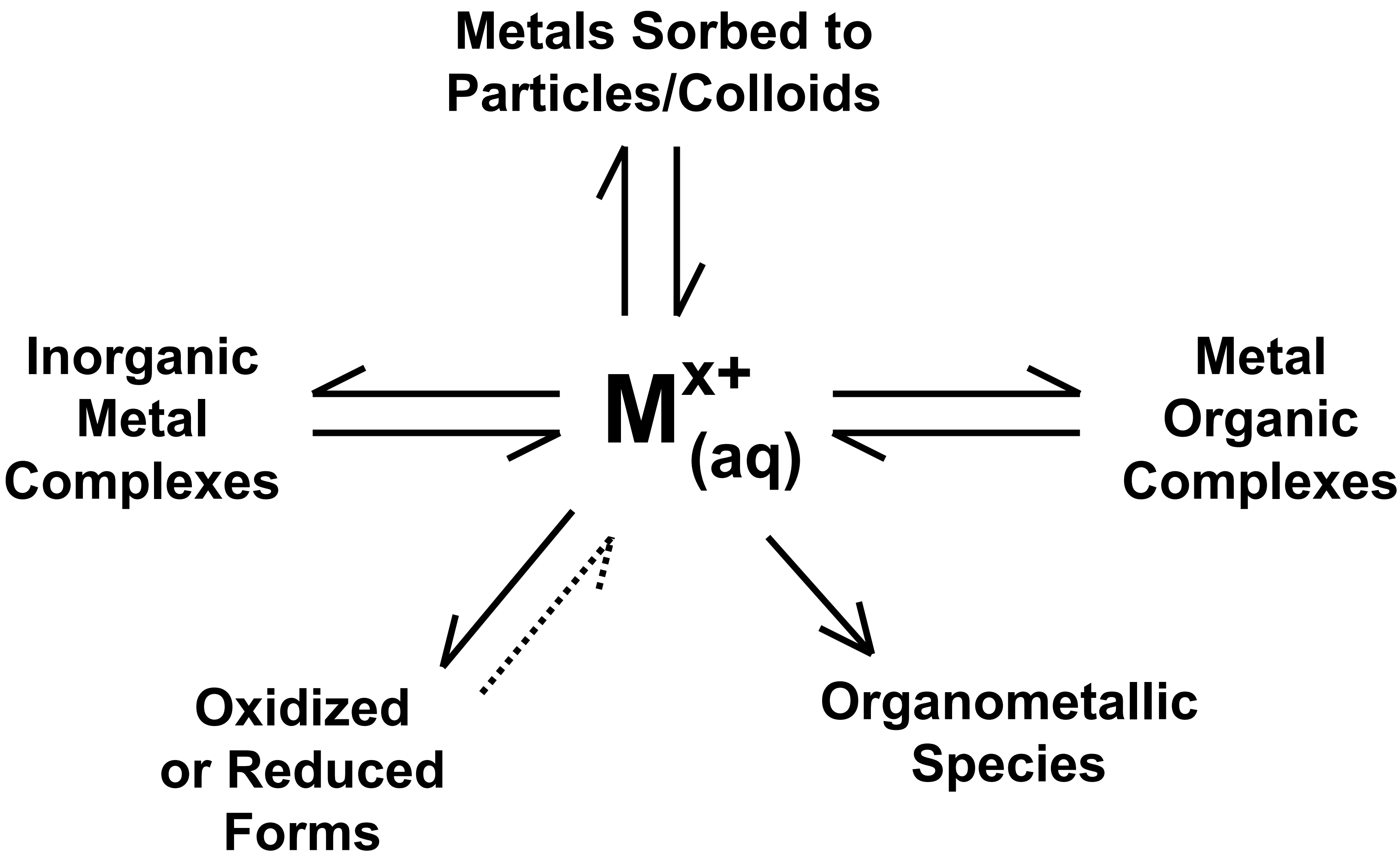
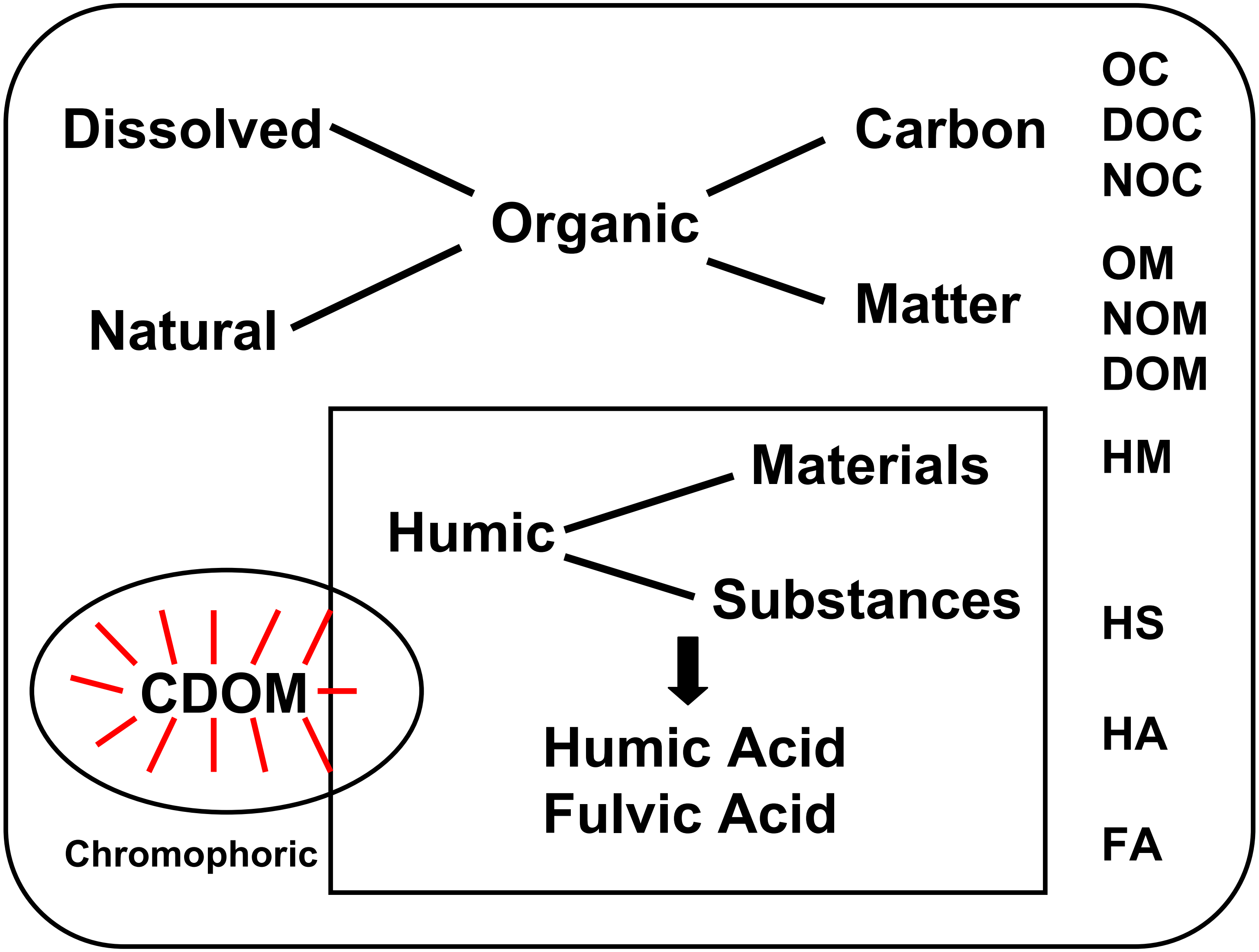
Dissolved Metal Species



Dissolved Organic Nomenclature



Metal Organic Complexes

M^{x+}

NOM^{y-}

NOM^{y-}

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

NOM^{y-}

M^{x+}

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

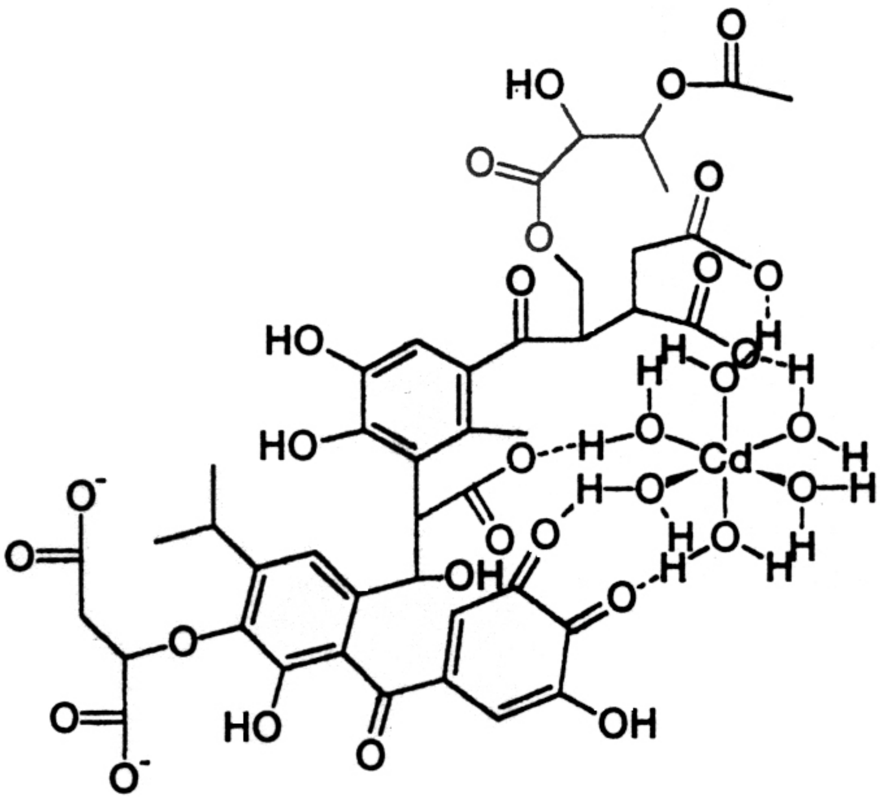
M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

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

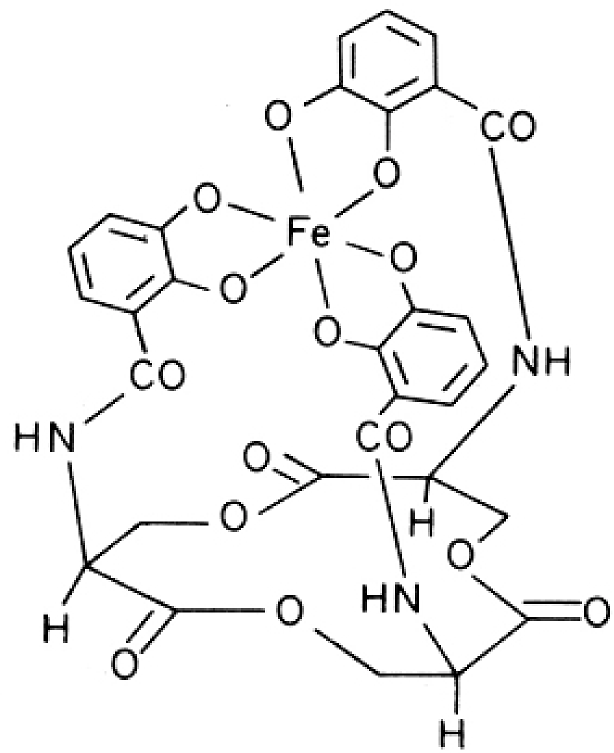
$M\text{-}NOM^{(y-x)-}$ = metal complex of natural organic matter

Metal Complexation by Humic Materials

Outer Sphere Binding vs Inner Sphere Binding

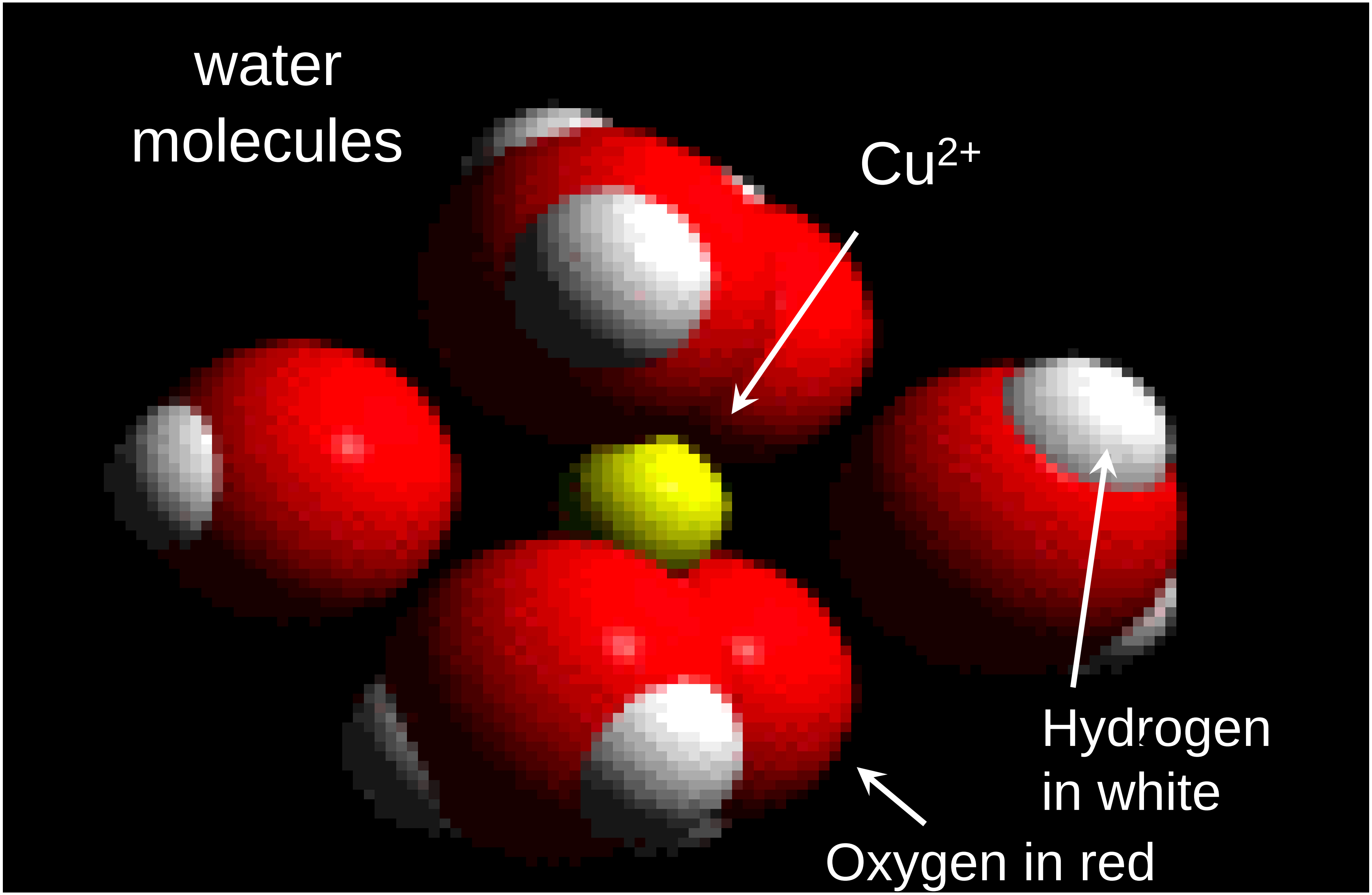


Leenheer et al. (1998)

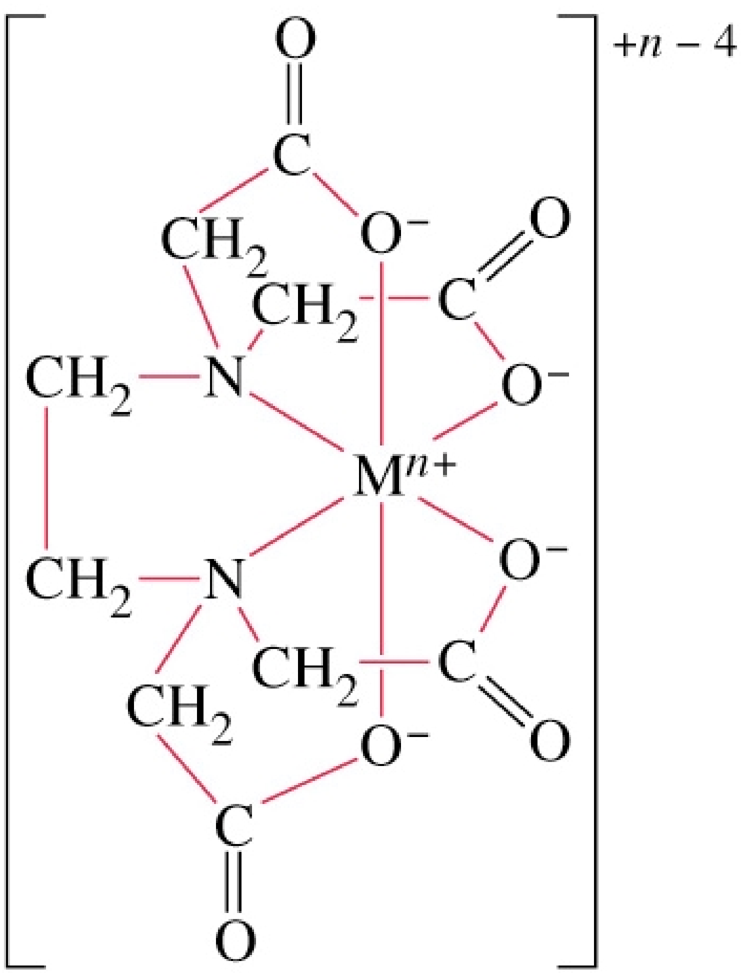


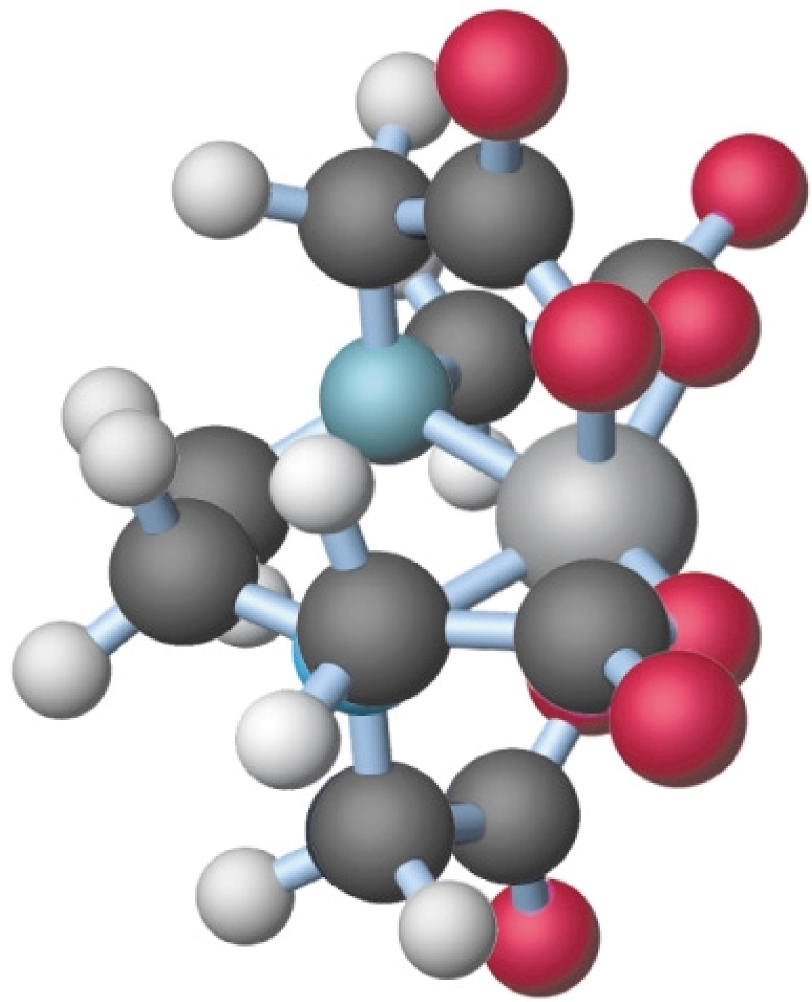
Morel (1983)

Primary Hydration Shell of Cu^{2+}

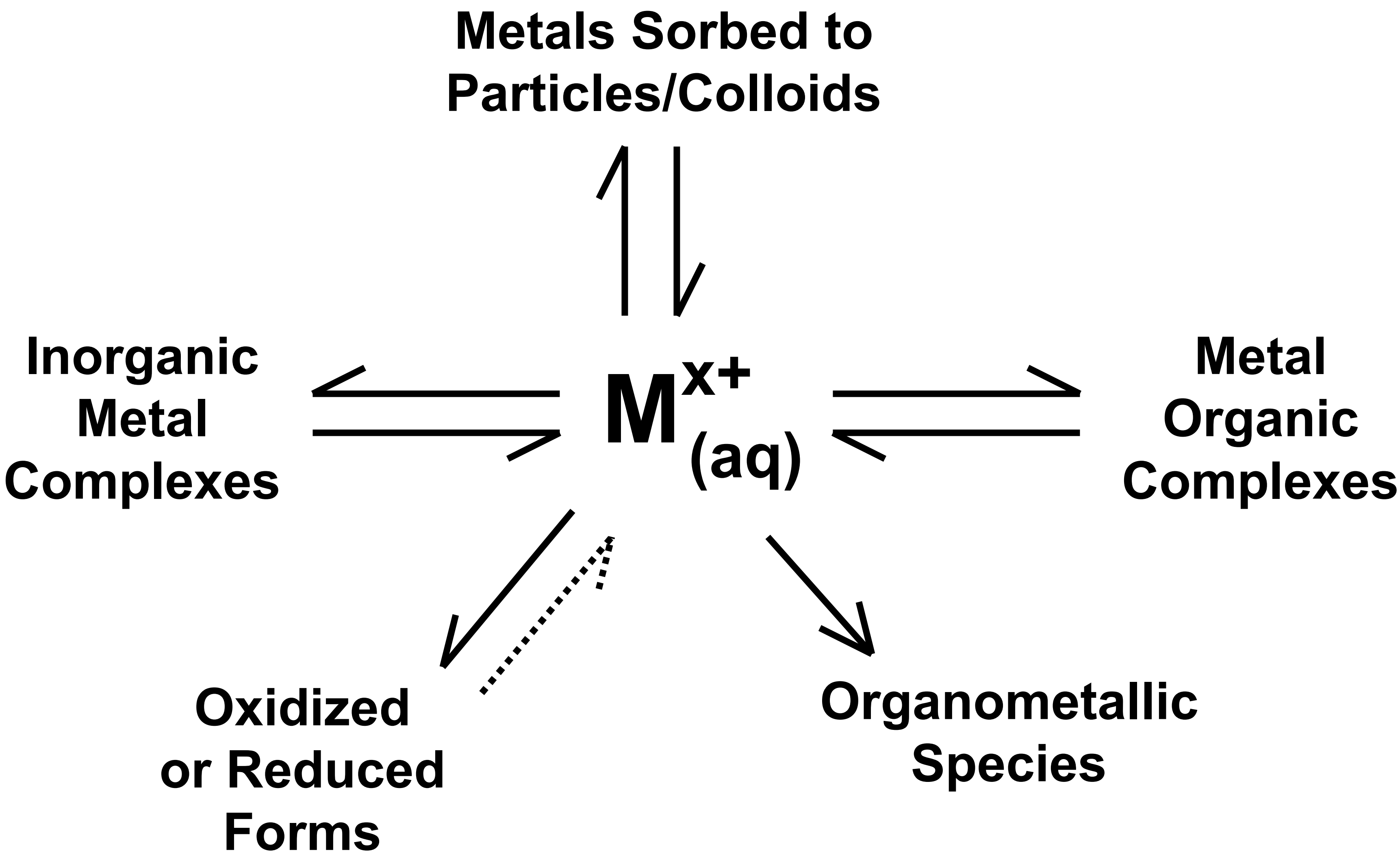


Metal Ion Complexation by EDTA (chelate effect)





Dissolved Metal Species



Metal Inorganic Complexes

M^{x+}

SO_4^{2-}

CO_3^{2-}

SO_4^{2-}

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

$M\text{-}CO_3^{(x-2)}$

M^{x+} CO_3^{2-}

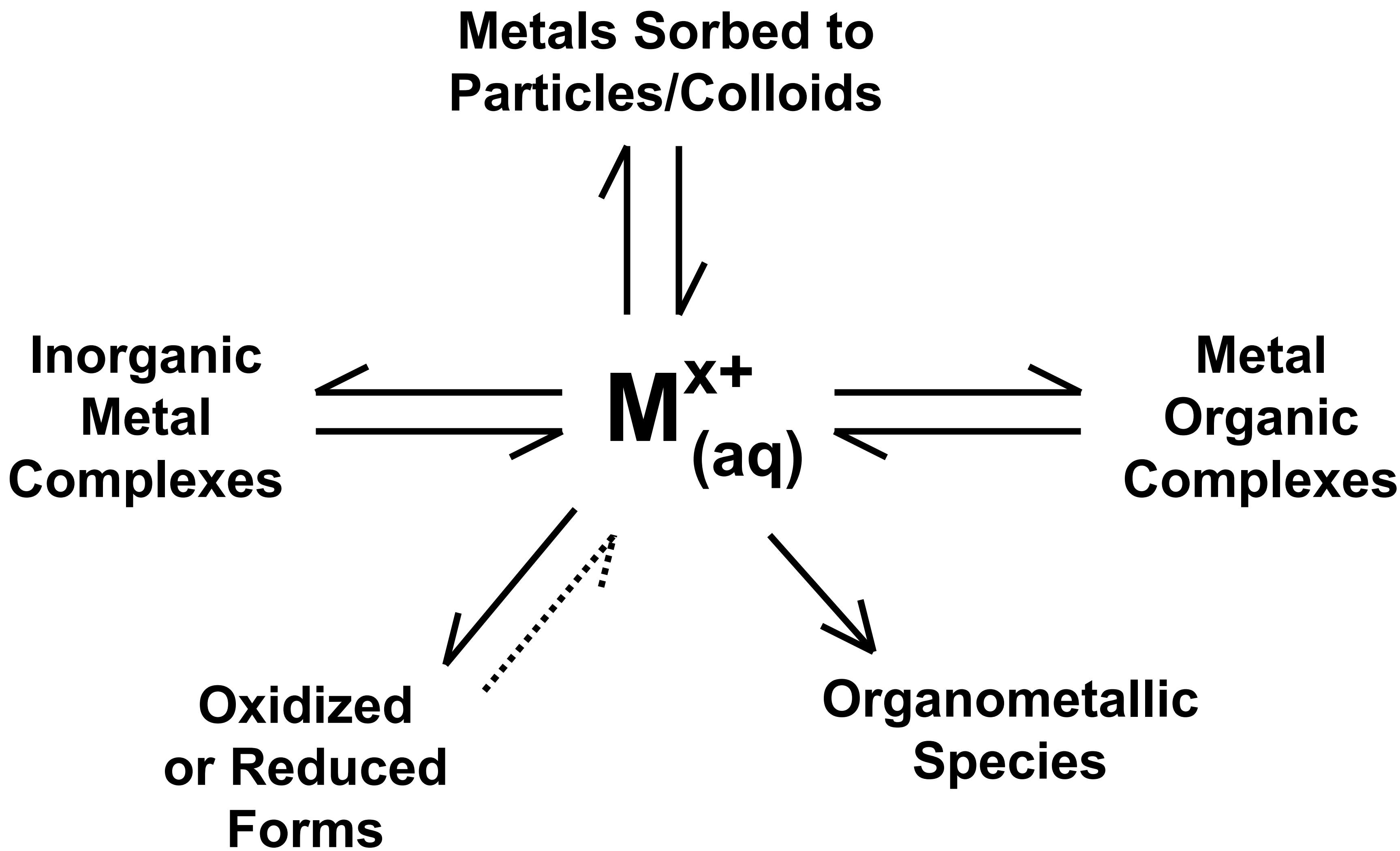
$M\text{-}Cl^{x-1}$ $M\text{-}SO_4^{(x-2)}$

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

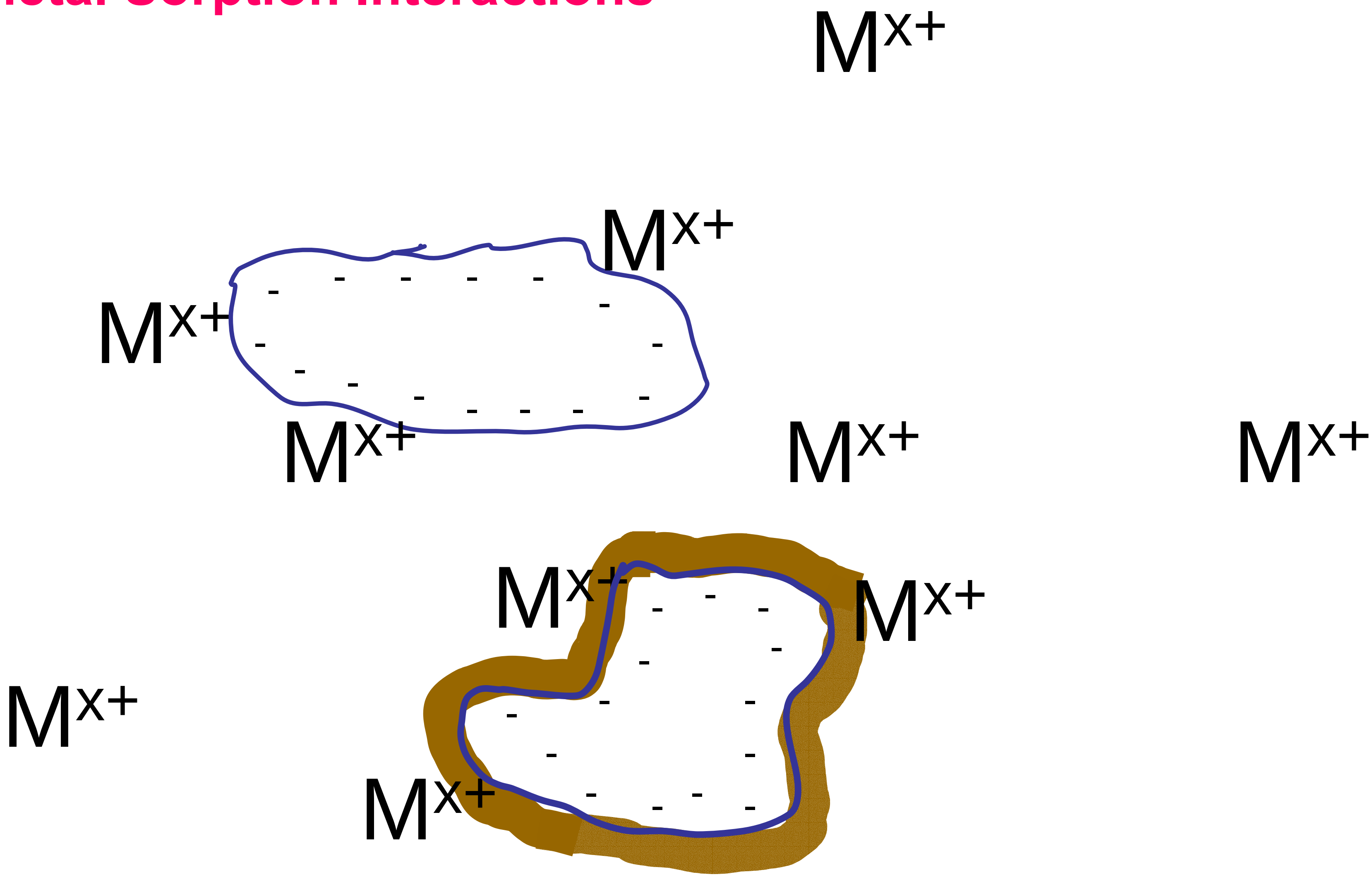
CO_3^{2-}, SO_4^{2-}, Cl^- = inorganic ligands able to bind metal ions

$M\text{-}CO_3^{(x-2)}$, $M\text{-}Cl^{x-1}$= metal complex of carbonate, chloride, etc.

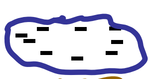
Dissolved Metal Species

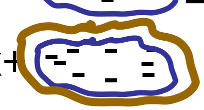


Metal Sorption Interactions

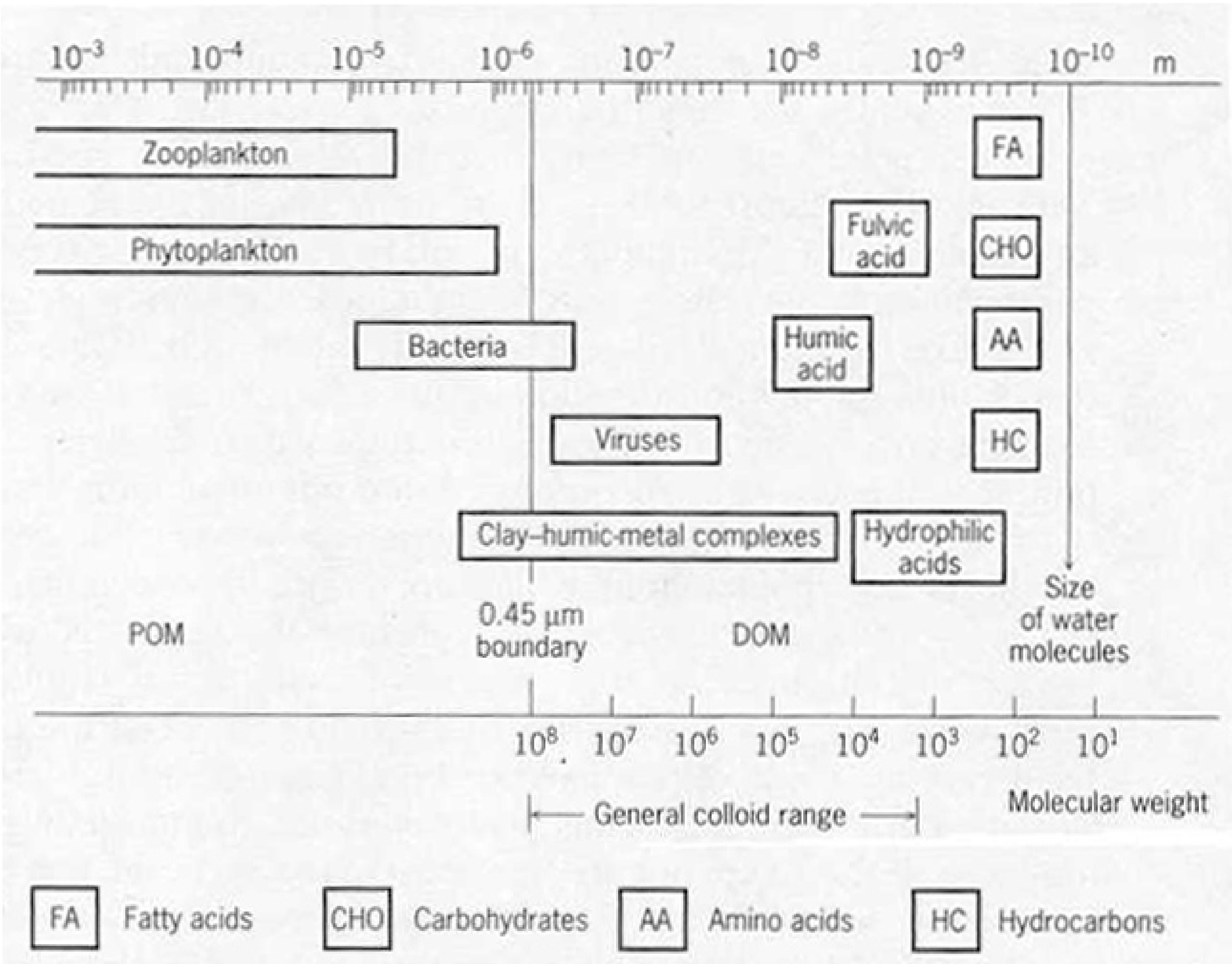


M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

 = natural colloid or particle with negative surface charge -

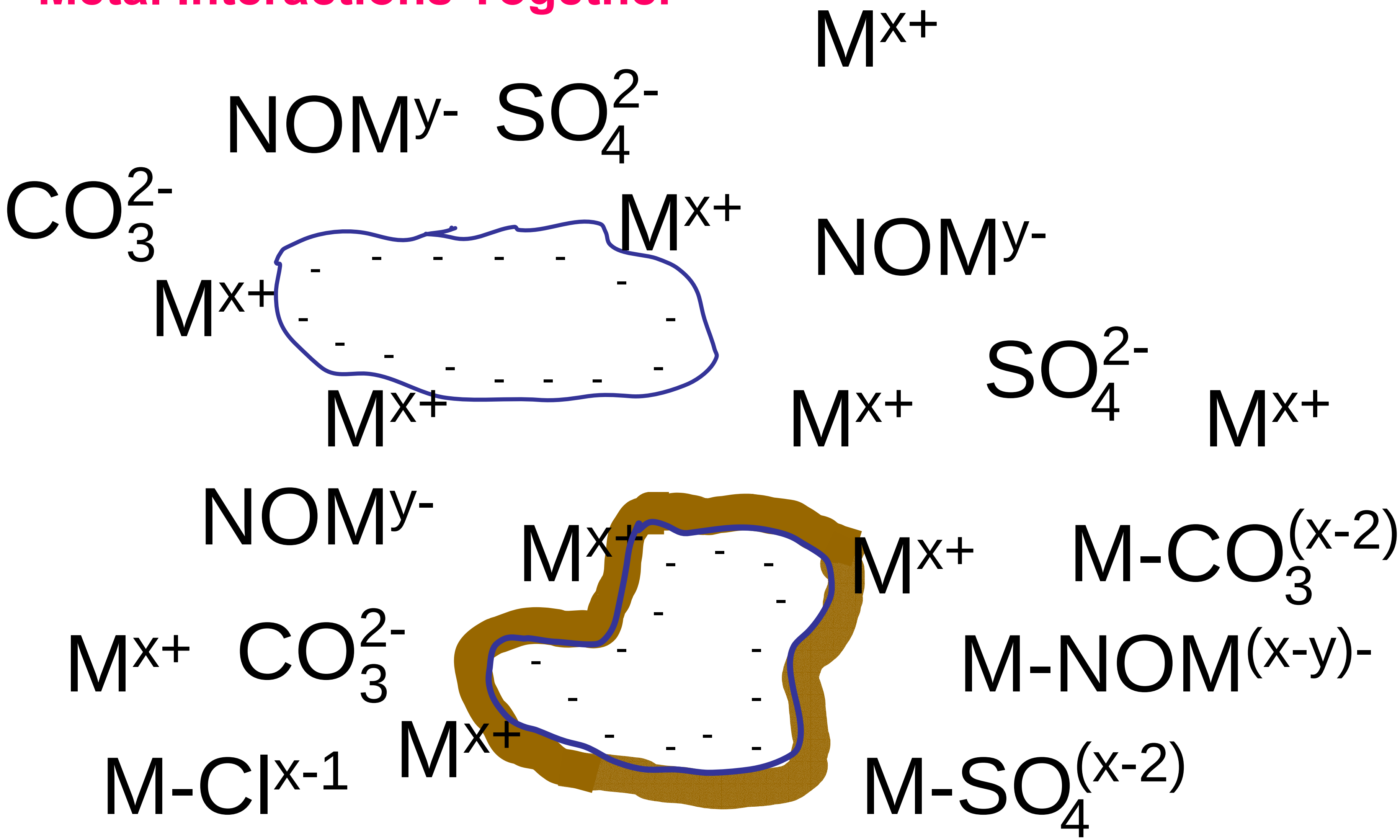
M^{x+}  = metal sorbed to particle or organic matter on particle

Organic Carbon Continuum



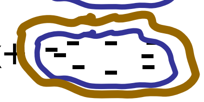
Libes, 1992

Metal Interactions Together

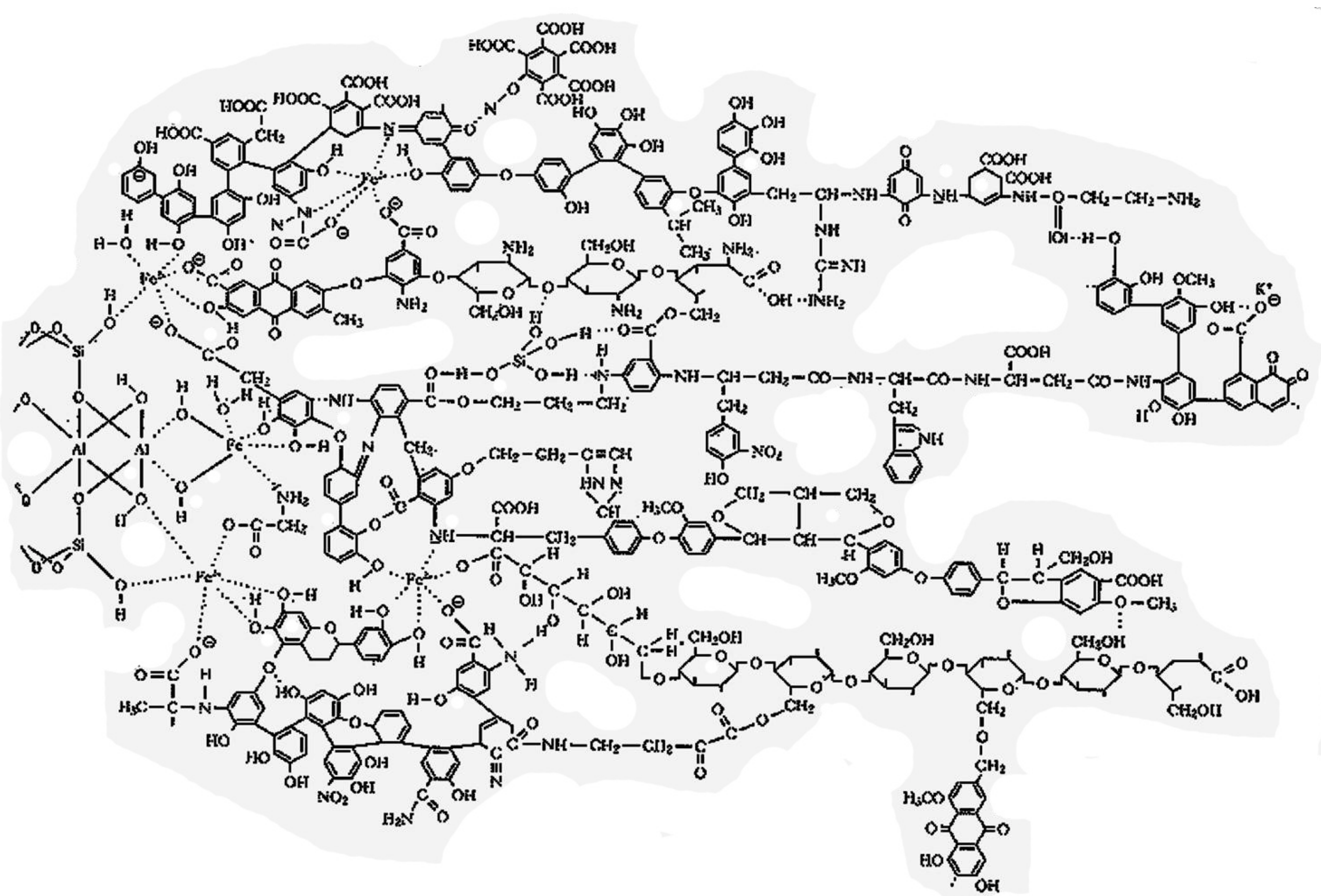


M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

 = natural colloid or particle with negative surface charge -

M^{x+}  = metal sorbed to particle or organic matter on particle

Metal-Organic-Clay Colloid



Kleinhempel reprinted from Albrecht Thaer Archiv (1970)

Table 4 **Determinations of the fraction of organically complexed copper in seawater**

Location	Percent Organic Cu	Technique	Reference
San Francisco Bay	80–92	CLE/DPCSV DPASV CRCP/GFAAS	Donat et al.[161b]
Indian Ocean	>99.7	CLE/DPCSV	Donat & van den Berg[48]
North Sea	>99.9	CLE/DPCSV	Donat & van den Berg[48]
Sargasso Sea	98.8	CLE/LP/GFAAS	Moffett et al.[122]
Sargasso Sea	93	CLE/DPCSV DPASV	Donat & Bruland[161a]
North Pacific	99.4–99.8	DPASV	Coale & Bruland[160,161]
New York coast	99.8	FPA	Hering et al.[208]
Biscayne Bay	99.6	CLE/LP/GFAAS	Moffett & Zika[159]
Narragansett Bay	99.9	CLE/SPE/GFAAS	Sunda & Hanson[158]
Coastal Peru	98	CLE/SPE/GFAAS	Sunda & Hanson[158]
North Atlantic	89–99.8	MnO_2 ads.	Buckley & van den Berg[157]
North Atlantic	98.8–99.4	CLE/DPCSV	Buckley & van den Berg[157]
South Atlantic	99.9	CLE/DPCSV	van den Berg[156]
Coastal Florida	98.7	Bioassay	Sunda & Ferguson[155]
Mississippi Plume	99.1	Bioassay	Sunda & Ferguson[155]
New York Bight	>95	DPASV	Huizenga & Kester[209]
Irish Sea	94–98	MnO_2 ads.	Van den Berg[126]

Note: CLE/DPCSV = Competitive ligand equilibration/differential pulse cathodic stripping voltammetry; CRCP/GFAAS = Chelating resin column partitioning/graphite furnace atomic absorption spectrometry; CLE/LP/GFAAS = Competitive ligand equilibration/liquid partitioning/graphite-furnace atomic absorption spectrometry; DPASV = Differential pulse anodic stripping voltammetry; FPA = Fixed potential amperometry; CLE/SPE/GFAAS = Competitive ligand equilibration/solid phase extraction/graphite-furnace atomic absorption spectrometry; MnO_2 ads. = Manganese dioxide adsorption.

Donat &Bruland 1995

Equilibrium Reaction & Expression

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

$$K = \frac{[M\text{-}NOM^{(x-y)-}]}{[M^{x+}][NOM^{y-}]}$$

K = equilibrium constant describing complexation reaction

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

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

measure | or maybe measure | or measure

<u>Metal Speciation</u> = determination of the forms of metal in equilibrium with NOM

Measurement must not disturb equilibrium

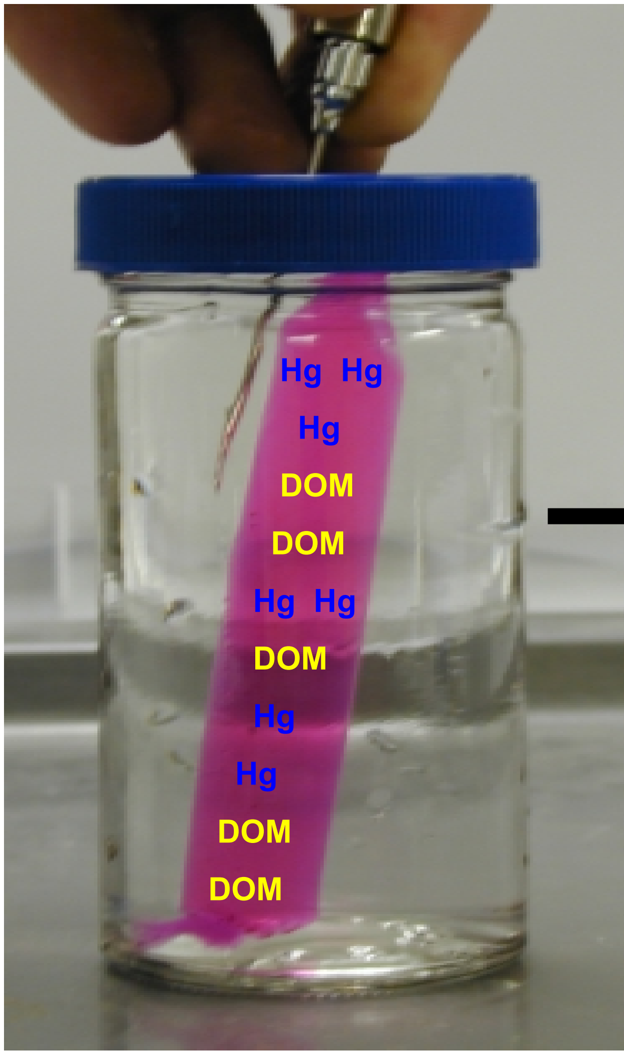
Analytical Speciation Methods

- Separation Methods
  - Equilibrium Dialysis
  - Chelating Resin Column Partitioning (CRCP)
- Direct Measurement
  - Differential Pulse Anodic Stripping Voltammetry (DPASV)
  - Differential Pulse Cathodic Stripping Voltammetry (DPCSV)
  - Fluorescence Quenching (FQ)
  - Competitive Ligand Equilibration (CLE)

Equilibrium Dialysis Method

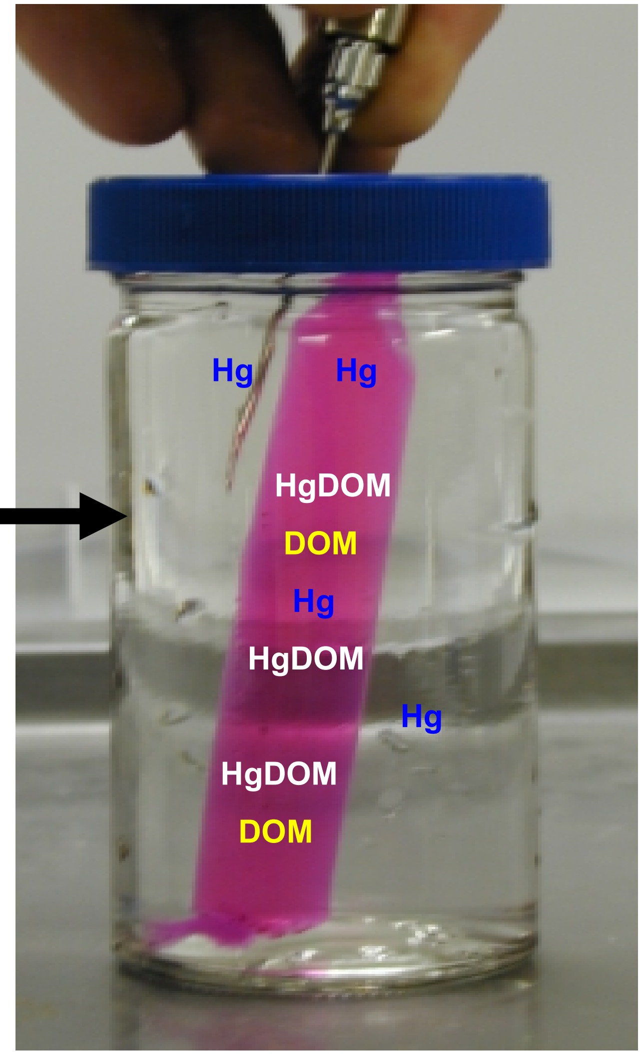
(Glaus, Hummel, Van Loon. Analytica Chimica Acta. 303 (1995) 321-331)

Initial

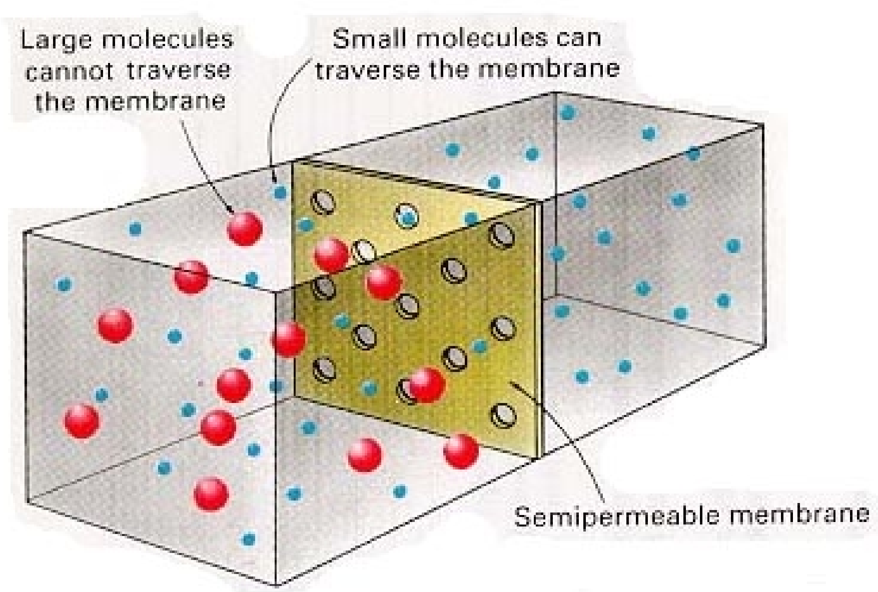


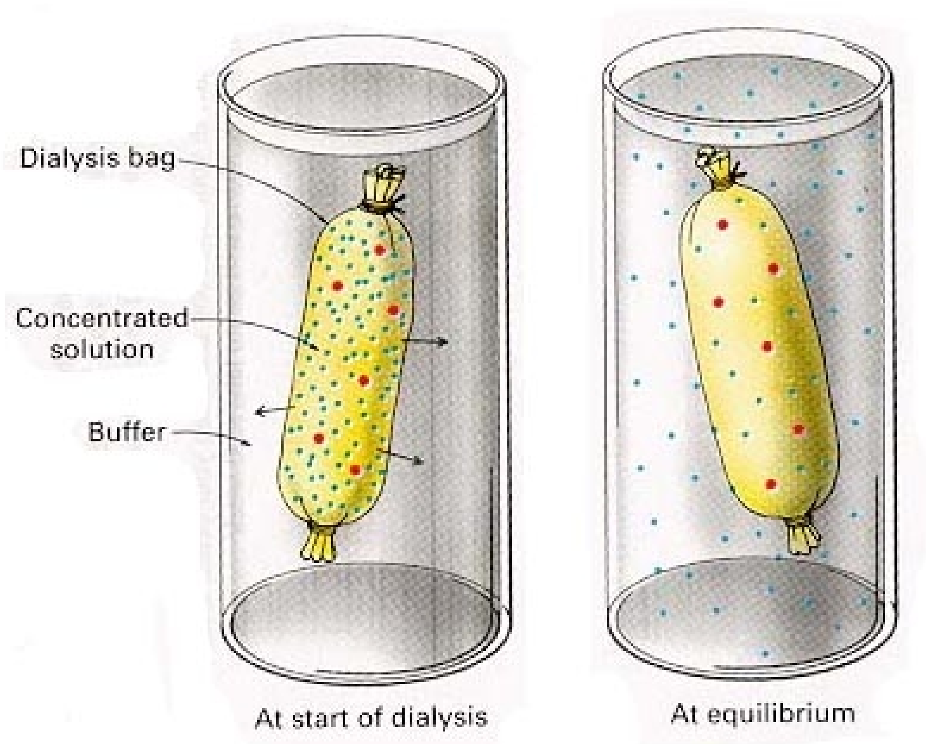
$$K_1 = \frac{[\text{Hg-DOC}]}{[\text{Free DOC}][\text{Free Hg}]}$$

Final



Dialysis Process

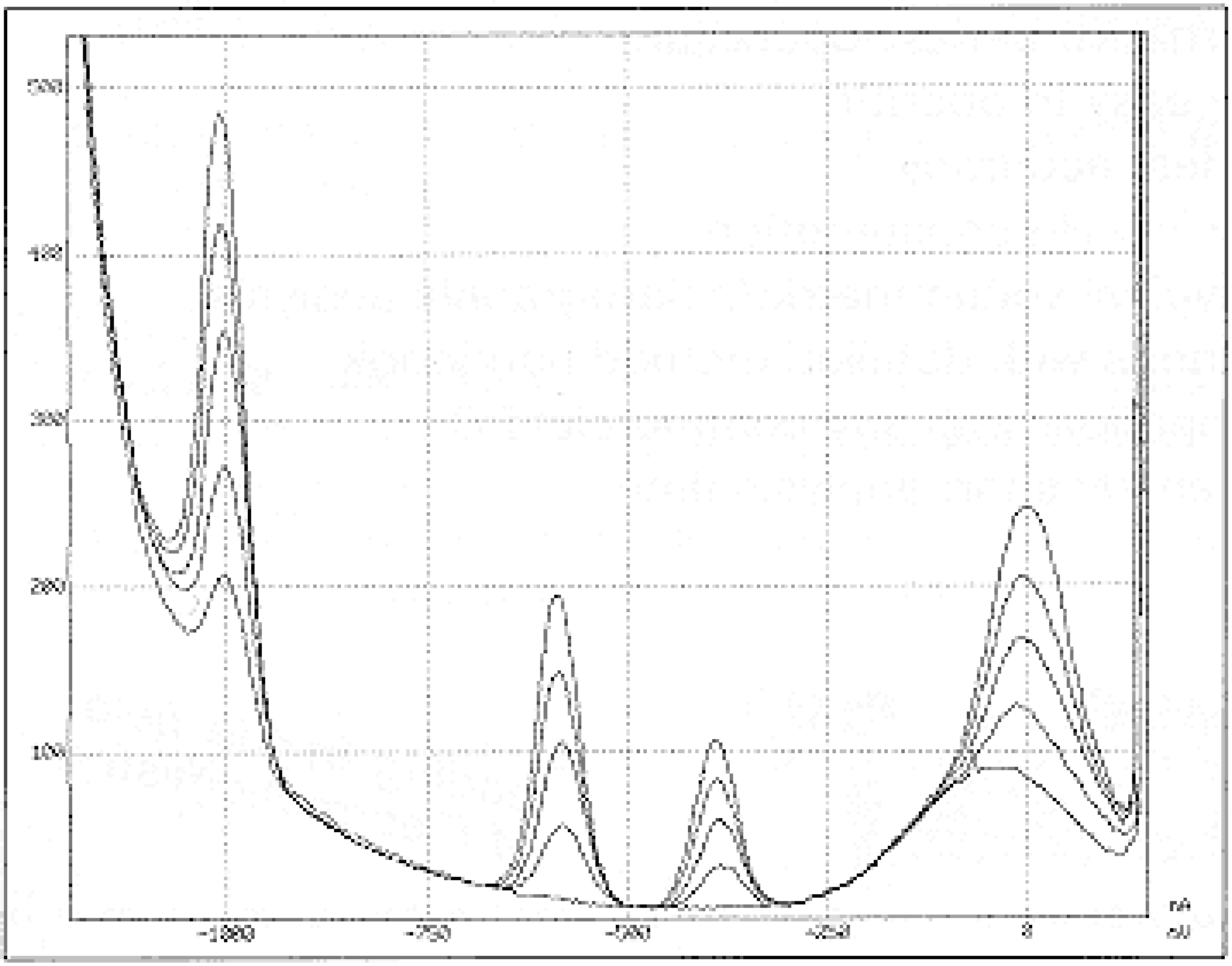




Typical Voltammetry Setup

Voltammogram (DPASV)

I



E (volts)