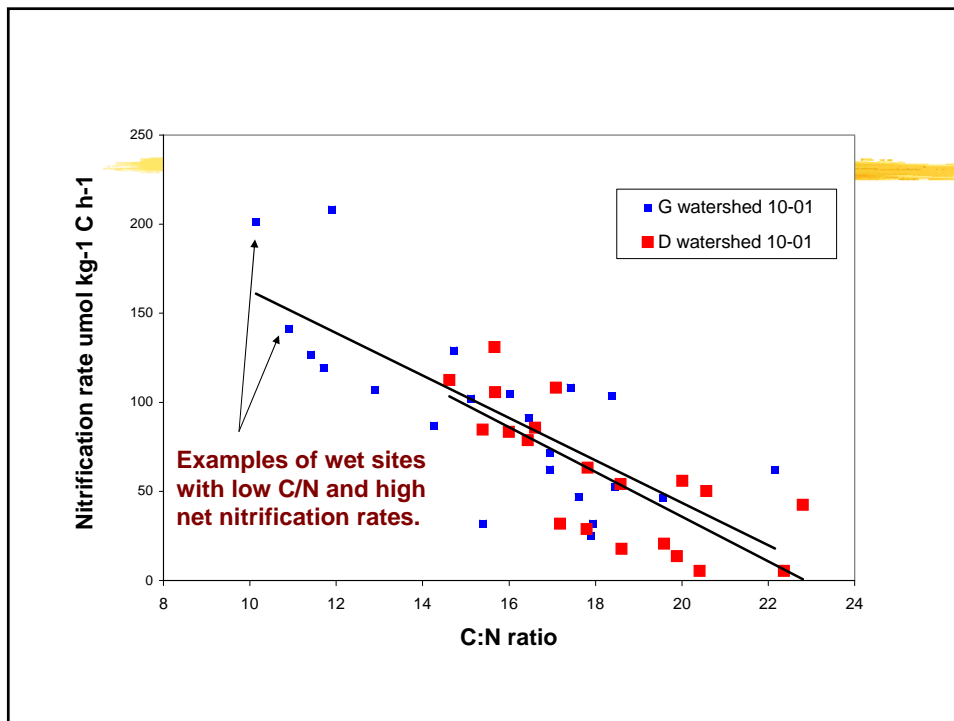


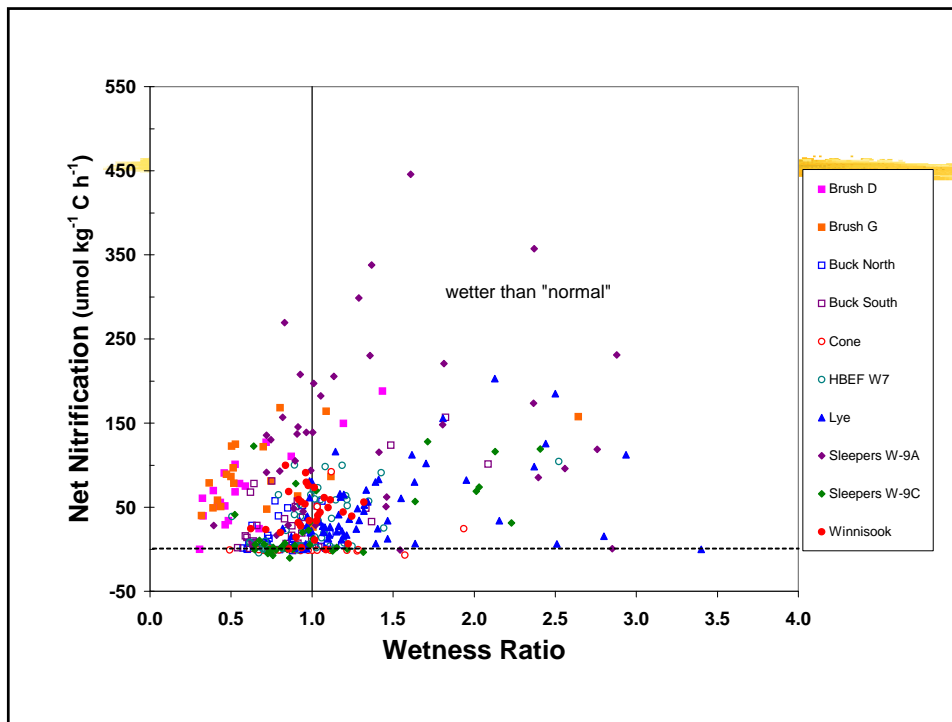
N redox

- Problems with thermodynamic approach
 - oxidized species (e.g. nitrate) are not "electroactive"
 - some reactions behave irreversibly
- Denitrification
 - usually carried out by heterotrophs that are facultative anaerobes and have specific enzymes capable of using N species as e^- acceptors
 - can be significant in flooded soils, riparian zones and wetlands

Denitrification

- nitrate > nitrite ($2 e^-$). NO_2^- is reactive and short-lived
- nitrite > nitric oxide ($1 e^-$). NO is reactive and not much is released to the atmosphere
- nitric to nitrous oxide ($1 e^-$). N_2O emissions can be significant and contribute to ozone depletion.
 - also a byproduct of nitrification (leaky pipe)
- nitrous oxide to dinitrogen ($1 e^-$). N_2 is relatively inert. Difficult to measure N_2 production.





Manganese

- More easily reduced than iron, less readily oxidized.
- Anoxic soils contain Fe²⁺. Introduction of oxygen will chemically oxidize it to Fe³⁺.
 - No microbes needed.
- In aerobic soils, Mn determines the redox status or poise
- Oxidized Mn is thermodynamically favored in the presence of O₂.
- However, abiotic oxidation below pH 7.5 is difficult to prove.

Manganese Oxides

- “Higher” oxides consist primarily of Mn(IV) octahedrally coordinated with O
- Birnessite (a layered Mn oxide) may contain as much as 20% Mn(III) and is thought to be common in soils.
- Mn oxides are relatively disordered in their “pure” state and are difficult to detect in soils, both because of this and because of low concentrations.
- The average amount of Mn in a soil is about 0.05% but this amount still may be important in determining a soil’s chemical behavior (especially metal sorption).

Mn(III)

- Mn(III) is extremely reactive and is not found as a free ion in solution.
- It may be stabilized in mineral structures or by complexation with hydroxy carboxylic acids (e.g. citrate) or pyrophosphate.
- Dismutation or disproportionation:
 - $2\text{Mn(III)} > \text{Mn(II)} + \text{Mn(IV)}$
- Reverse dismutation
 - $\text{Mn(II)} + \text{Mn(IV)} > 2\text{Mn(III)}$

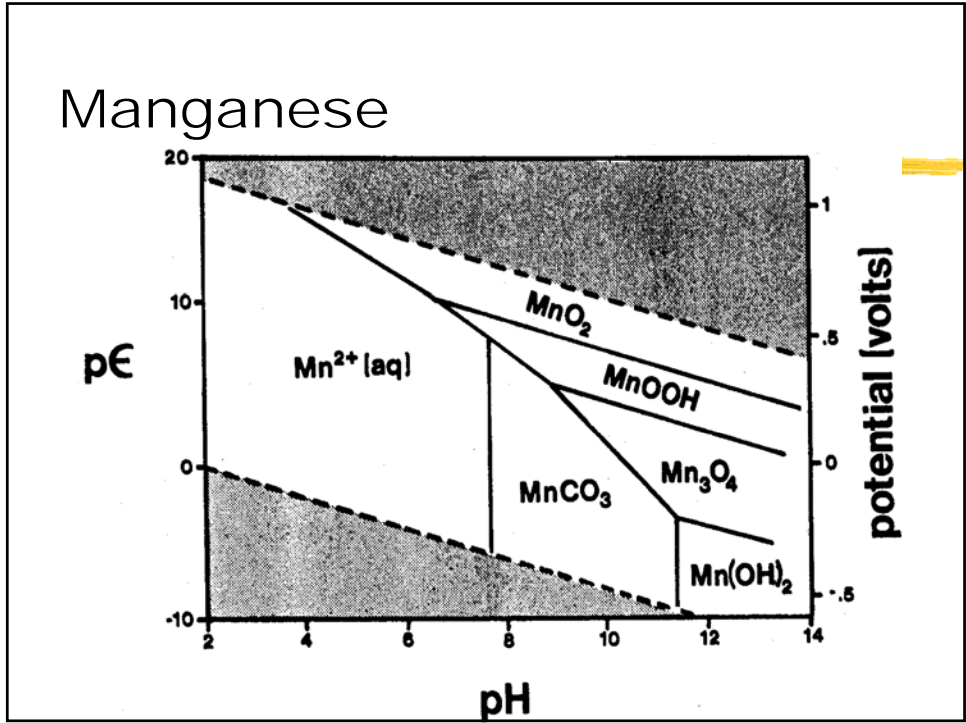
Mn oxide reactivity

- capable of oxidizing many metals, etc.
 - Cr(III) > Cr(VI) toxic, mobile
 - Co(II) > Co(III) immobile
 - Pu(III,IV) > Pu(VI) toxic, mobile
 - As(III) > As(V) less toxic
 - Se(IV) > Se(VI)
- Mechanism: sorption, electron transfer, release or incorporation into structure.
- Because Mn oxides are poorly ordered, surface reactivity is difficult to determine. Lattice vacancies may create sites for sorption and e^- transfer.

Mn oxide reactivity (cont.)

- capable of oxidizing many organics
 - polyphenols (hydroquinone)
 - ascorbic acid
 - oxalate
- may cause oxidative polymerization
- may be involved in humus formation
- may be the key to life

Manganese



Manganese

