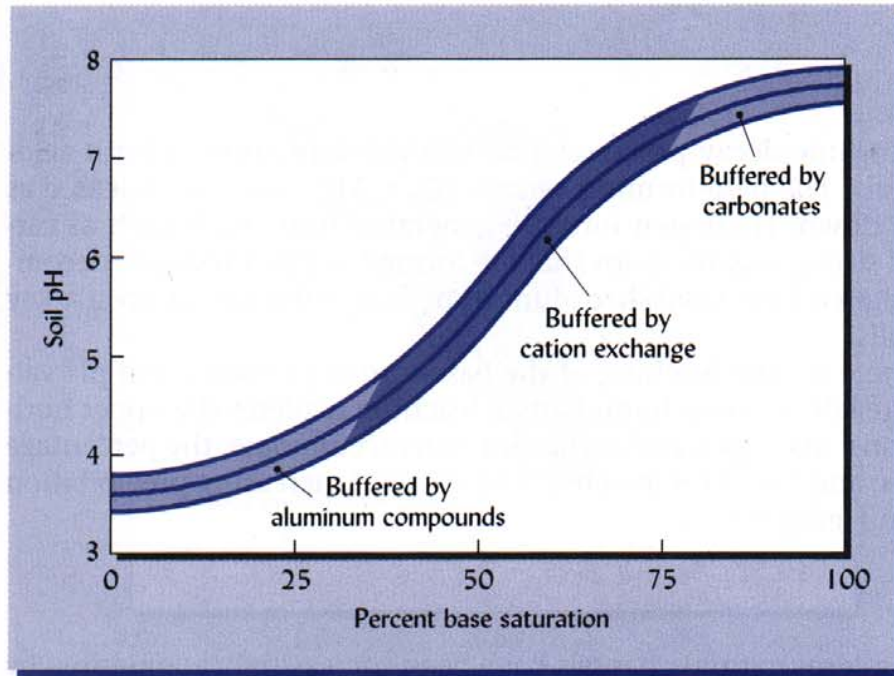
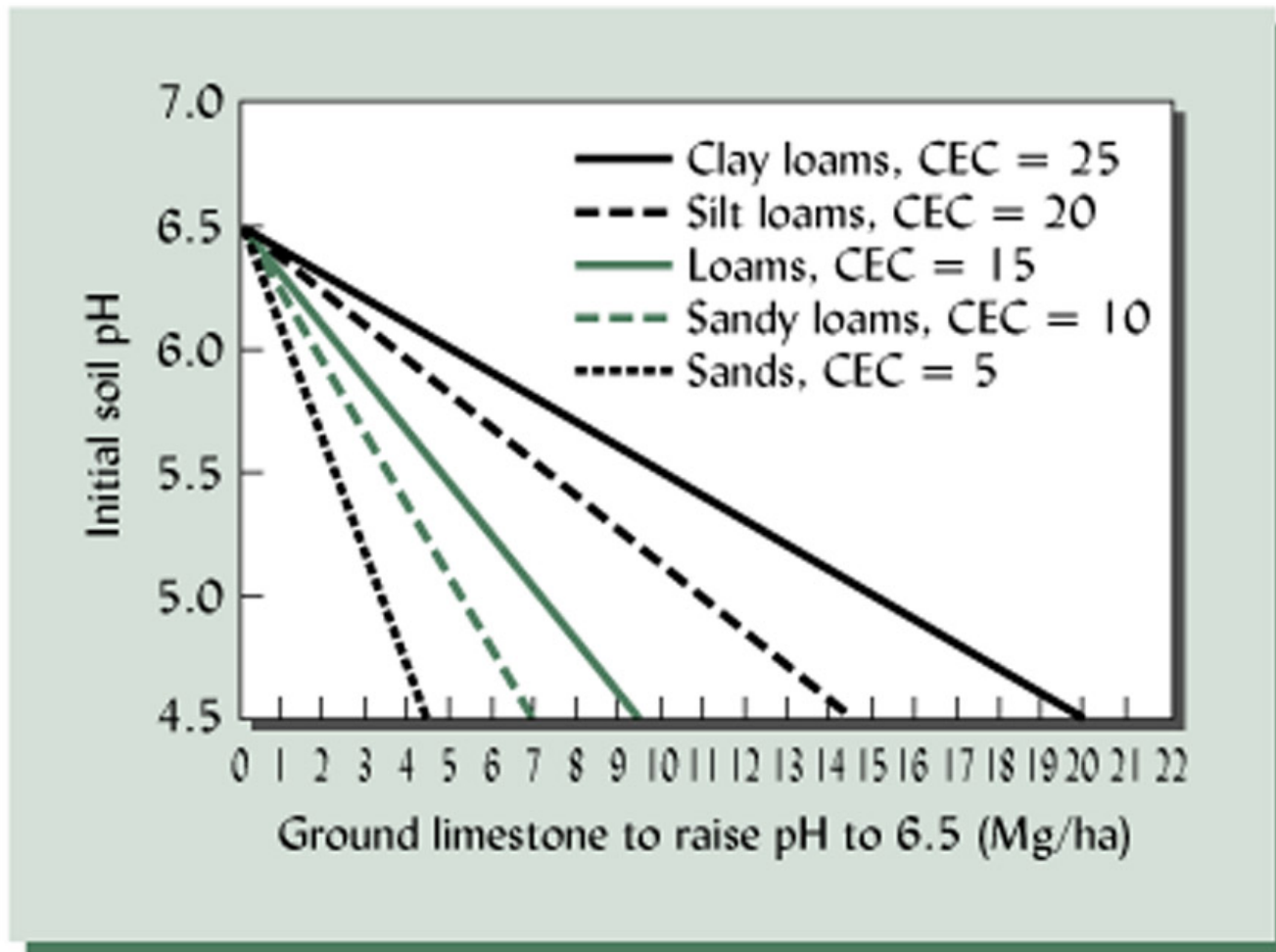


FIGURE 9.6 The relationship between percent base saturation and soil pH of Vermont soils, the appropriate pH range where three major buffering mechanisms are most effective: aluminum compounds at low pH, cation exchange at intermediate pH, and carbonates at high pH values. Although there is much variation from one soil to another in the pH-base saturation relationship, the three major mechanisms shown for buffering soils usually pertain. [Magdoff and Bartlett (1985)]

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.

(Fig 9.7 p374 B&W13th)

Effect of soil texture on lime requirement (Fig 9.24)



Change in pH over time with liming in a cropping system

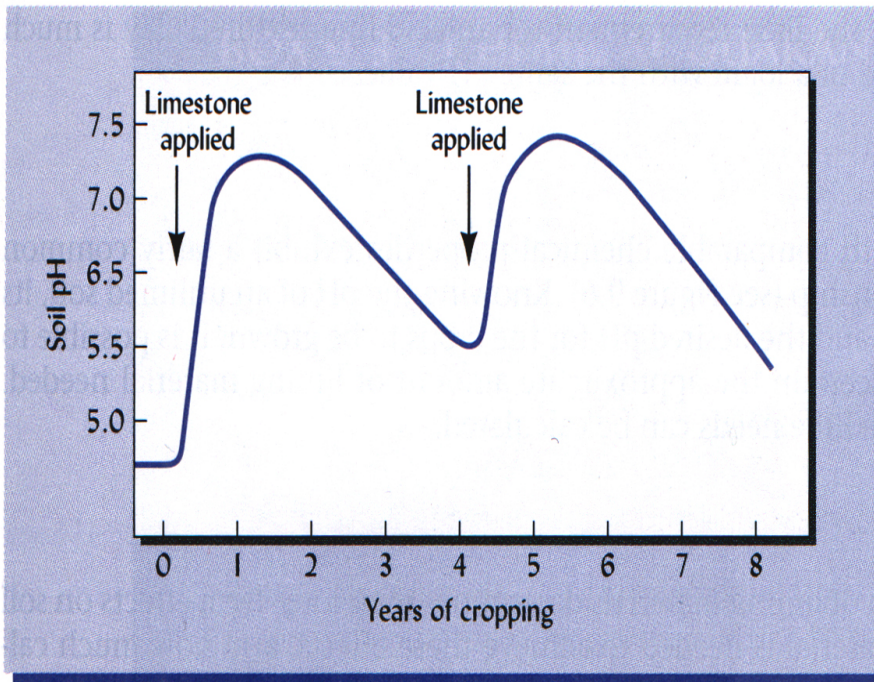


FIGURE 9.16 Diagram to illustrate why repeated applications of limestone are needed to maintain the appropriate chemical balances in the soil. Soil pH likewise increases after 4 to 8 Mg/ha (3.5 to 4.5 tons/acre) of limestone is applied to a temperate region soil. The pH reaches a peak after about one year. Leaching and crop removal deplete the calcium and magnesium and, in time, the pH decreases until a renewed application of limestone is necessary.

Brady, N.C., and R.R. Weil. 2000. *Elements of the Nature and Properties of Soils*. Prentice-Hall, New Jersey.



Summary: pH, The Master Variable

- Tiny concentration of H^+ has big effect on plant nutrient uptake, biotic community
- Optimum pH for microbes and plant nutrient availability = 5.5-7.0
- Easy to measure pH, both active and residual
- Cheaply and relatively easily managed in organic and conventional agricultural systems with the addition of lime

Study questions

- B and W Chapter 9. Soil Acidity. # 1-10