

Polymerization



Monomers combine with the loss of some simple molecule (usually H_2O)

- condensation reaction: A (usually stepwise) reaction in which two or more reactants (or remote reactive sites within the same molecular entity) yield a single main product with accompanying formation of water or of some other small molecule, e.g. ammonia, ethanol, acetic acid, hydrogen sulfide.
- Maillard reaction—polymerization between sugars and amino acids produce melanoidins
 - Too much heterocyclic N to be pathway in soils

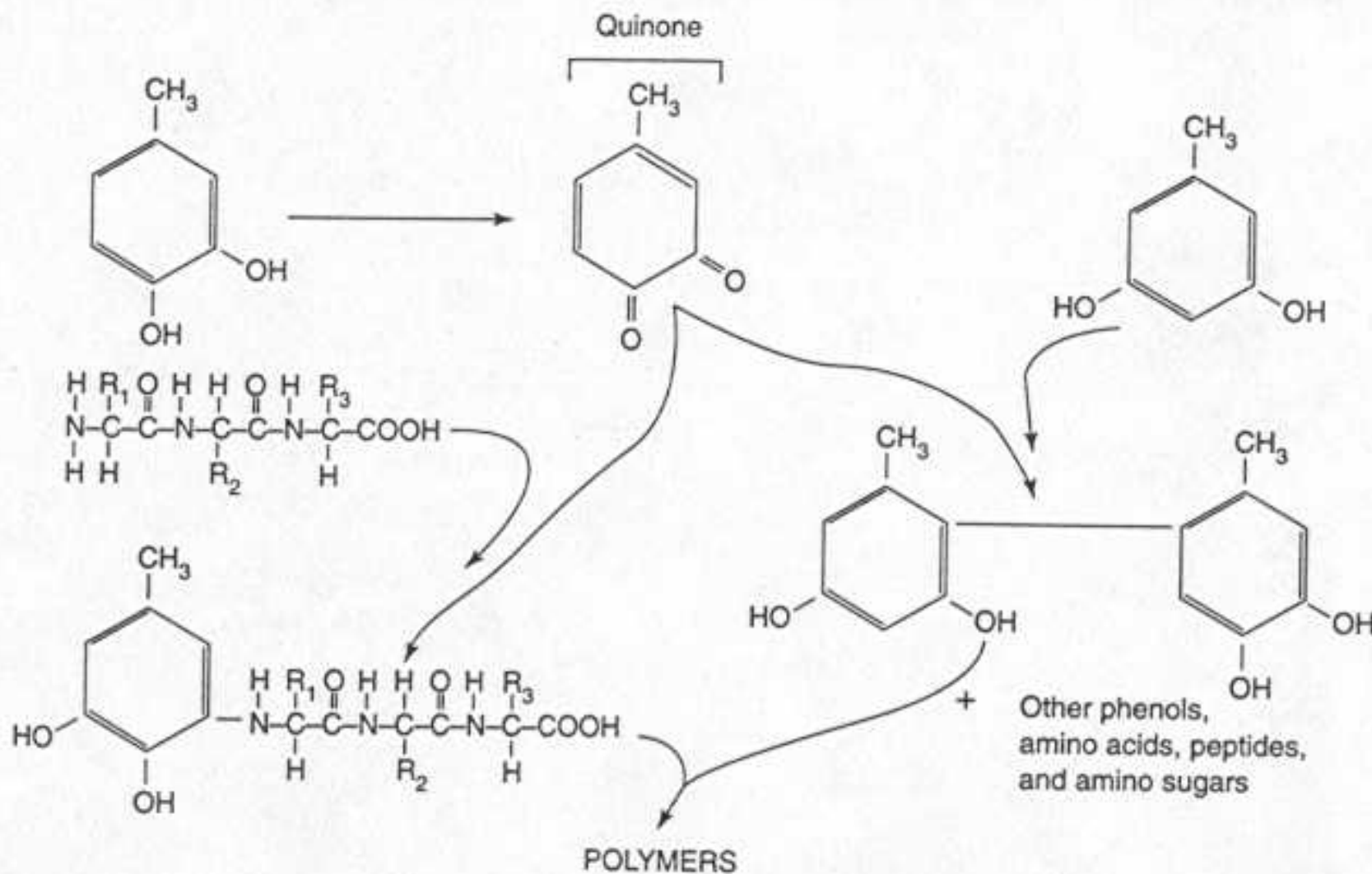


Figure 11-18 Possible condensation or polymerization reactions of phenols involving quinone formation that result in the production of humic polymers. *Adapted from Burns and Martin (1986). Used with permission.*

Many pathways to humics



■ Lignin theory

- Initial product is humin—relatively low in O
- Humic and fulvic acids follow

■ Polyphenol theory

- Reactions between quinones and amino acids
- Initial products are high in O (fulvic and humic acids)

A new theory of formation



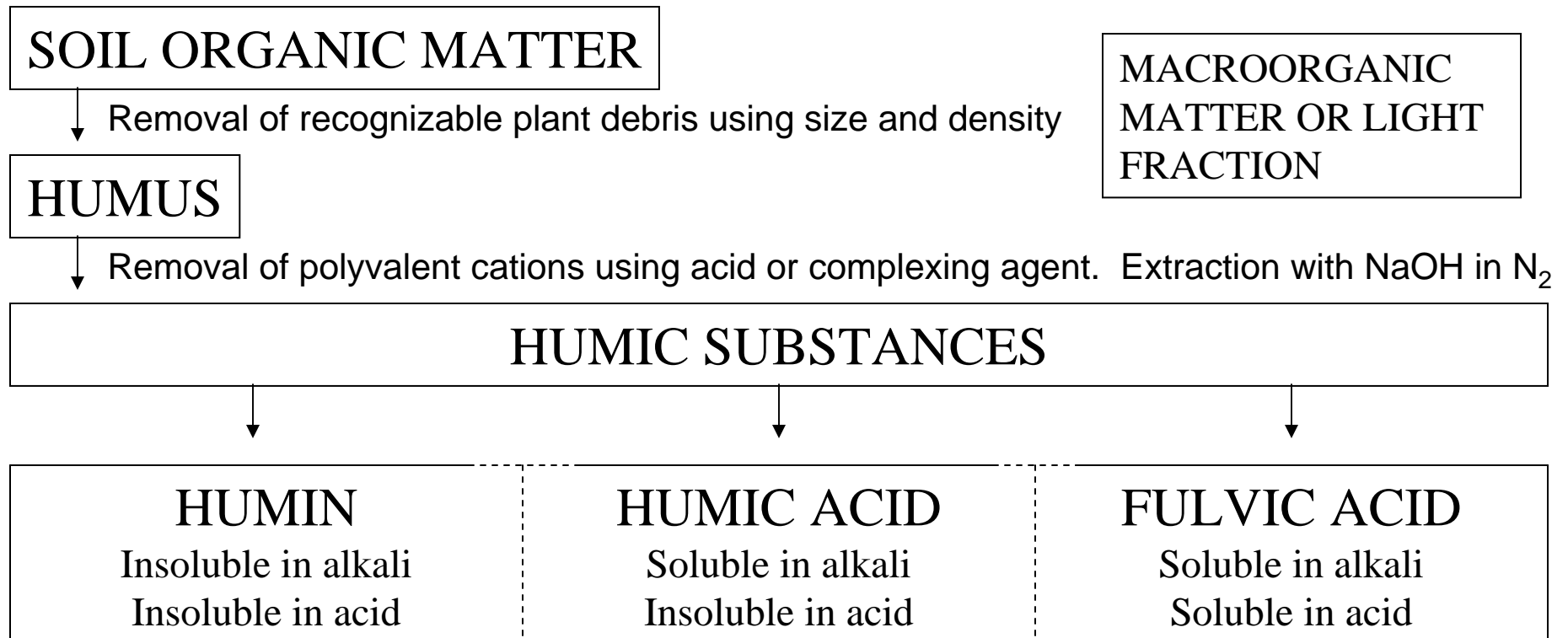
- humics aren't actually macromolecules
- instead, they are supramolecular associations of relatively small molecules
- self organized into micelle-like structures
 - hydrophobic portions inward
 - hydrophilic portions in contact with solution
- these structures can also build up on clay surfaces

Chemistry of SOM



- Definitions (from text)
- Composition
- Structure
- Reactivity
- Metal Binding
- Clay - Humus complexes

Chemical Fractions of SOM



Operationally defined: method determines results

Structure

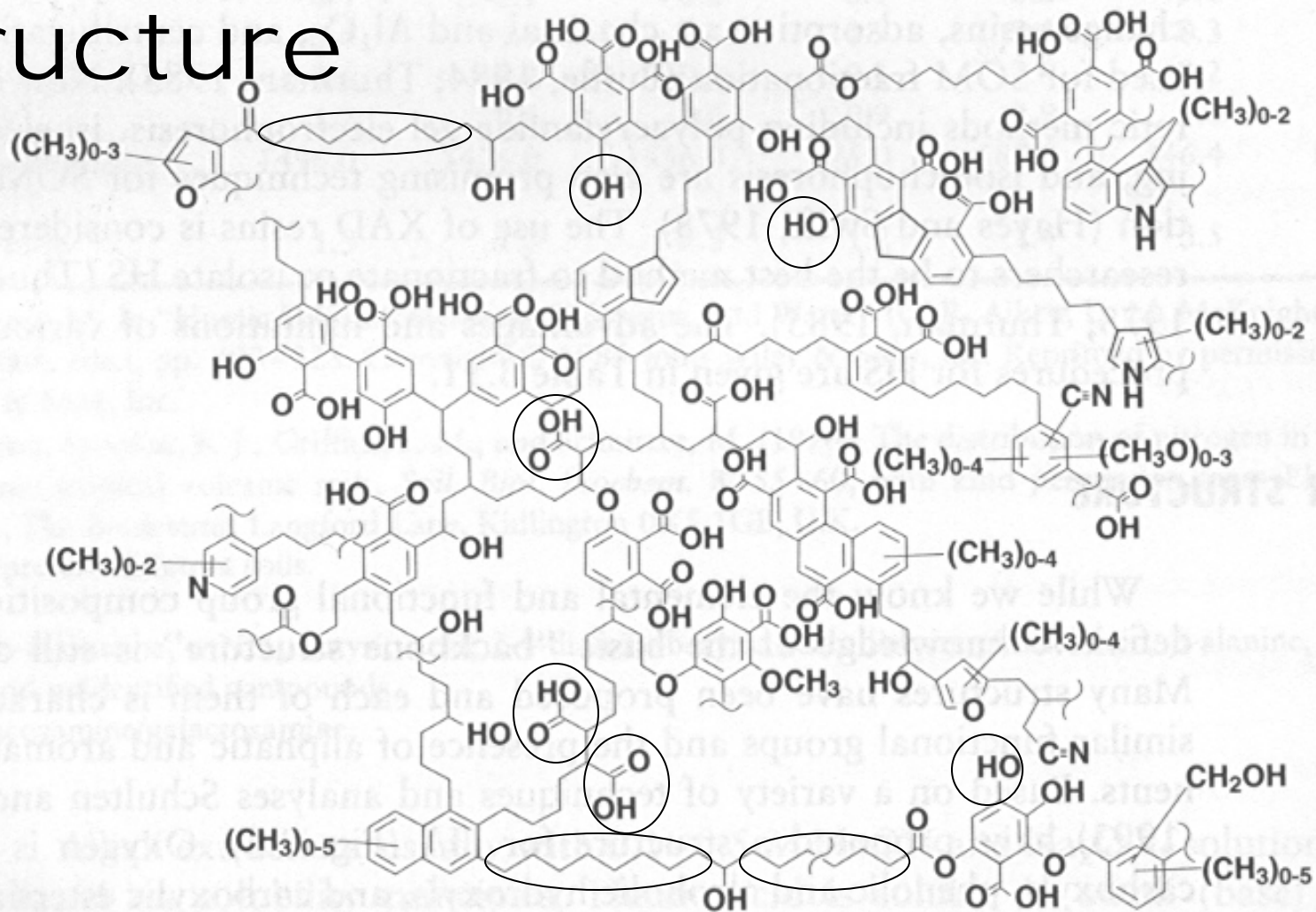


FIGURE 3.5. Schematic of humic acid structure. From Schulten and Schnitzer (1993), with permission from Springer-Verlag.

Chemical Fractions of SOM

HUMIN	HUMIC ACID	FULVIC ACID
Insoluble in alkali Insoluble in acid	Soluble in alkali Insoluble in acid	Soluble in alkali Soluble in acid

<u>Molecular weight decreasing</u>				
10 ⁶	100 000	10 000		1000
<u>Cation exchange capacity (cmol kg⁻¹) and acidity increasing</u>				
100?	300	500		1000
<u>Carbon content (g kg⁻¹) decreasing</u>				
550	620	560	520	430
<u>Oxygen content (g kg⁻¹) increasing</u>				
340	290	360	440	510
<u>Nitrogen content (g kg⁻¹) decreasing</u>				
46	55		41	7
<u>Hydrogen content (g kg⁻¹) variable</u>				
55	29	67	33	50

Nuclear Magnetic Resonance



- Nuclei 'spin' and many have a 'magnetic moment'.
- In NMR, the sample is placed in a strong magnetic field, pulses of RF energy excite the nuclei, the 'resonance frequency' is measured as the nuclei return to their ground state (relax).
- Different environments around the nuclei will give different frequencies and these can be quantified.
- Solid state 'magic angle' NMR is used on soils
- Paramagnetic substances interfere (e.g. Fe)

Nuclear Magnetic Resonance

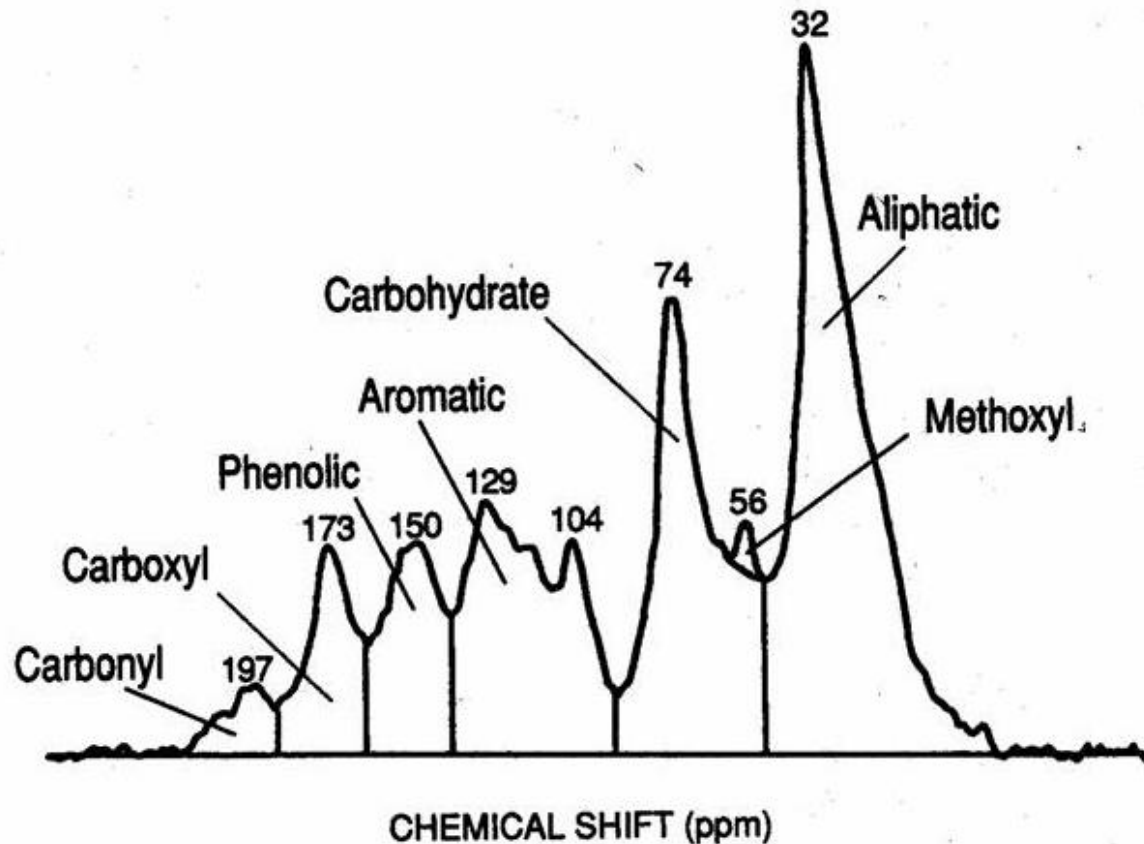


Fig. 2-5. Different C types at 95-cm depth in virgin soil at a site in transition to a bog in Quebec, shown in a CPMAS ^{13}C NMR spectrum (modified from Preston et al., 1987).

Decomposition shown by NMR

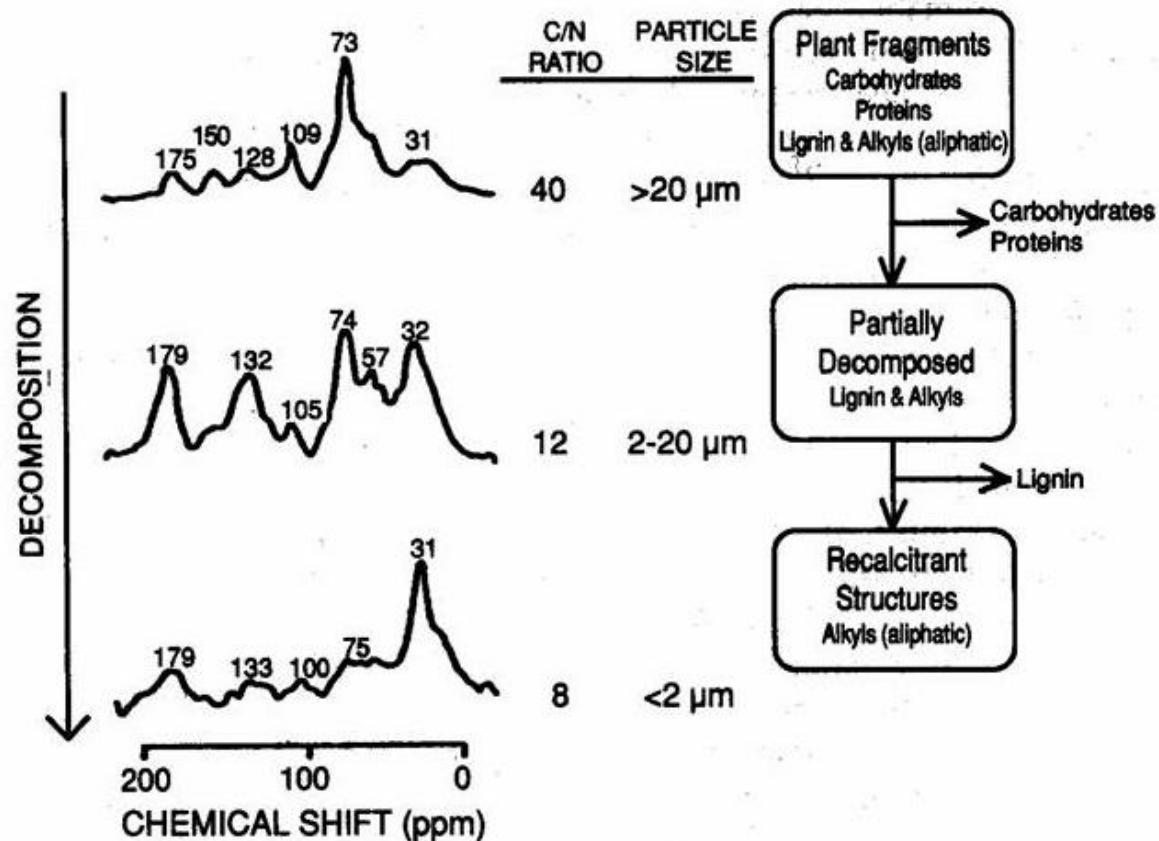


Fig. 2-6. Decomposition of soil OM in the A horizon of a South Australia wheat (*Triticum aestivum*) pasture Mollisol as a function of particle size. Parallel changes are shown in CPMAS ¹³C NMR spectra and the C/N ratio (modified from Baldock et al., 1992).

Reactivity



- Up to 100% of the CEC of soils is due to Organic Matter.
- Functional groups
 - carboxyl R-C(=O)-OH
 - quinone Ar=O
 - phenolic OH Ar-OH
 - enols R-CH=CH-OH

Reactivity



- The charge on SOM is pH dependent.
 - Above about pH 3, SOM has a negative charge.
 - Dissociation of carboxylic groups (low pH range)
 - Dissociation of phenolic groups (higher pH range)
 - Source of buffering
- However, the CEC in most forest soils does not change with pH.

Acidity constants (K_a)



HCOOH	17.7×10^{-5}
CH ₃ COOH	1.75×10^{-5}
CH ₃ CH ₂ CH ₂ COOH	1.52×10^{-5}
Cl CH ₂ COOH	136×10^{-5}
Cl ₂ CHCOOH	5530×10^{-5}
Cl ₃ CCOOH	23200×10^{-5}
CH ₃ CH ₂ CH Cl COOH	139×10^{-5}
CH ₃ CH Cl CH ₂ COOH	8.9×10^{-5}
Cl CH ₂ CH ₂ CH ₂ COOH	2.96×10^{-5}

Metal Binding



The total binding capacity of HA for metal ions is about 200 - 600 $\mu\text{mol g}^{-1}$.

- About 33% of this total is due to the retention on CEC sites.
- Complexation:
 - Adsorption
 - Specific Adsorption
 - Chelation

Soil forming factors and OM



- Time: Rapid initial accumulation of OM that reaches equilibrium within 110-1500 years.
- Climate: affects vegetative production/decomp.
- Vegetation: Large differences between grasslands and forest soils, and between tree species.
- Parent material: Finer texture usually has higher OM—sorption by clays, physical protection in micro pores, less aeration.
- Topography: Drainage class has an effect.