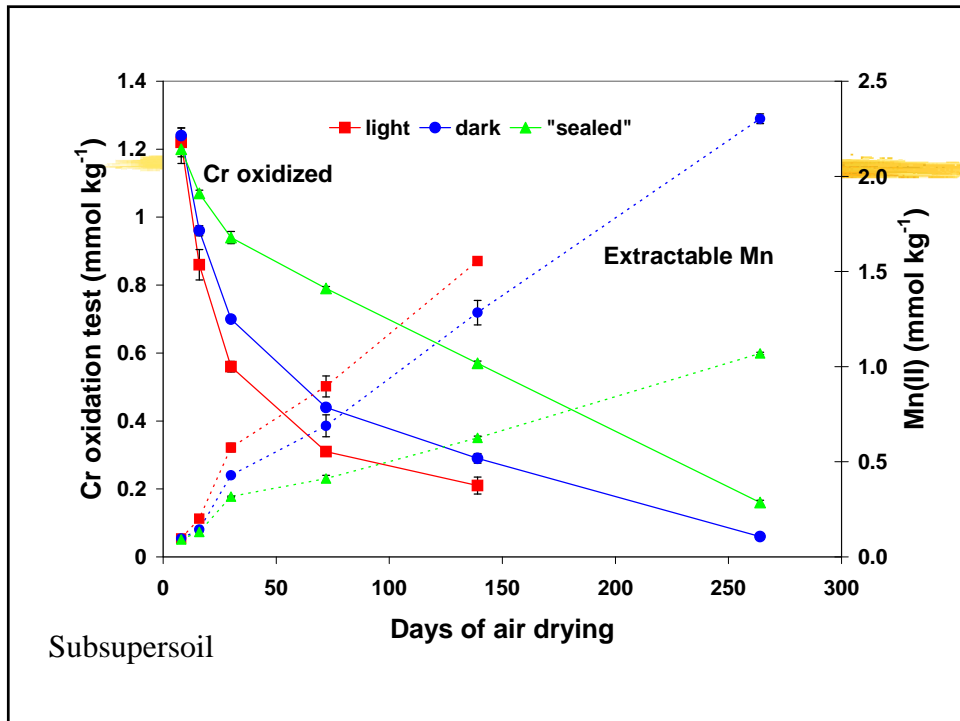
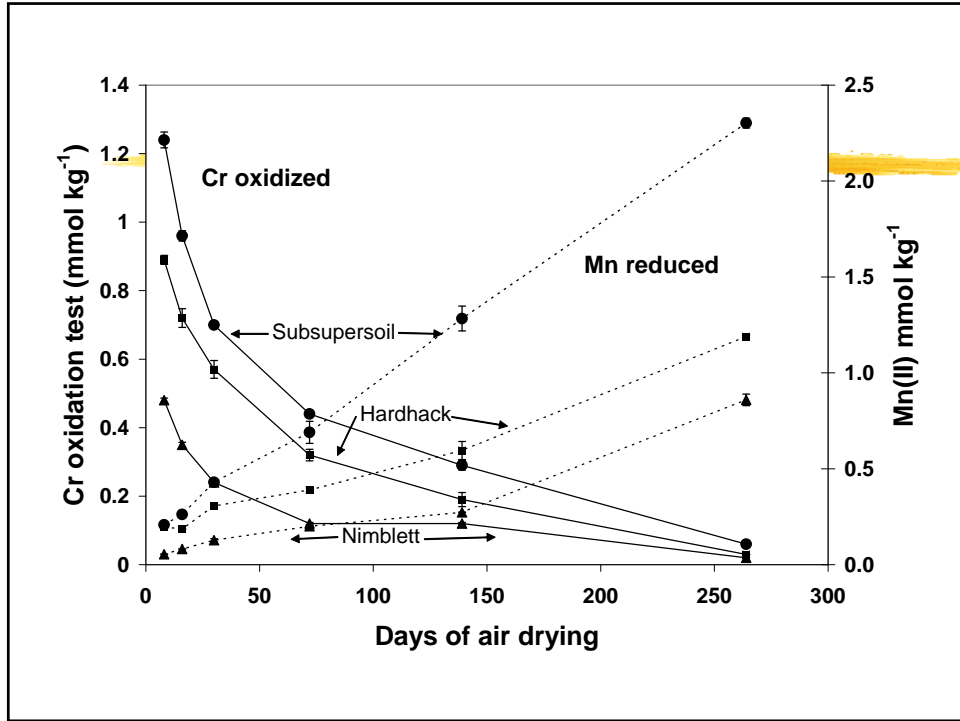


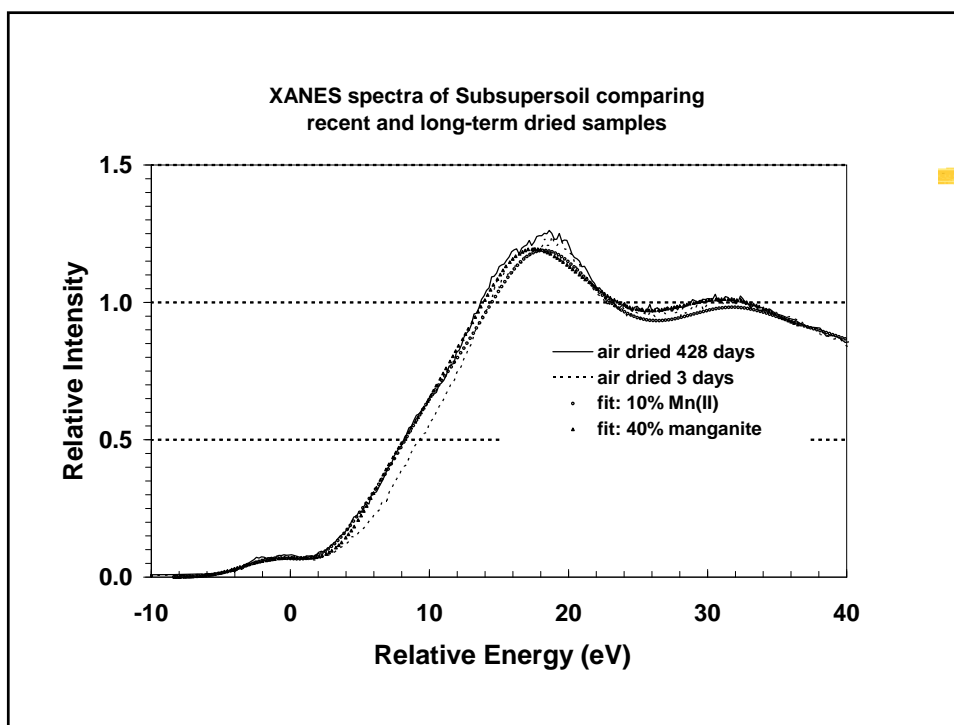
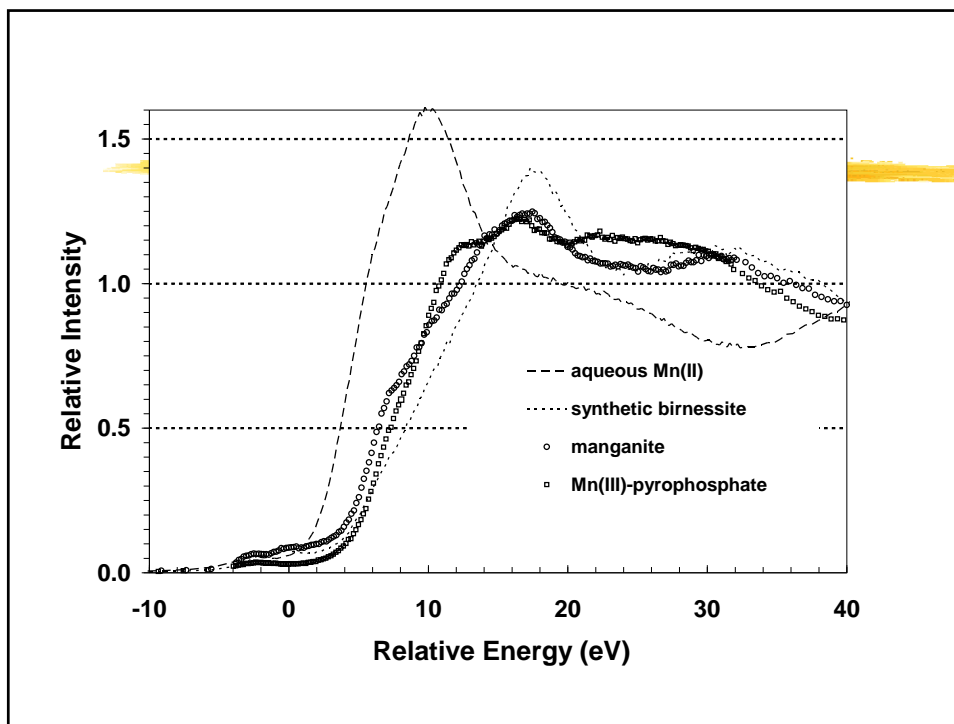
## Soil vs. dirt

- Soils are often dried, ground and sieved before chemical analysis.
- This provides a homogenous sample from which repeated measurements can be taken.
- However, it has been found that many soil characteristics will change.
  - Organic matter becomes more soluble
  - Manganese reduces and becomes more soluble
  - Phosphorus is often less soluble but not consistently

## Soil vs. dirt

- Bartlett R.J., and B.R.James. 1980. Studying dried, stored, laboratory soil samples--some pitfalls. *Soil Sci. Soc. Am. J.* 44:721-4.
- Fujimoto C.K., and G.D.Sherman. 1945. The effect of drying, heating, and wetting on the level of exchangeable manganese in Hawaiian soils. *Soil Sci. Soc. Am. J.* 10:107-12.
- Ross D.S., H.C. Hales, G.C. Shea-McCarthy, and A. Lanzirotti. 2001. Sensitivity of soil Mn oxides: drying and storage cause reduction. *Soil Sci. Soc. Am. J.* 65:736-743.
- Shindo H., and P.M.Huang. 1982. Role of Mn(IV) oxide in abiotic formation of humic substances in the environment. *Nature (London)* 298:363-5.
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## Lowry-Brønsted acids

- loss or gain of protons
  - Lewis acid accepts an electron pair
- strong vs. weak acids
  - low vs. high  $pK_a$
- Carbonic acid is a special case of a weak acid
  - controls the pH of most natural waters

## Complex ions and ion pairs

- ion pair—soluble weak association of two charged ions.
  - Outer sphere—ligand does not replace water
- complex ion—metal and ligand (other than water) form a soluble “species”
  - Inner sphere—ligand replaces water
- solvation complex—metal plus primary hydration sheath (ligand is water)

## Types of complexes

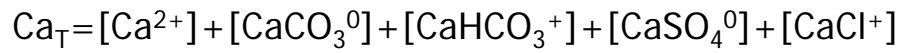
- monodentate—one bond
  - Cu-acetate
- bidentate—two bond
  - Cu-oxalate
- polydentate (chelates)
  - Cu-citrate
  - Cu-EDTA
- $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

## Metal-fulvate interactions

- Strong sites (type 1)—inner sphere multidentate
  - dominate at low metal/high fulvate conc.
  - two carboxylic or phenol/carboxylic groups
- Weak sites (type 2)—outer sphere and monodentate
  - important when type 1 sites become saturated
  - H bonding or single bond with carboxylic group

## Speciation

- Analysis of soil solution gives total ion concentration. This is the sum of:
  - free (hydrated) ion
  - complexed ion



## Speciation Modeling

- Computer programs
  - GEOCHEM
  - MINTEQA
  - SOILCHEM

Equilibrium models  
Thermodynamic database