Chemical Oceanography

Metal Geochemistry

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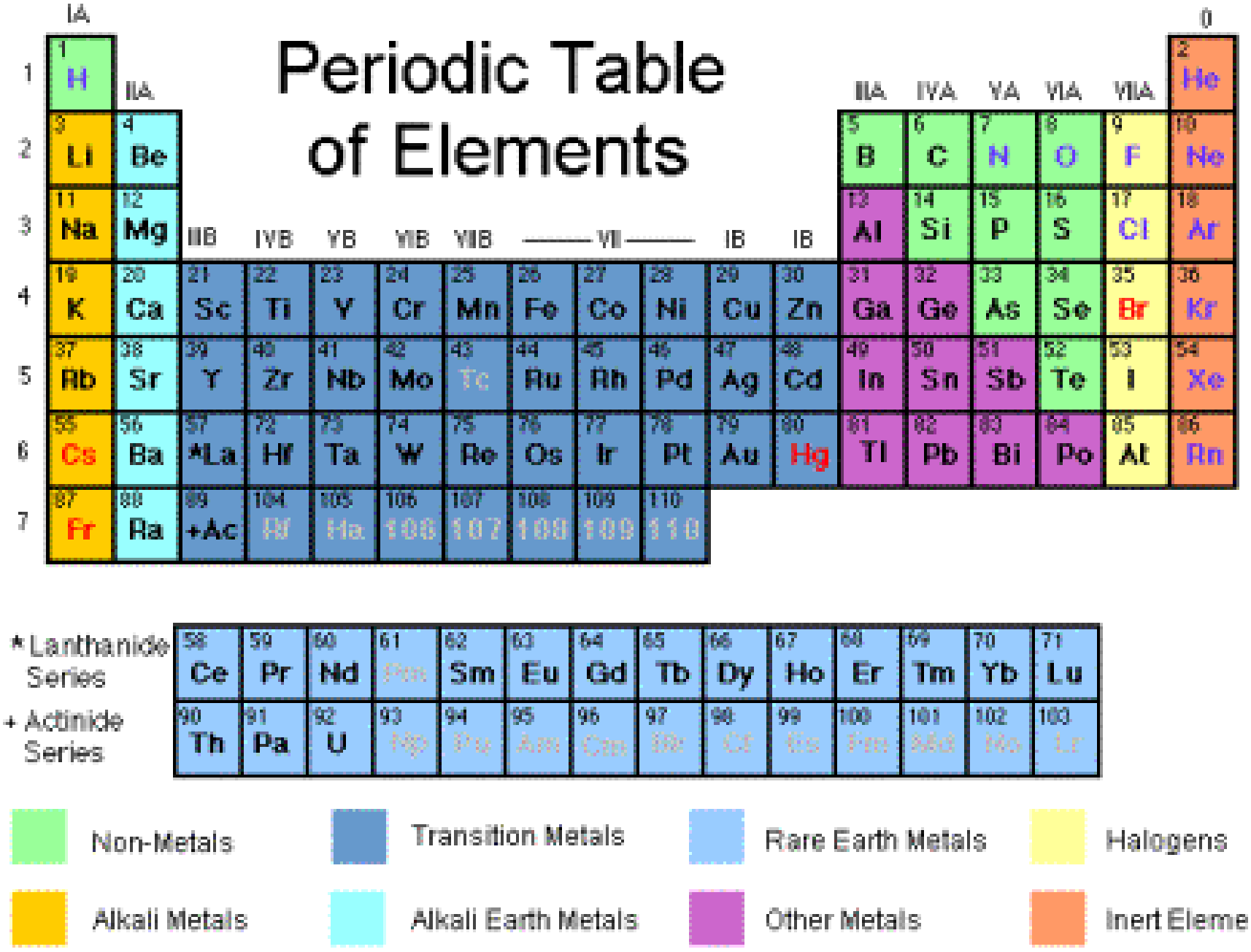
Metal Geochemistry

- Read Emerson & Hedges Chapter 12
- Read paper Donat & Bruland (1995)
- Read paper by Nieboer & Richardson (1980)

(Papers are posted on website for today's class)

Periodic Table of Elements



Concerned with Metal Ions (Geochemistry)

- Typically cations (Cu^{2+}, Cd^{2+})
- Some anions (CrO_4^{2-}, MoO_4^{2-}, AsO_4^{3-})
- General properties of interest
  - Reactivity
    - Redox – oxidation/reduction reactions
    - Complexation or Sorption
    - Speciation – forms
  - Cycling – ultimate fate
  - Transport – mobility
  - Toxicity/Bioavailability/Bioaccumulation

Biogeochemical Processes

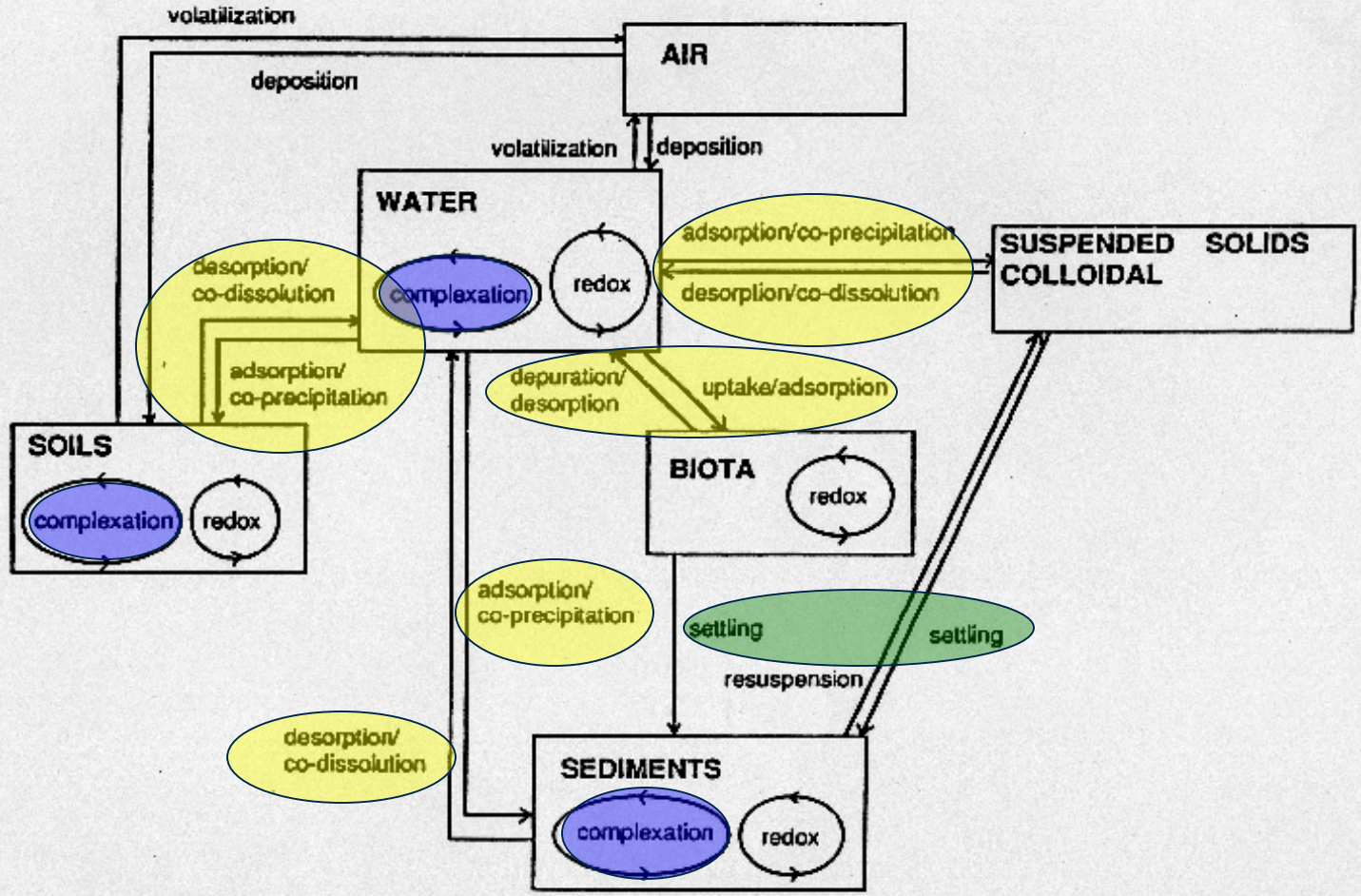


Figure 3.1. Schematic diagram of processes controlling the biogeochemical cycling of metals in aquatic environments.

Classification Schemes for Metals

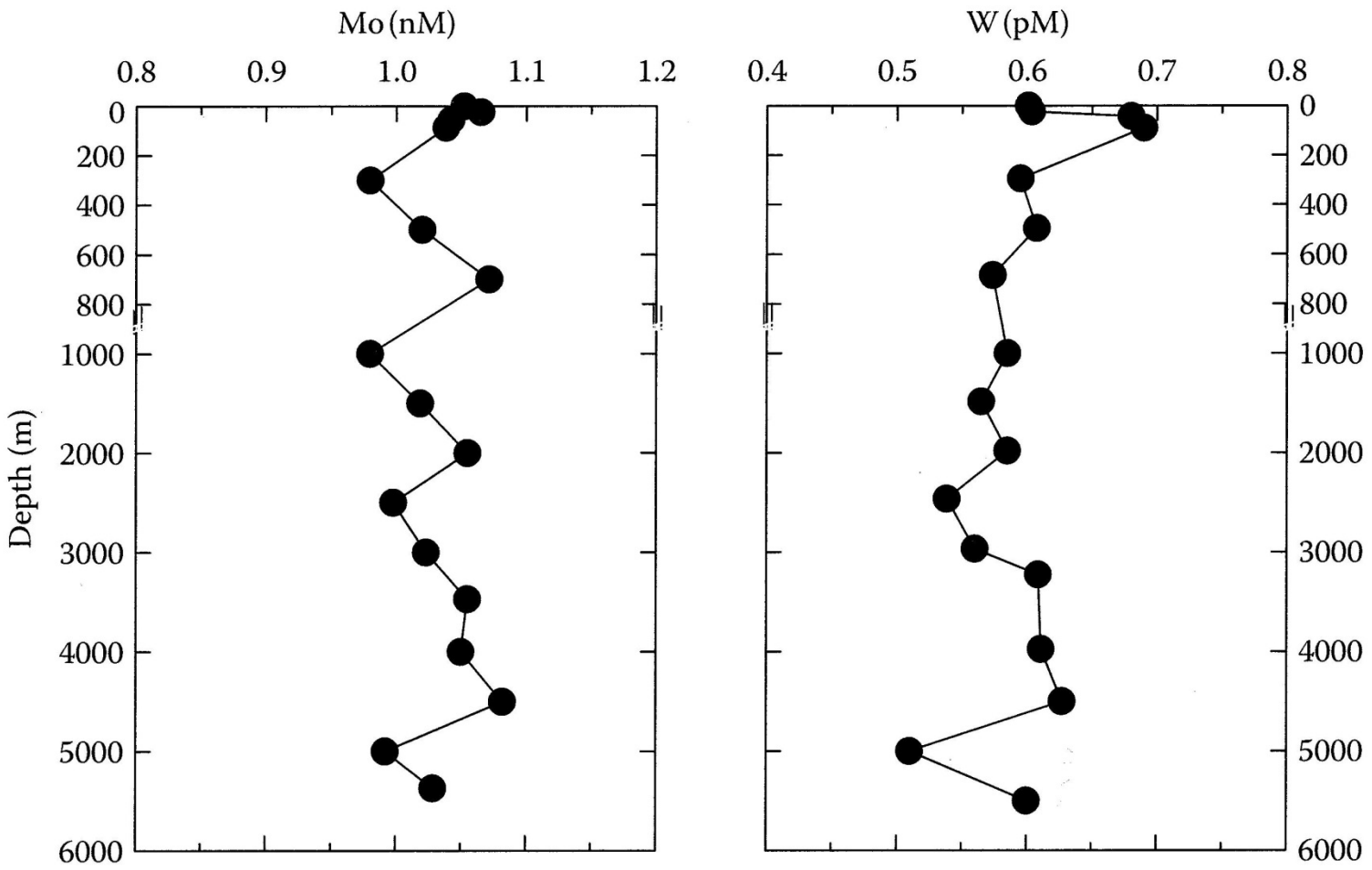
- Concentration – Major, Minor, Trace
- Biological Reactivity – Biolimiting, Biointermediate, Biounlimited, Noncycling
- Chemical Reactivity – d^0, d^{10}, Intermediate or Class A, Class B, Intermediate
- Overall Reactivity – Nutrient Type, Particle Reactive, Other
- Environmental Origin – Crustal, Pollutant (anthropogenic)

Concentration levels

- Major ions – discussed previously
  metals & non metals (Ca^{2+}, Mg^{2+}, Na^{+} , K^{+})
- Minor ions – some mention (Ba^{2+}, Sr^{2+}, etc.)
- Trace ions (Trace Metals) – all the rest
- Millero
  - Major: 0.05 to 750 mM
  - Minor: 0.05 to 50 μM
  - Trace: 0.05 to 50 nM

Depth Profiles for Mo & W

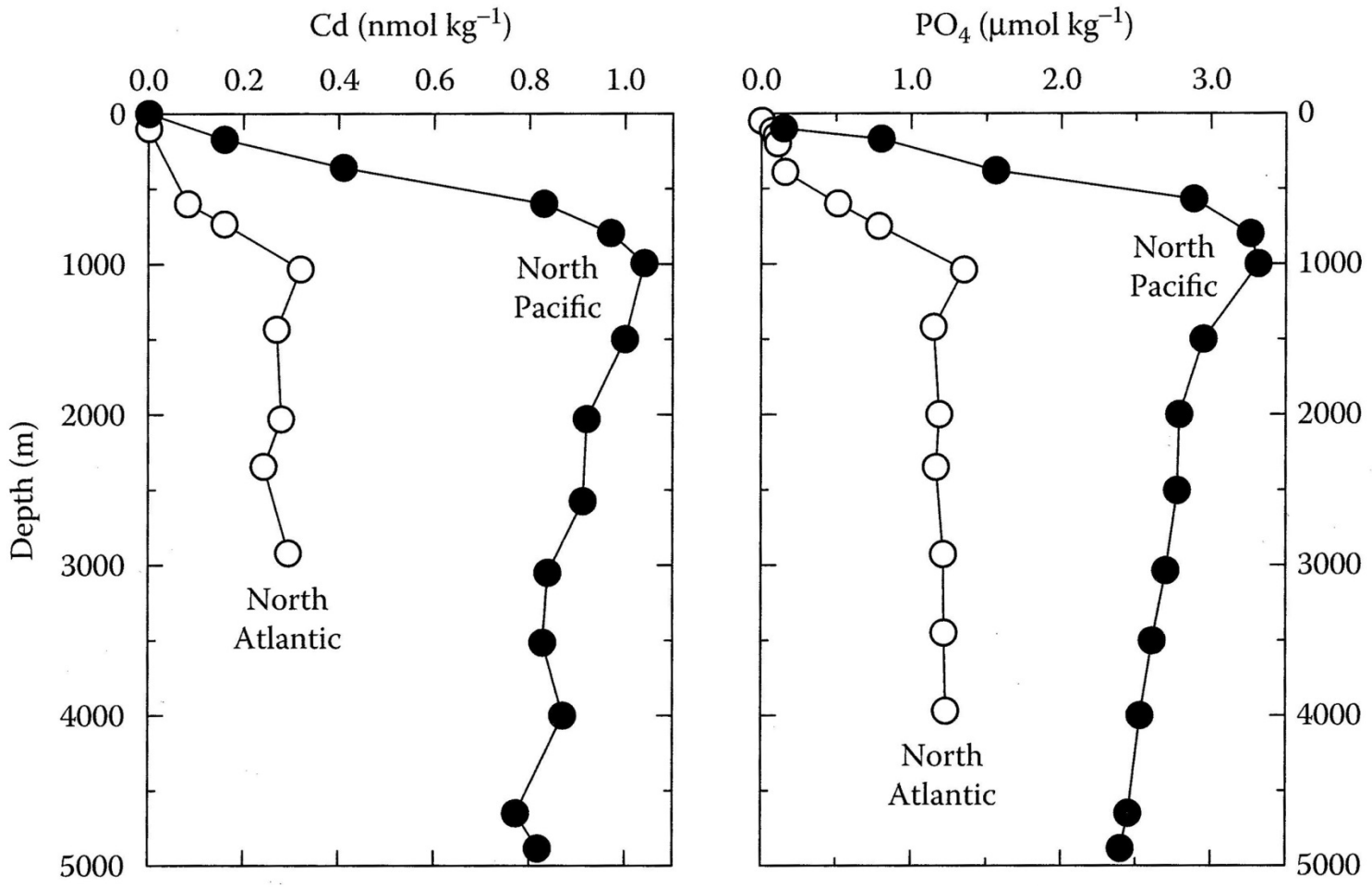
Conservative behavior (Millero 2006)



Major Components, Rb^+, Cs^+, etc.

Depth Profiles for Cd & P

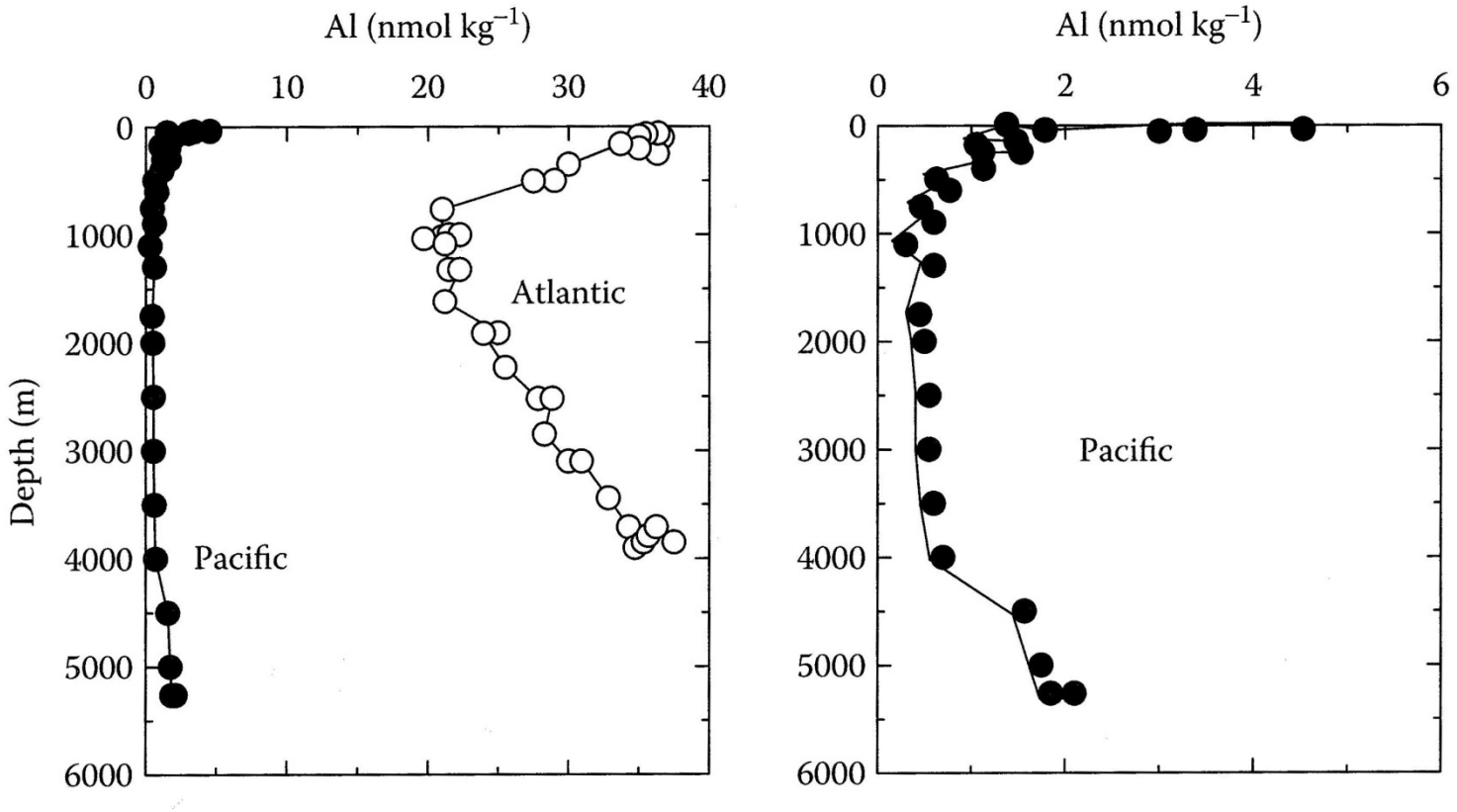
Nutrient behavior (Millero 2006)



Nitrate, Silicate, Zinc, Barium, etc.

Depth Profiles for Al

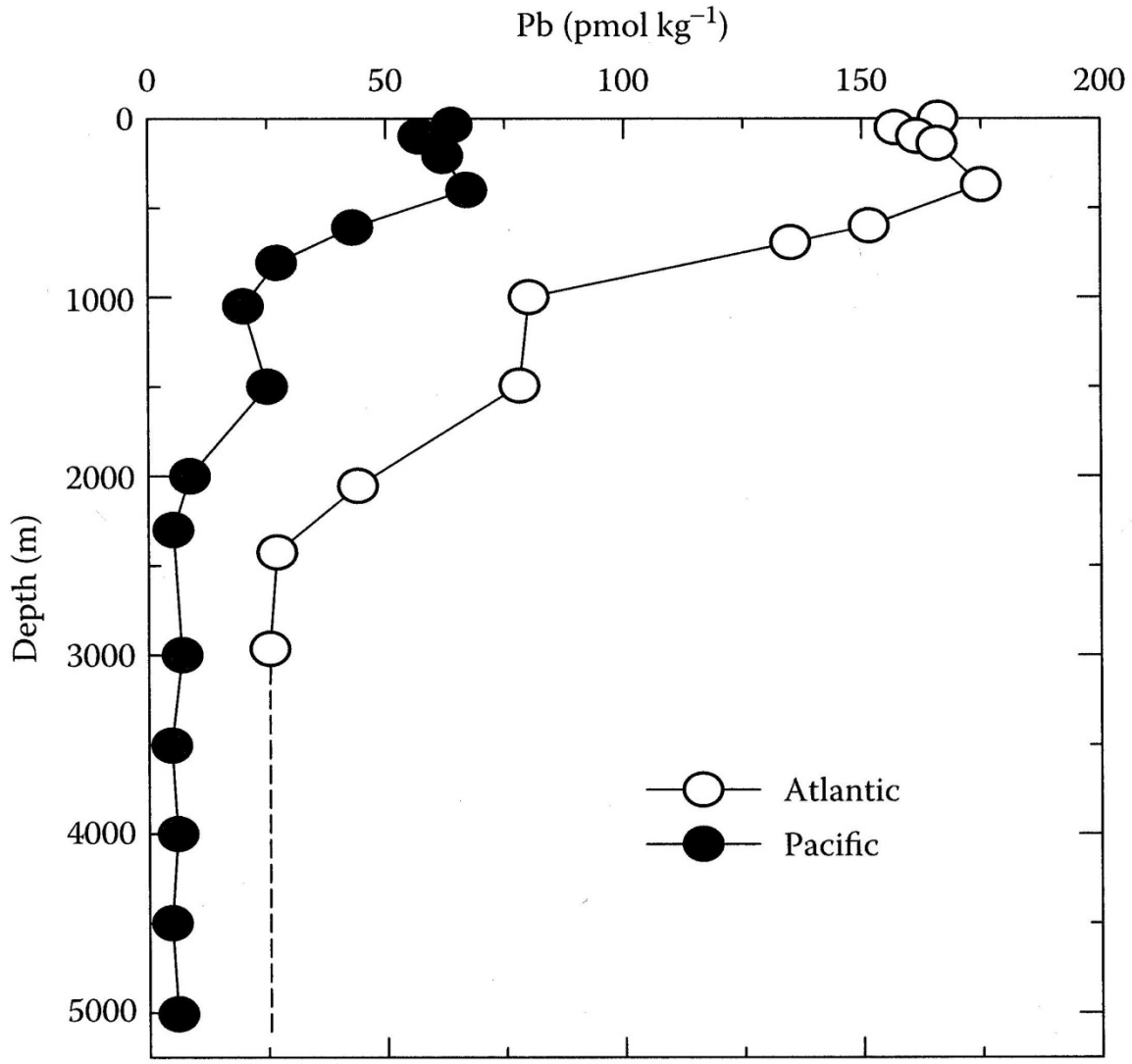
Mid-depth minimum (Millero 2006)

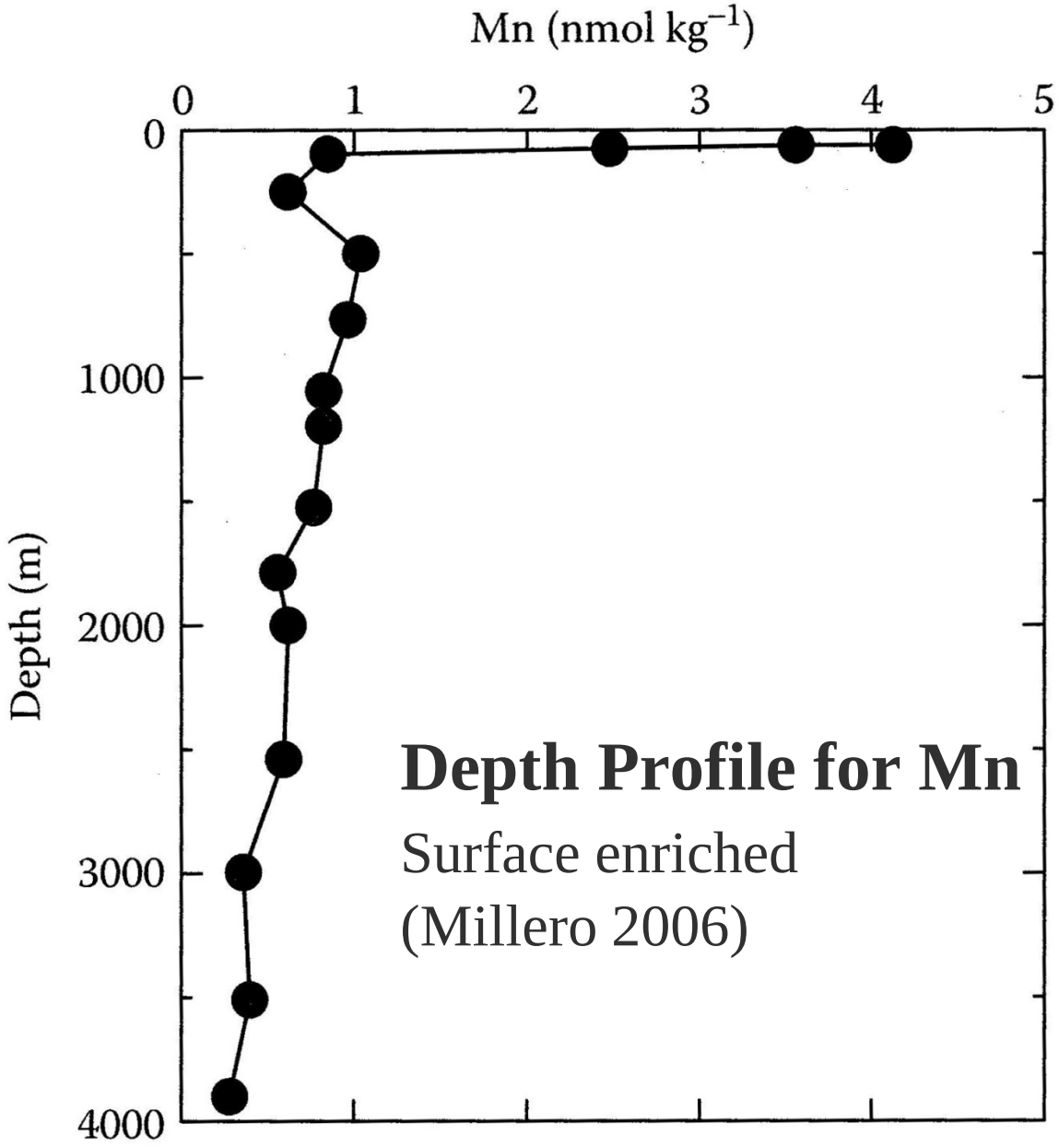


Copper, Tin, etc.

Depth Profiles for Pb

Surface enriched (Millero 2006)

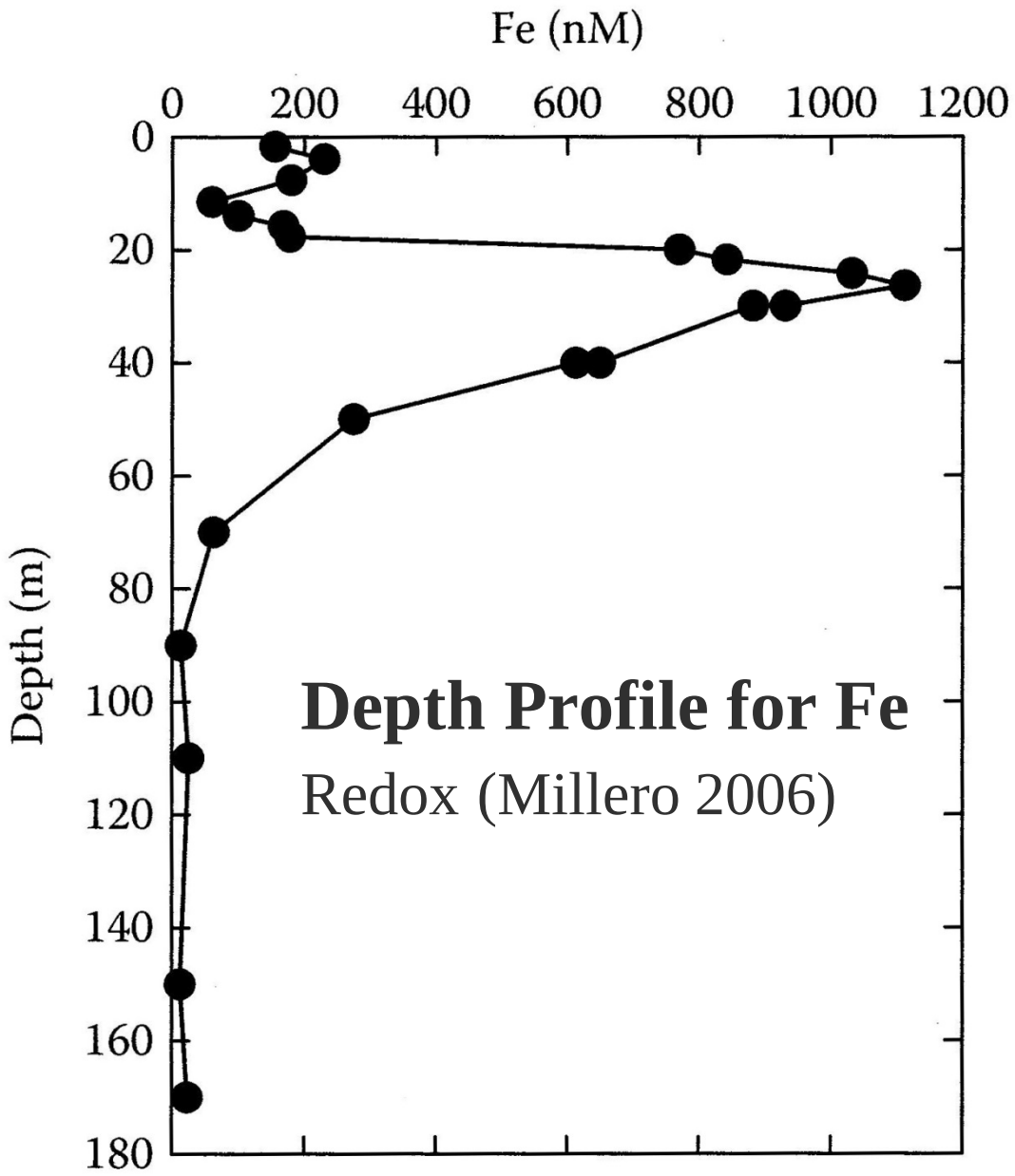




Depth Profile for Mn

Surface enriched

(Millero 2006)

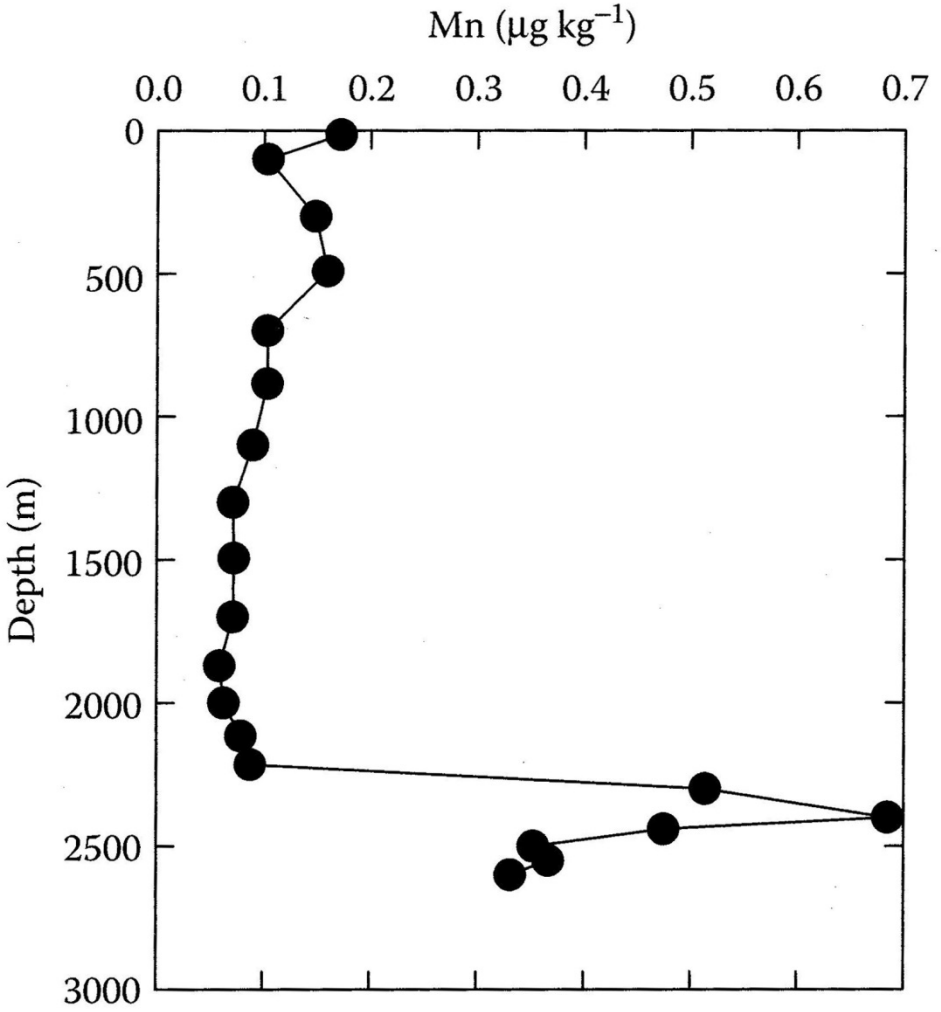


Depth Profile for Fe

Redox (Millero 2006)

Depth Profile for Mn

Anomolous (Millero 2006)



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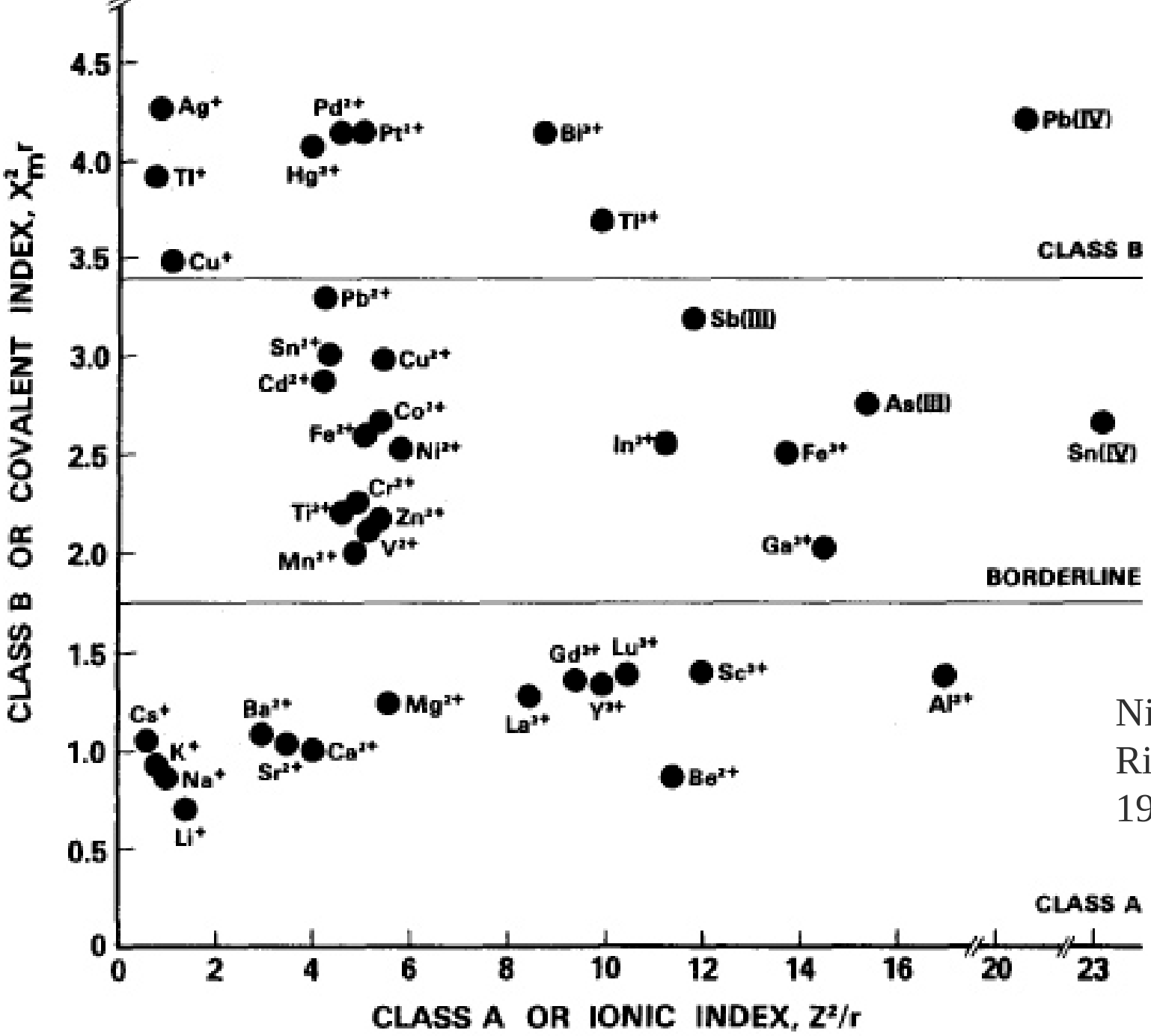
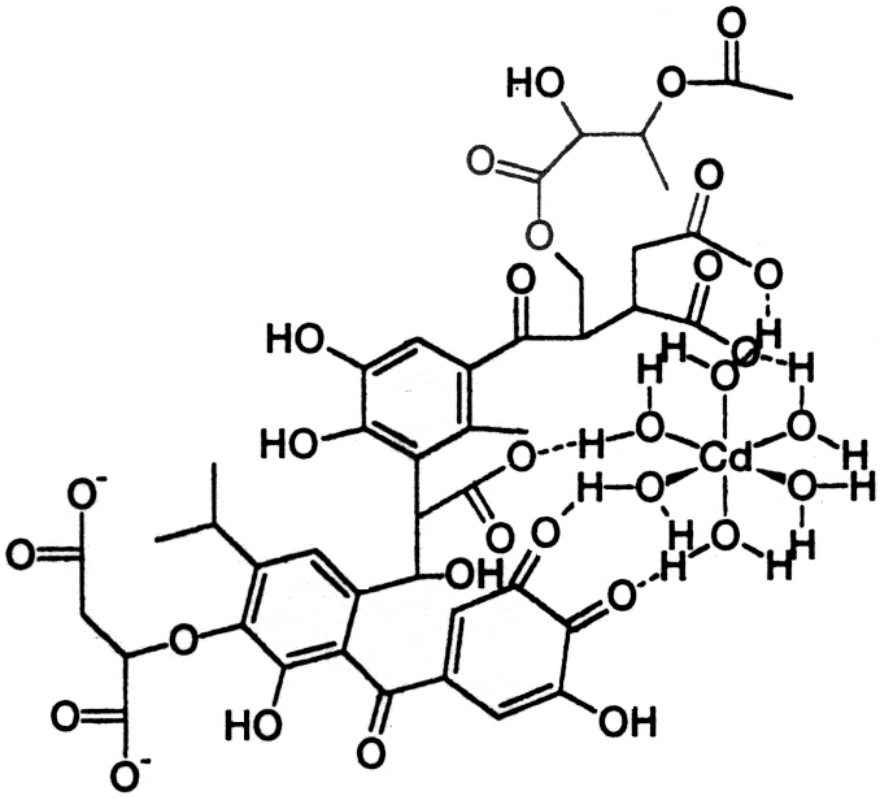


Nieboer & Richardson 1980

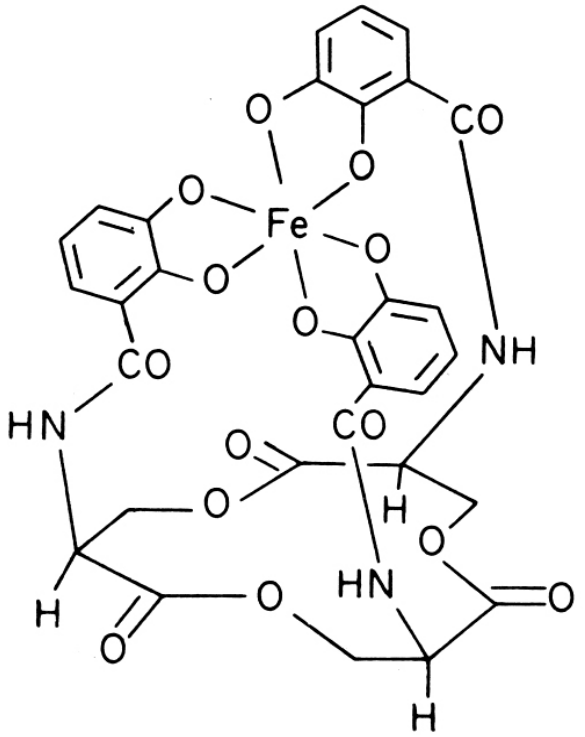
Importance of Humic Materials

Global Carbon Reservoir
Take Part in Interfacial Phenomena
Undergo Coagulation and Aggregation
Involved in Photochemical Reactions
Contain Radicals
Known Reducing Agents
Methylate Metals
Form Chlorinated Species, THMs DBPs
Detoxify Metals
Limit Bioavailability of Metals
Alter Solubility
Influence Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria

Metal Complexation by Humic Materials



Leenheer et al. (1998)



Morel (1983)

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Limit Bioavailability of Metals

Alter Solubility

Influence Transport

Bind Metals & Organic Pollutants

Terminal Electron Acceptor for Bacteria

Humic material will aggregate & may“salt out” with cations

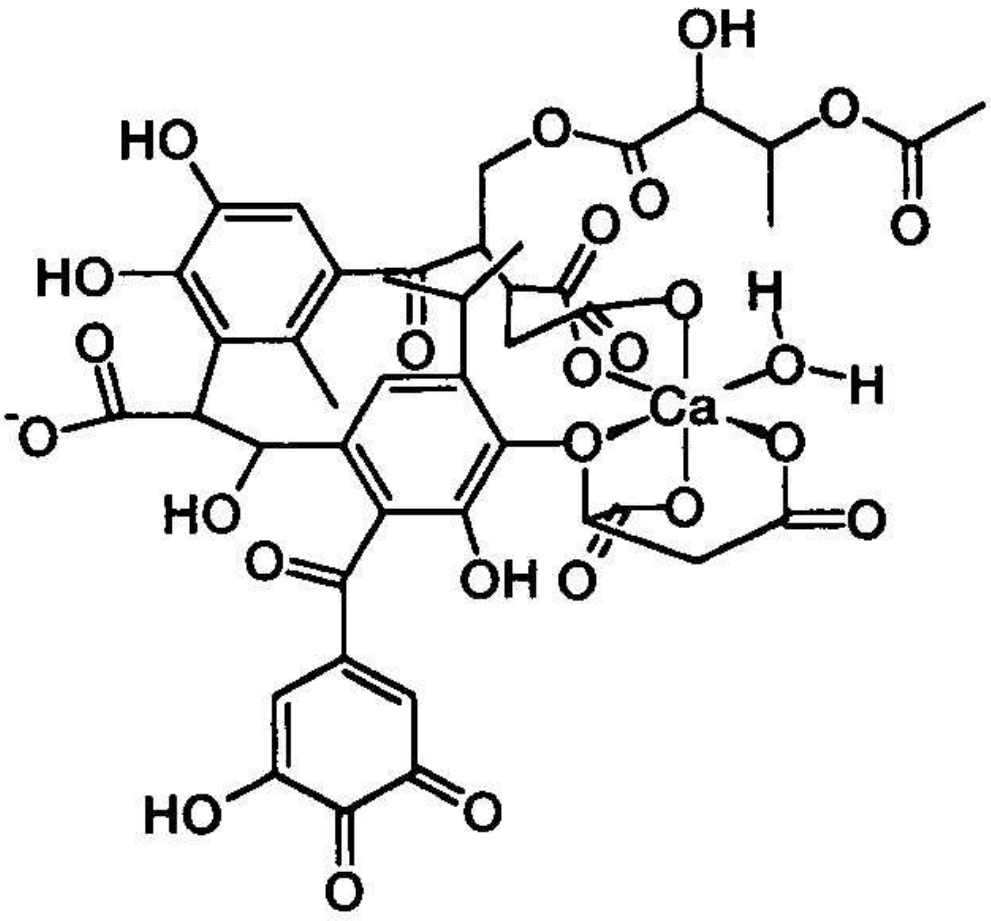
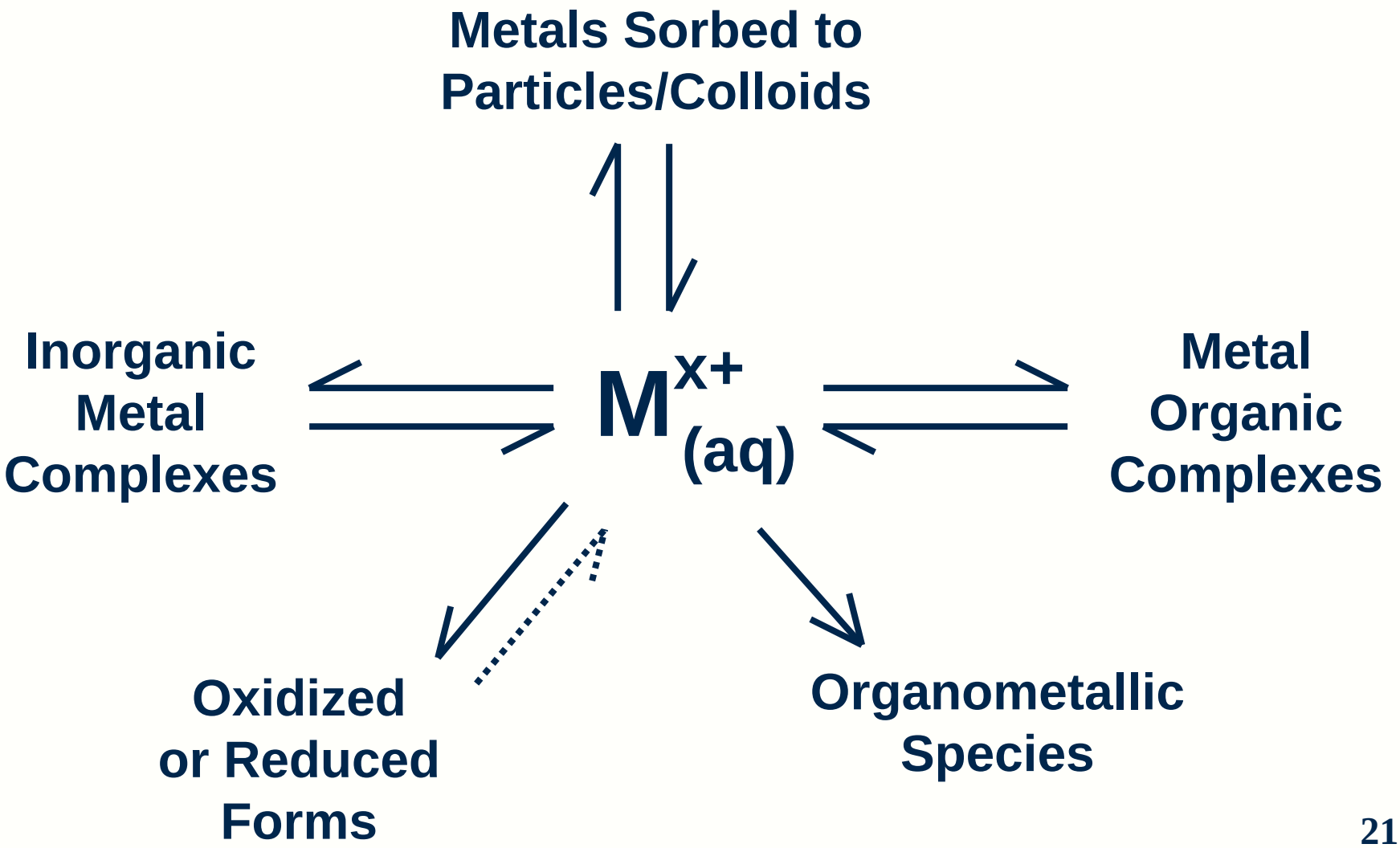


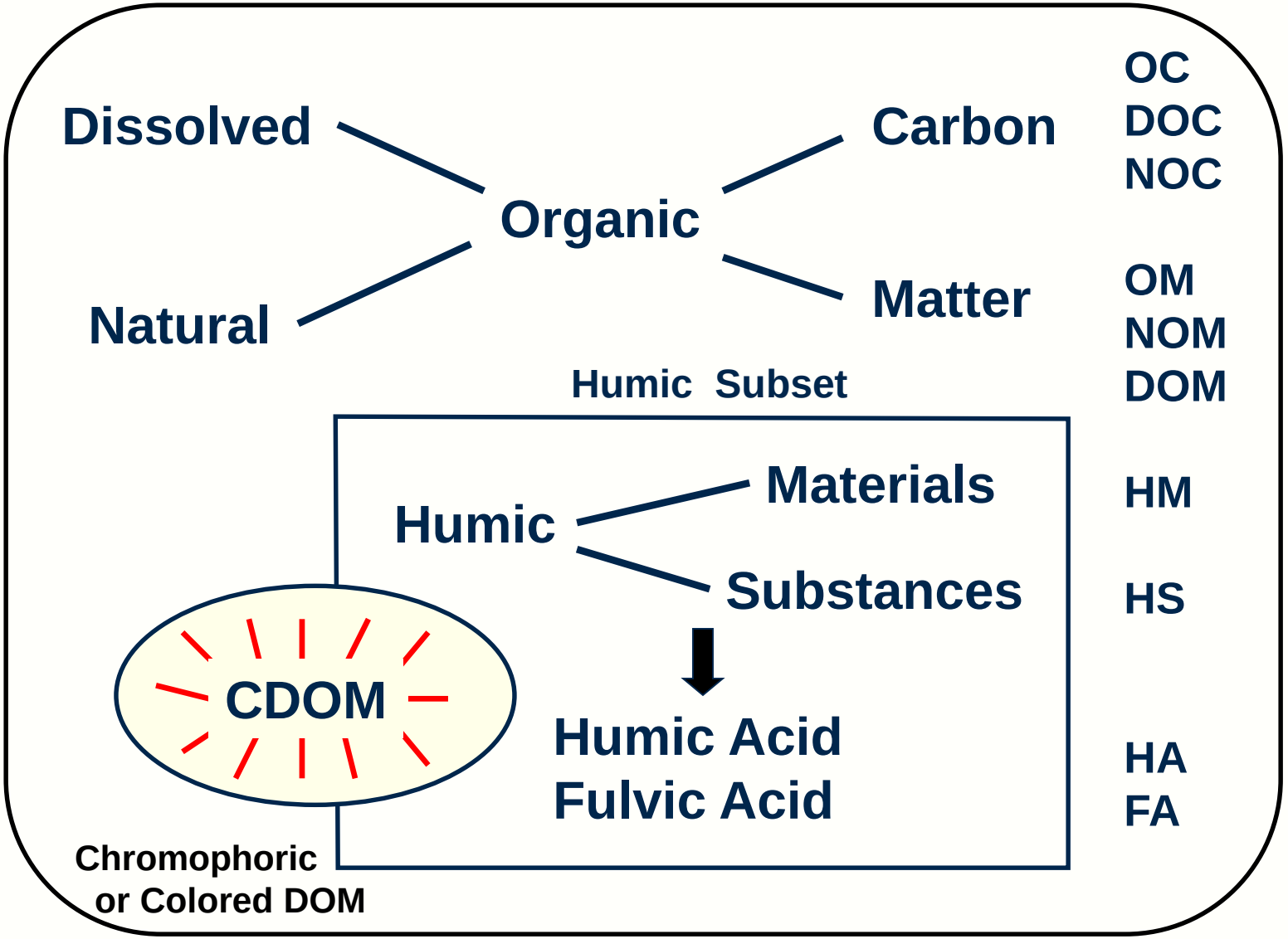
FIGURE 6. Structural model of a calcium inner-sphere complex

Leenheer, J.A. et al. (1998) Environ. Sci. Technol. 32, 2410

Dissolved Metal Species



All Dissolved Organic Compounds



Metal Organic Complexes

M^{x+}

NOM^{y-}

NOM^{y-}

M^{x+} M^{x+}

NOM^{y-}

M^{x+} $M\text{-}NOM^{(x-y)-}$

M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

NOM^{y-} = natural organic matter of varying negative charge y-

$M\text{-}NOM^{(y-x)-}$ = metal complex of natural organic matter