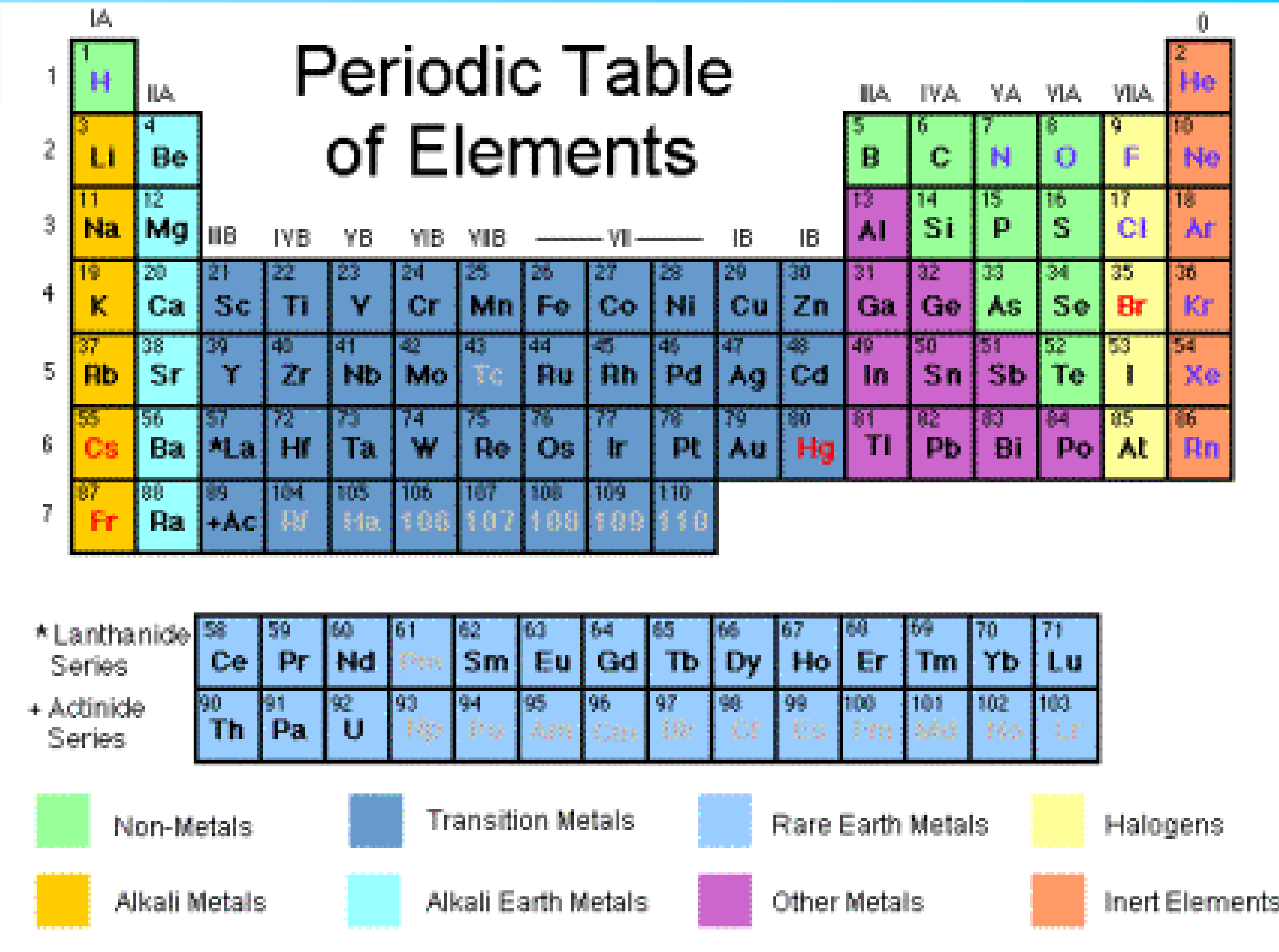
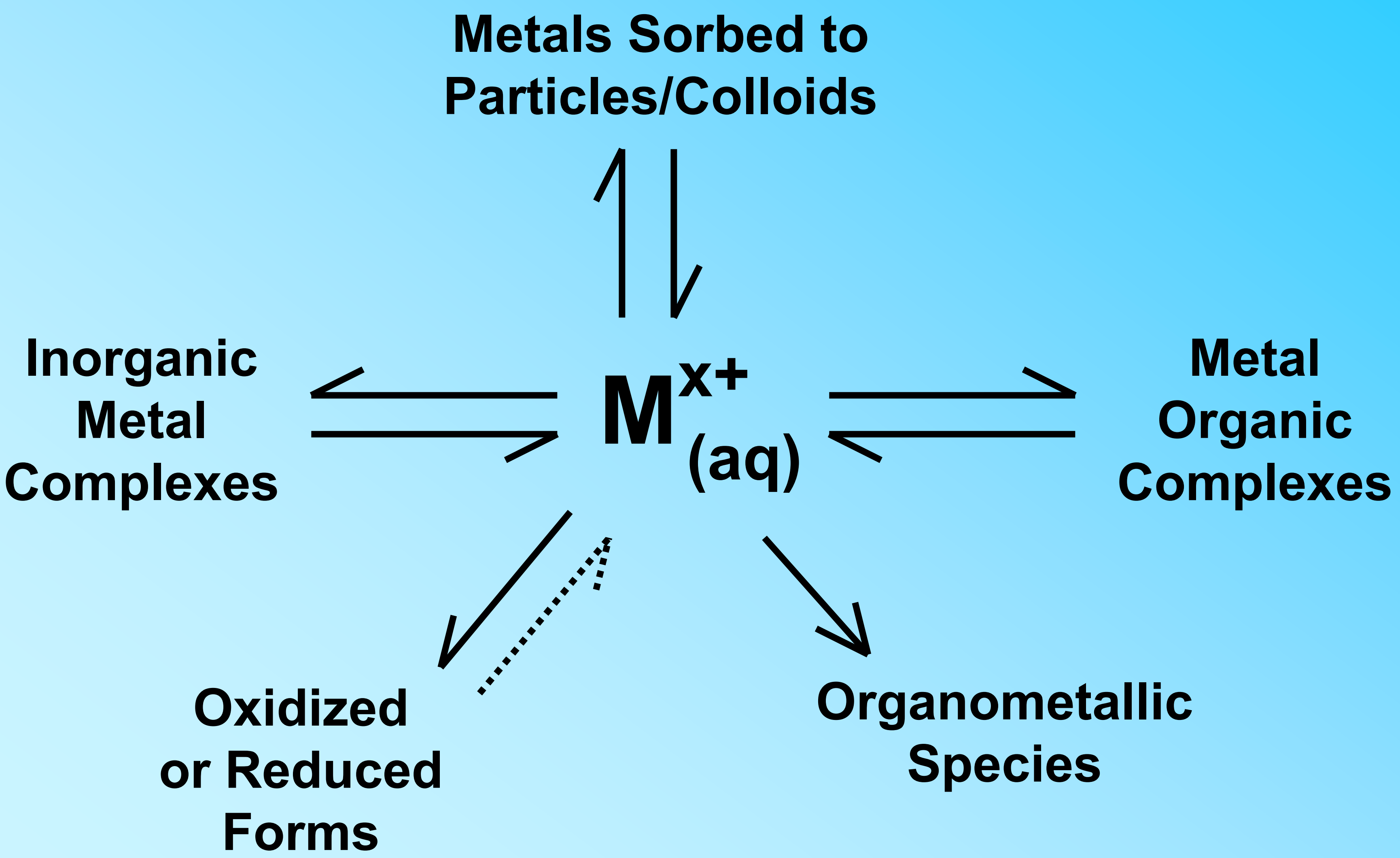


http://www.mbari.org/science/upper-ocean-systems/chemical-sensor-group/periodic-table-of-elements-in-the-ocean/

Dissolved Metal Species



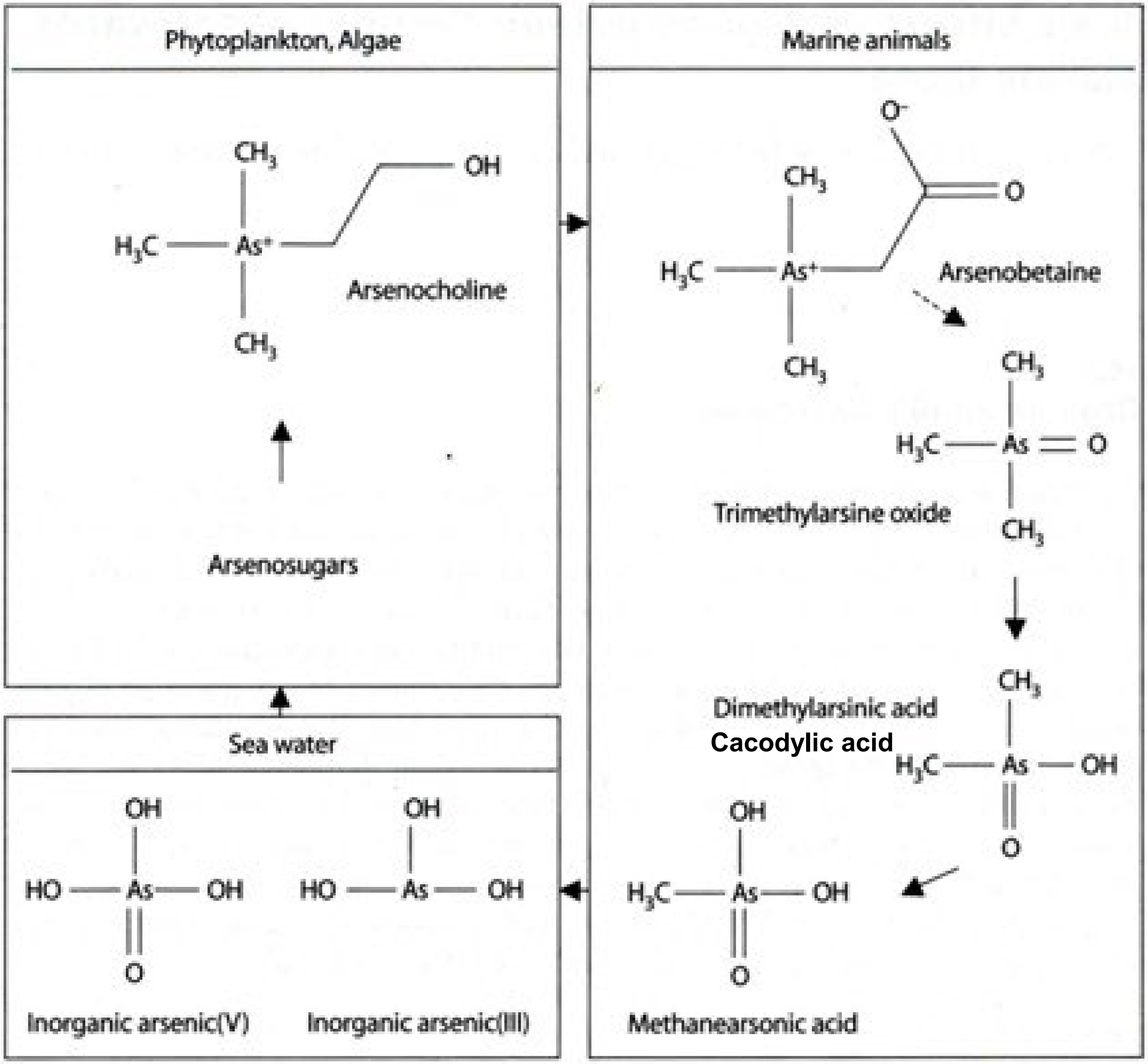


Fig. 15.1. A tentative arsenic cycle in marine ecosystems

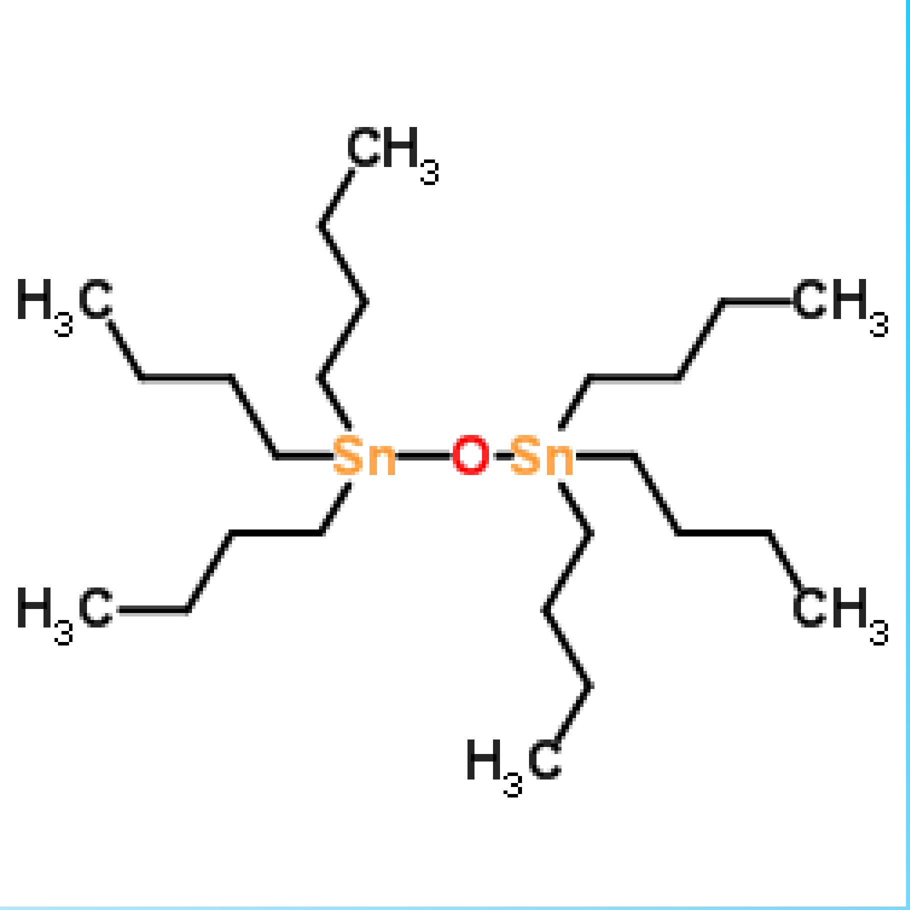
Organometallic Compounds - Contain organic functionality & metal center with a carbon-metal bond

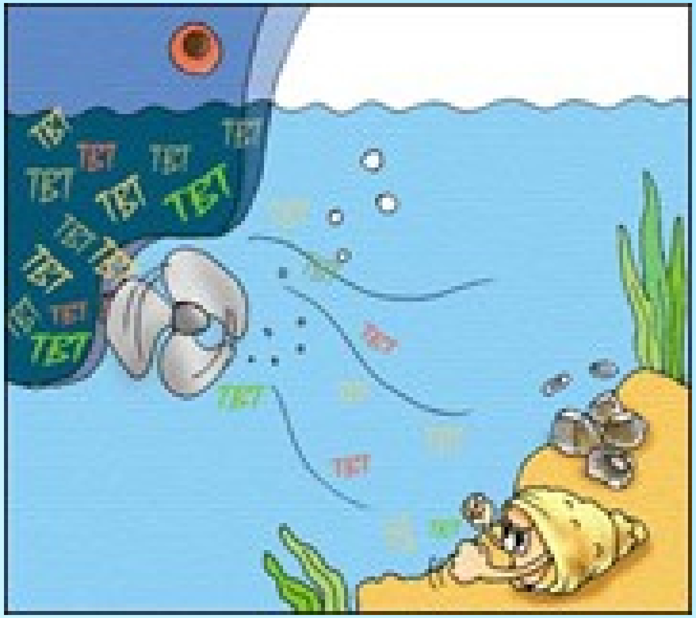
Tributyltin oxide

$[(C_4H_9)_3Sn]_2O$

Bis[tri-n-butyltin(IV)]oxide

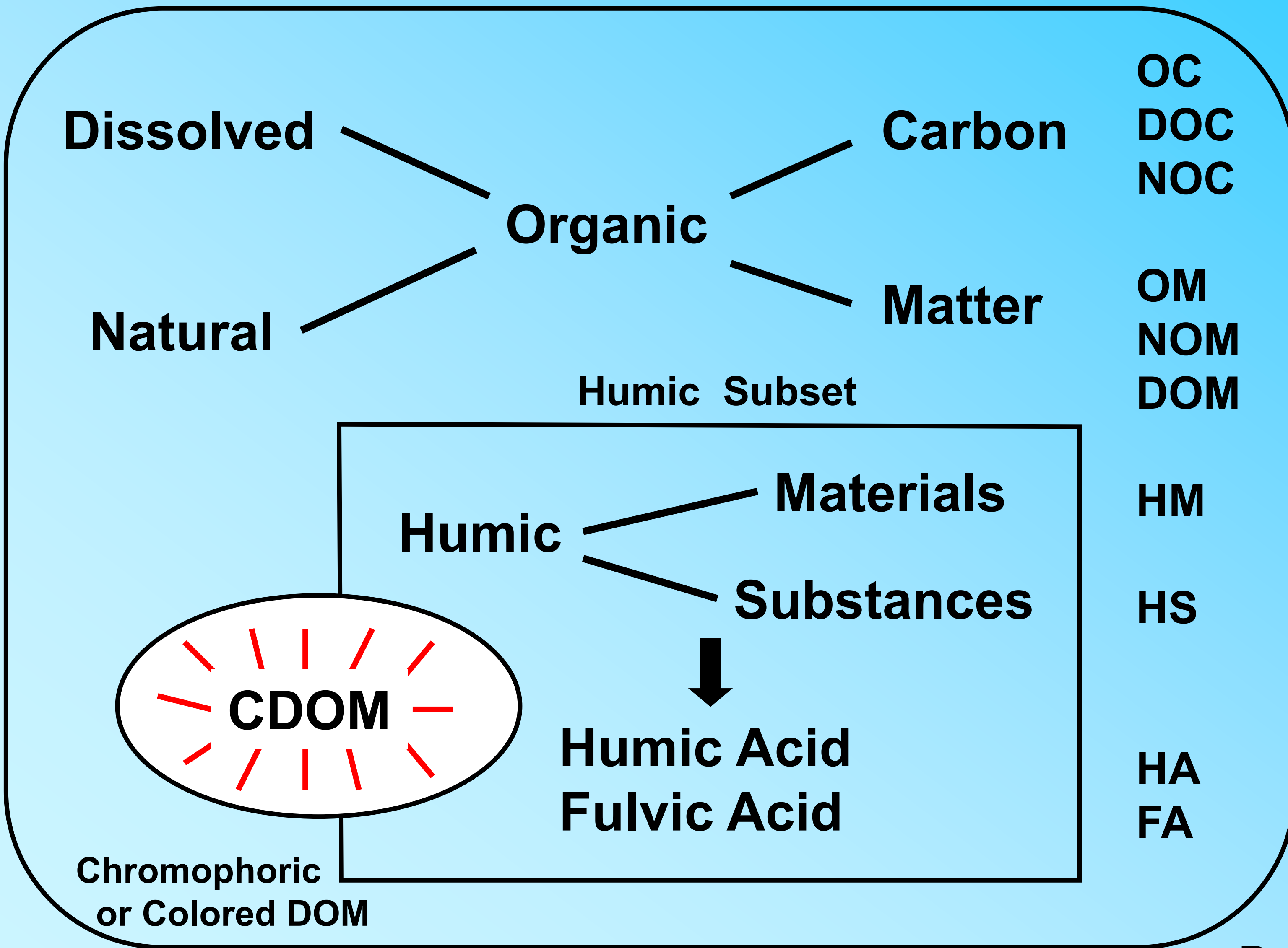
Used in antifouling paint on boat hulls from 1960s to 2008





Dissolved Organic Nomenclature

All Dissolved Organic Compounds

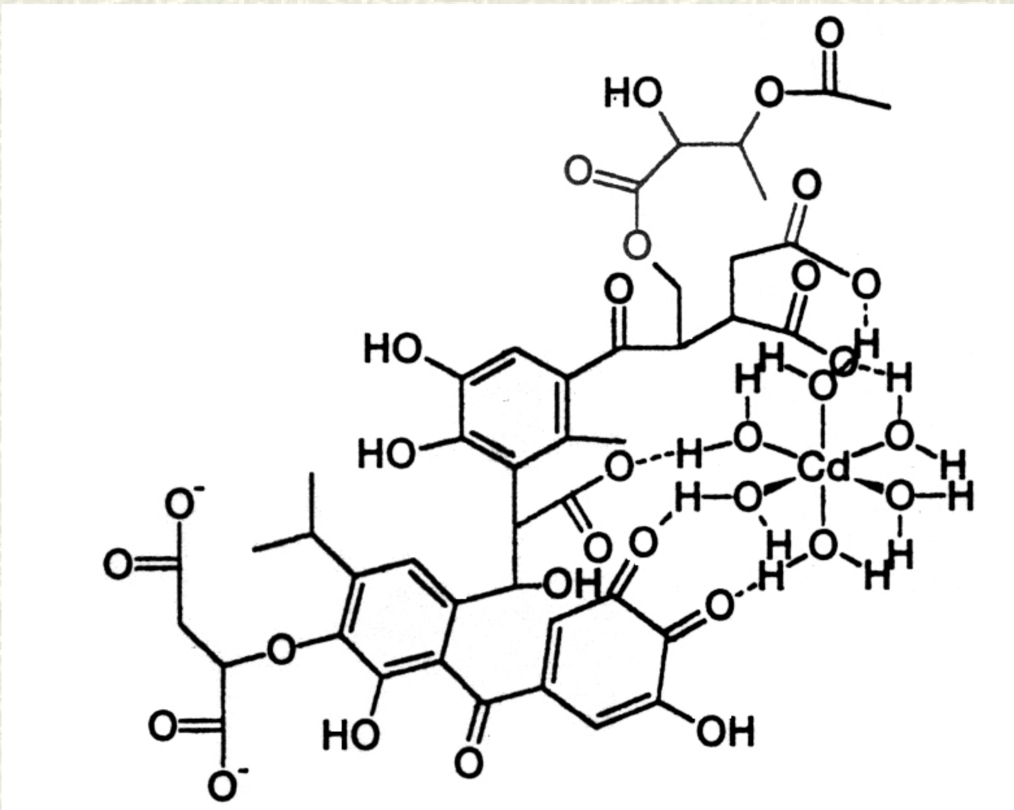


Ryan & Zhu 2013

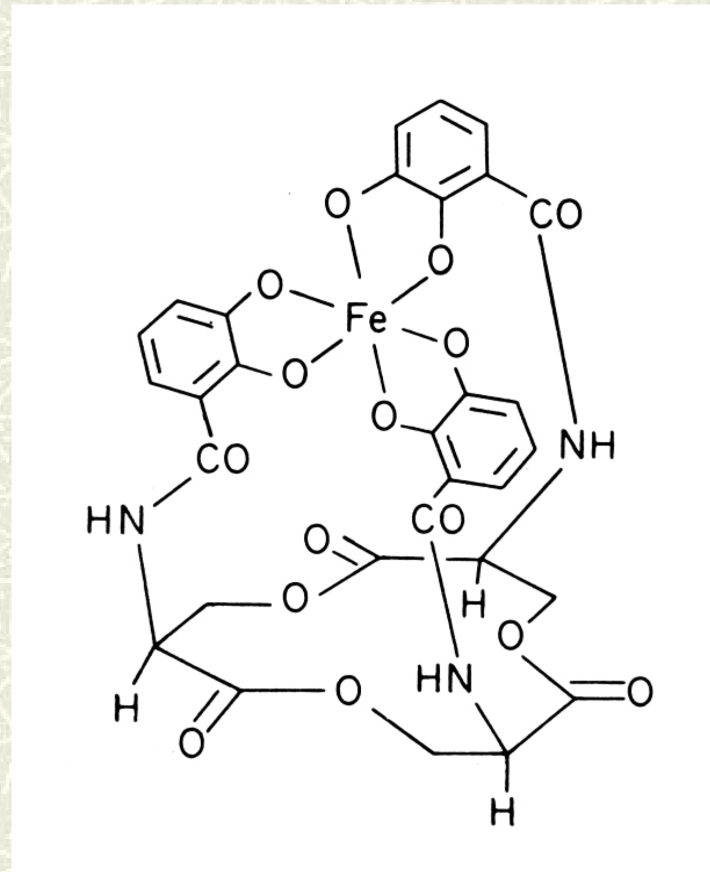
Importance of Humic Materials

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



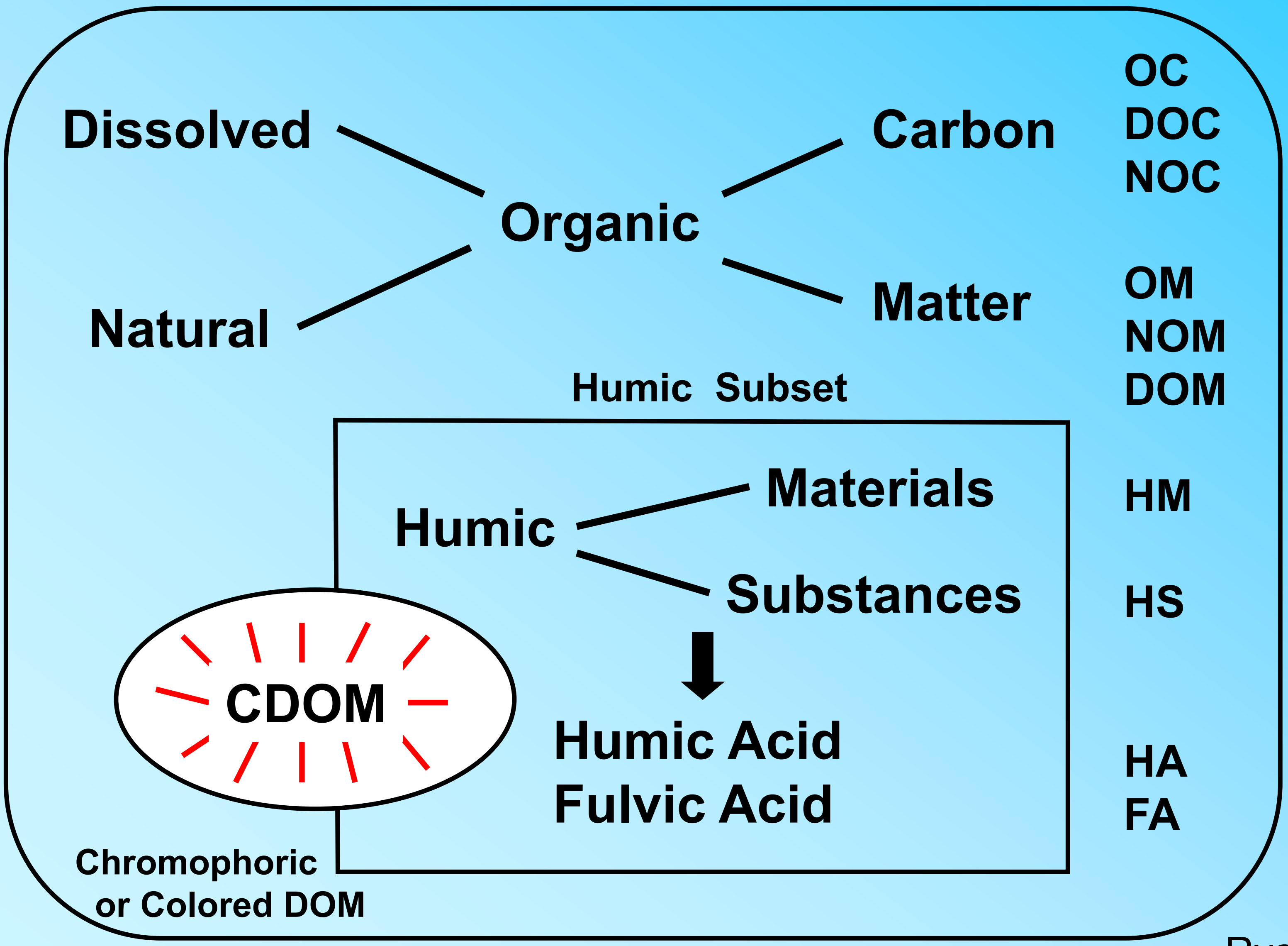
Leenheer et al. (1998)



Morel (1983)

Dissolved Organic Nomenclature

All Dissolved Organic Compounds



Ryan & Zhu 2013

Metal Organic Complexes

M^{x+}

NOM^{y-}

NOM^{y-}

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

NOM^{y-}

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

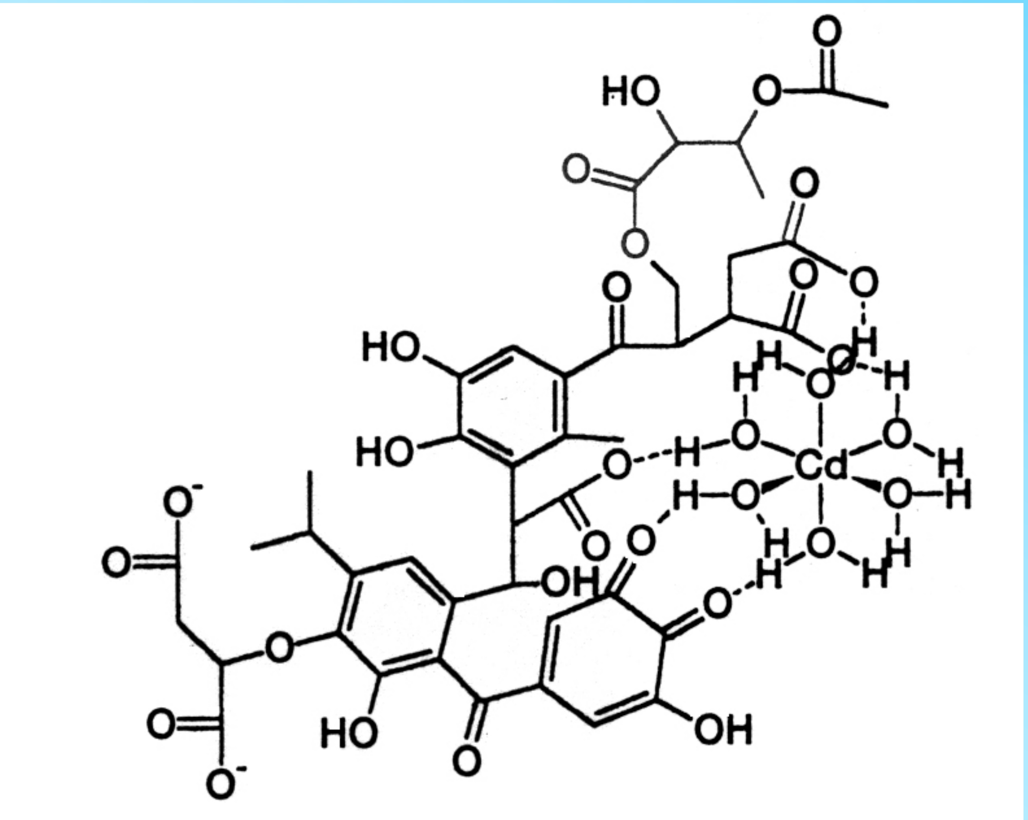
M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

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

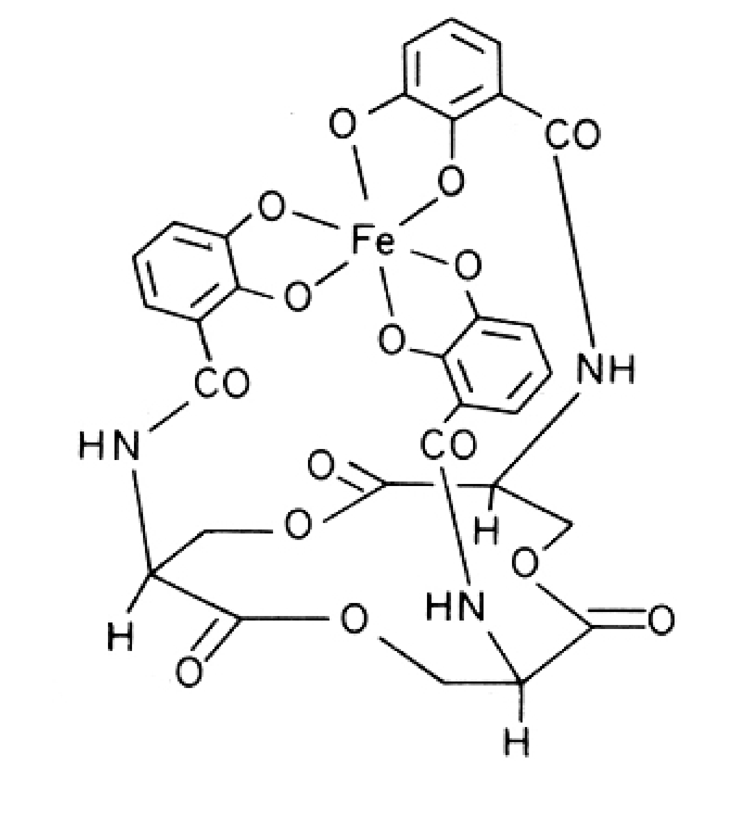
$M\text{-}NOM^{(y-x)-}$ = metal complex of natural organic matter

Metal Complexation by Humic Materials

Outer Sphere Binding vs Inner Sphere Binding



Leenheer et al. (1998)



Morel (1983)

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

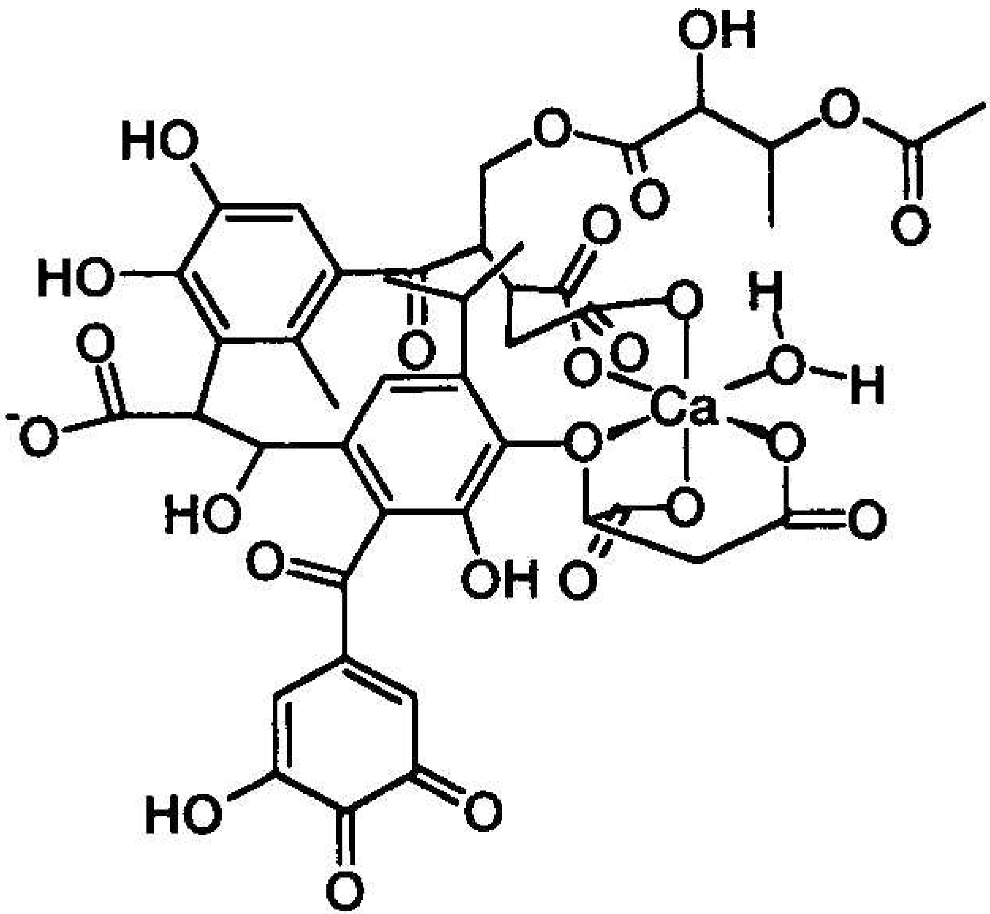


FIGURE 6. Structural model of a calcium inner-sphere complex

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

Importance of Humic Materials

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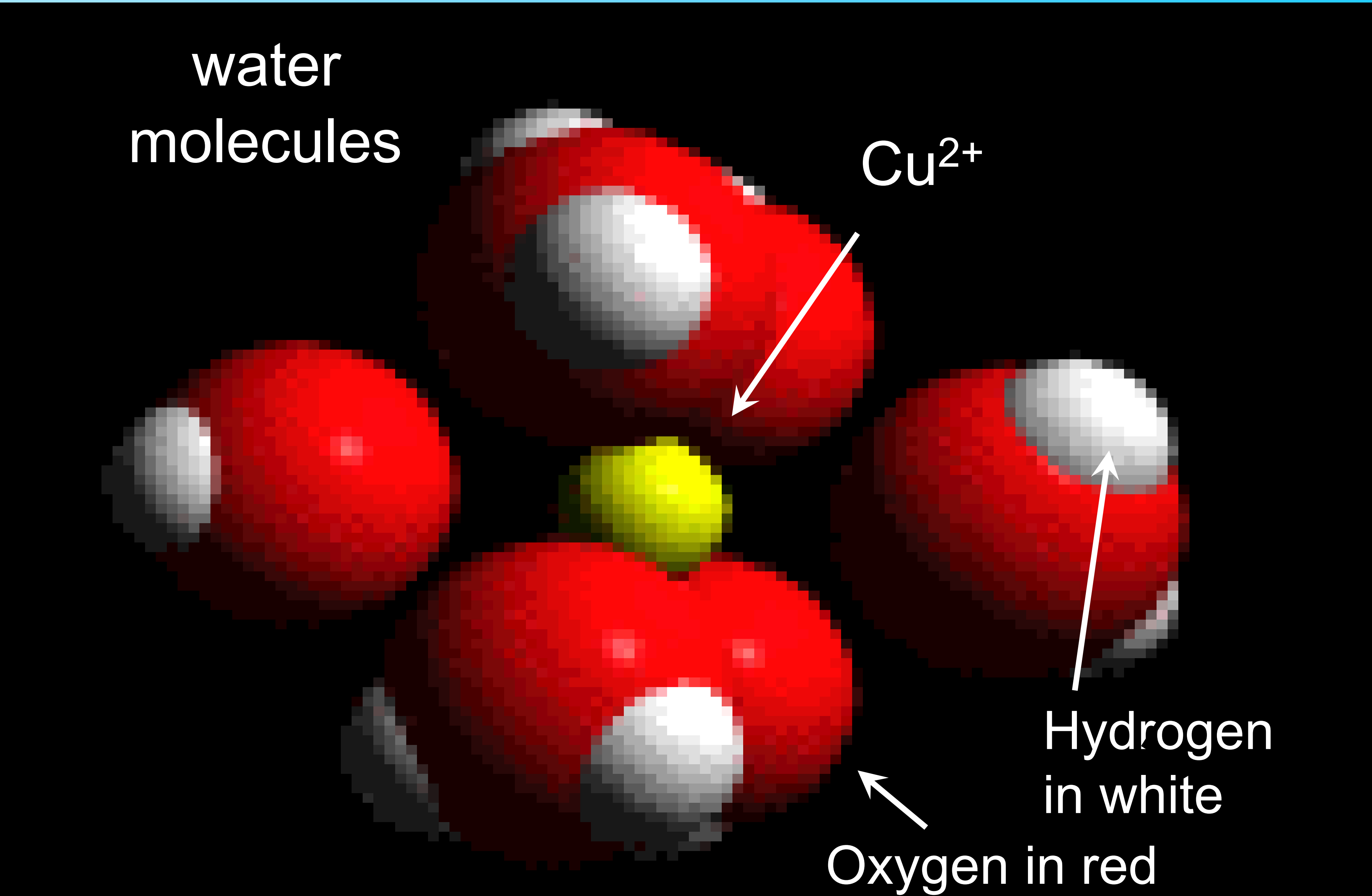
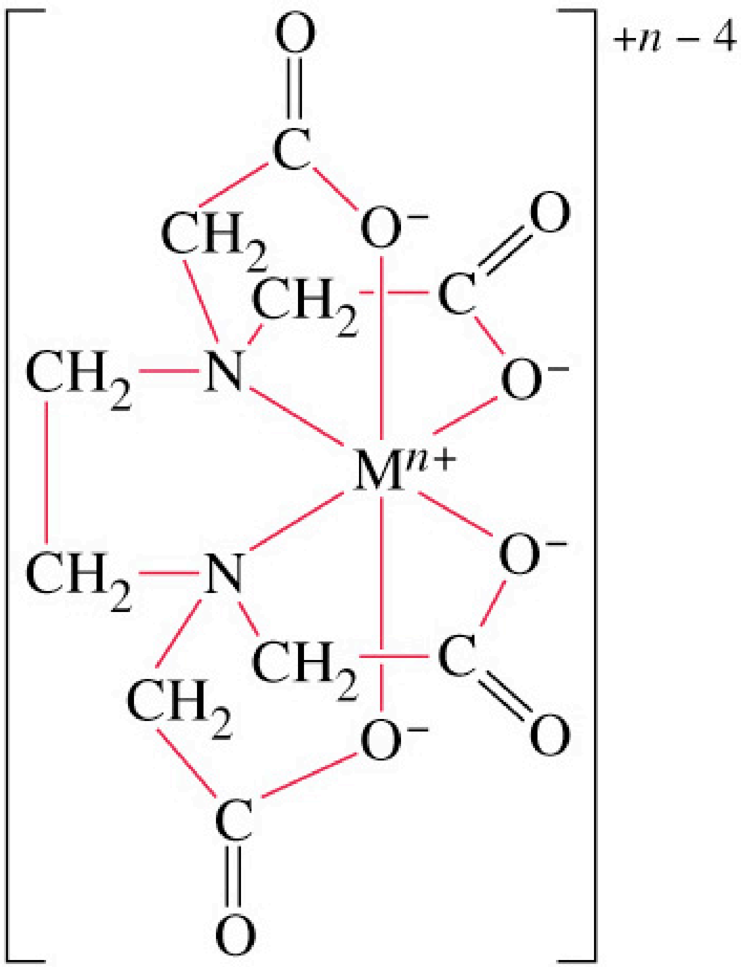
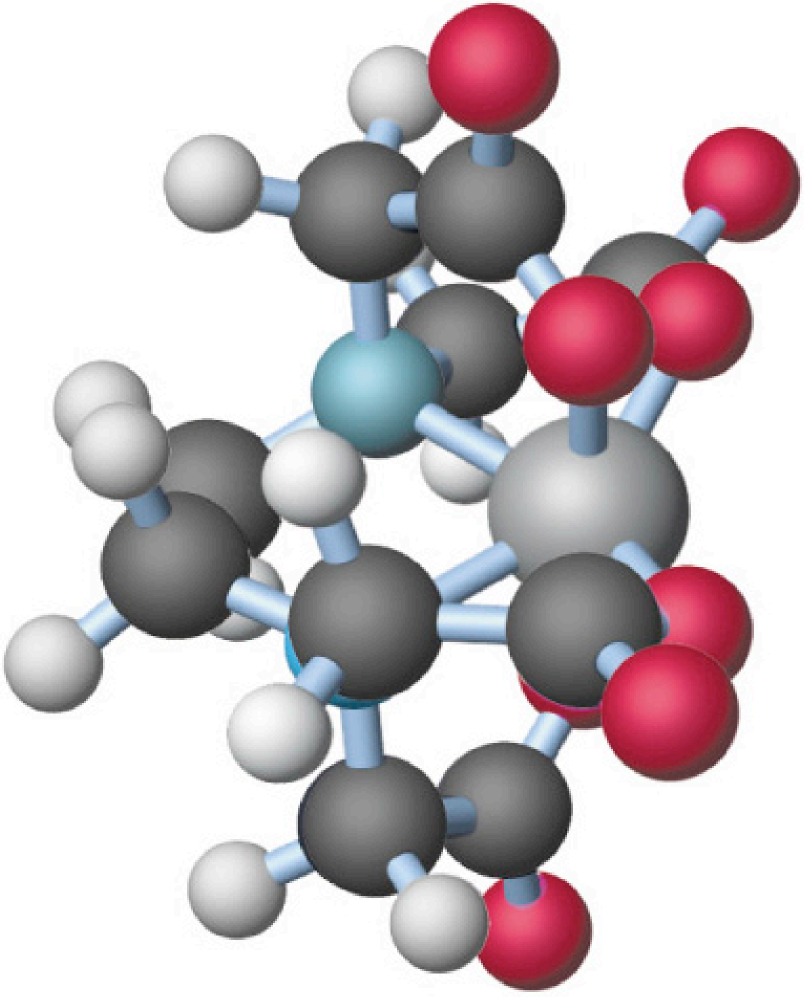
Alter Solubility
Influence Transport
Bind Metals & Organic Pollutants
Terminal Electron Acceptor for Bacteria

Primary Hydration Shell of Cu^{2+}

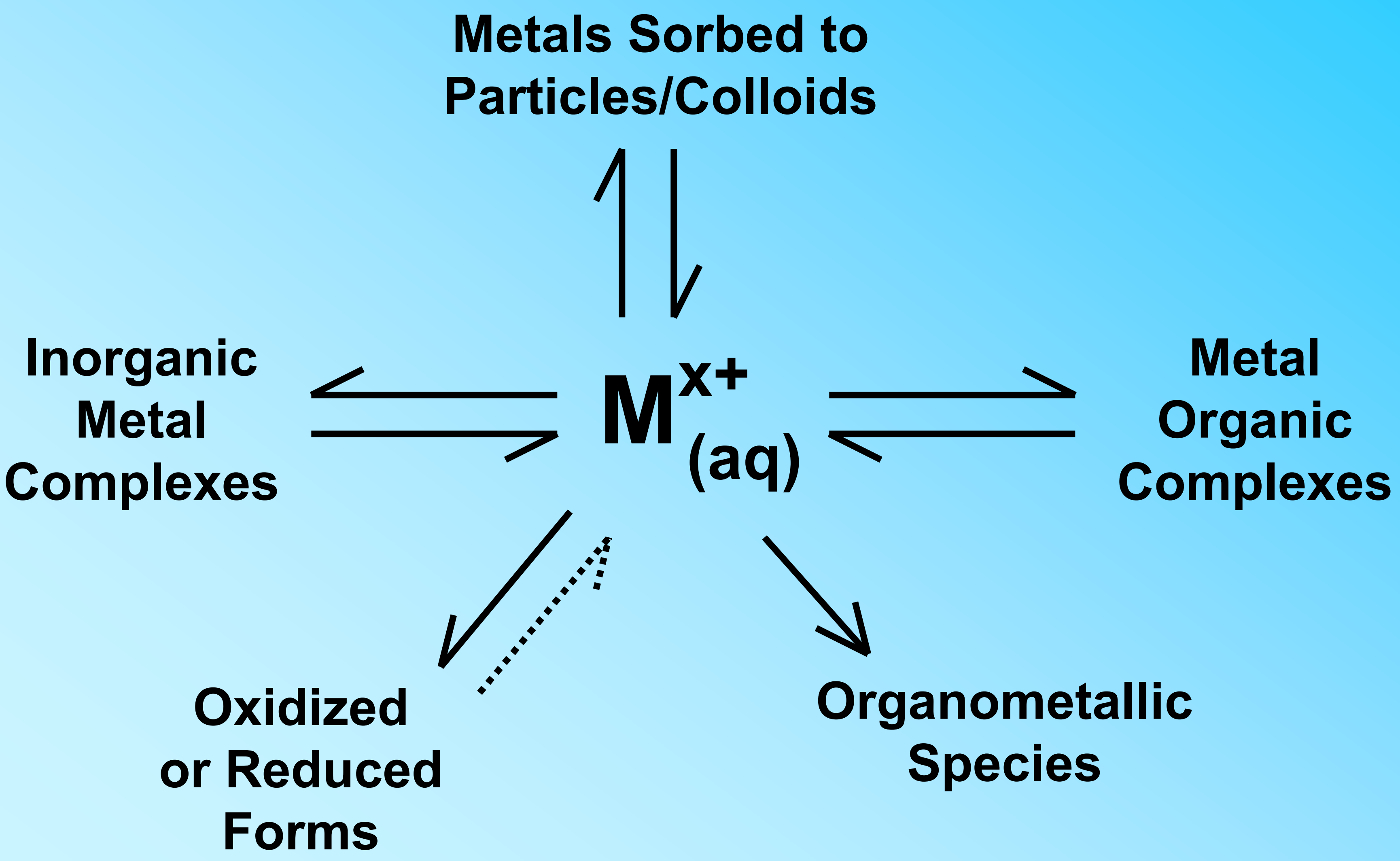


Metal Ion Complexation by EDTA (chelate effect)





Dissolved Metal Species



Metal Inorganic Complexes

M^{x+}

SO_4^{2-}

CO_3^{2-}

M^{x+} SO_4^{2-} M^{x+}

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

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

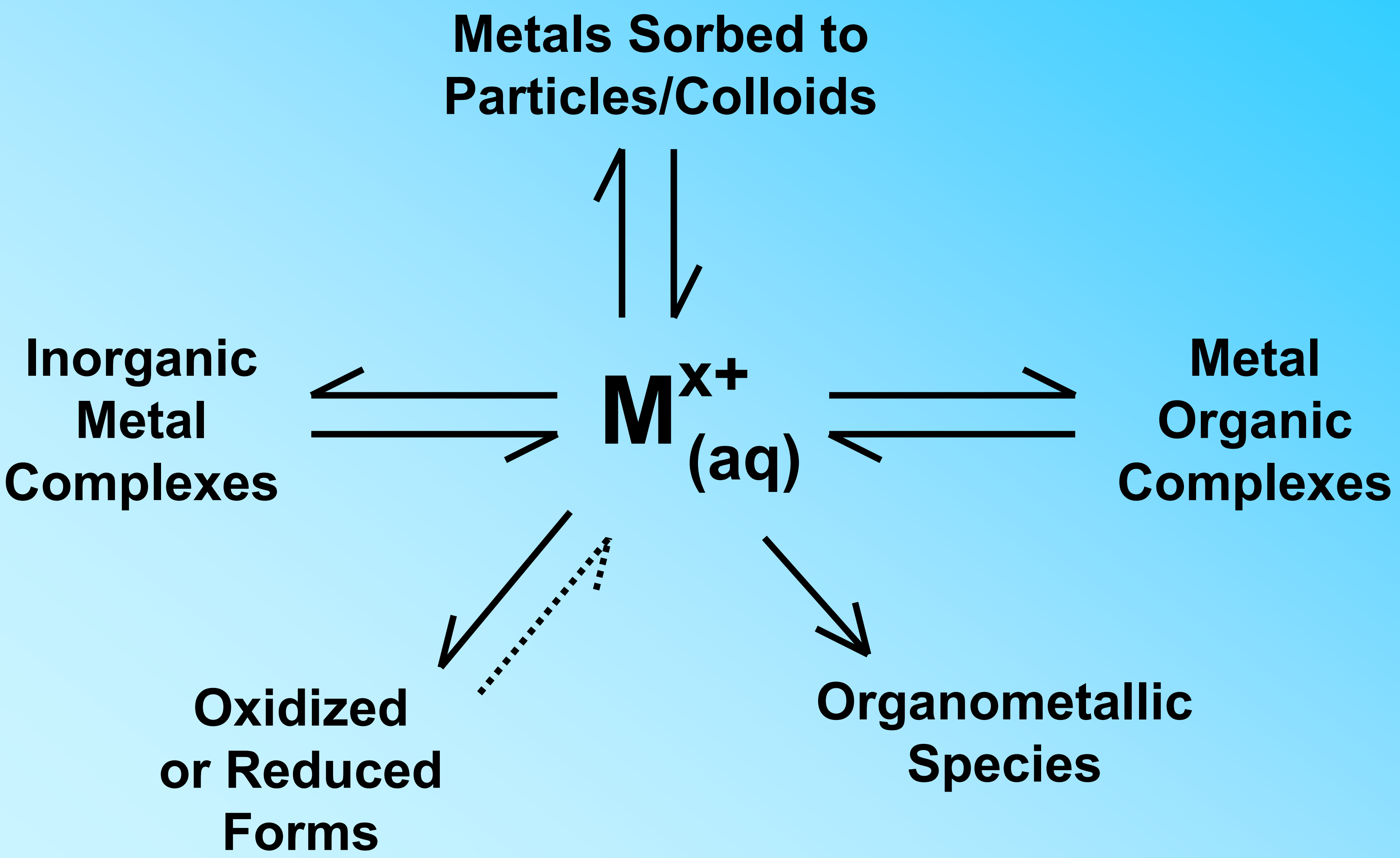
$M\text{-}Cl^{x-1}$ $M\text{-}SO_4^{(x-2)}$

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

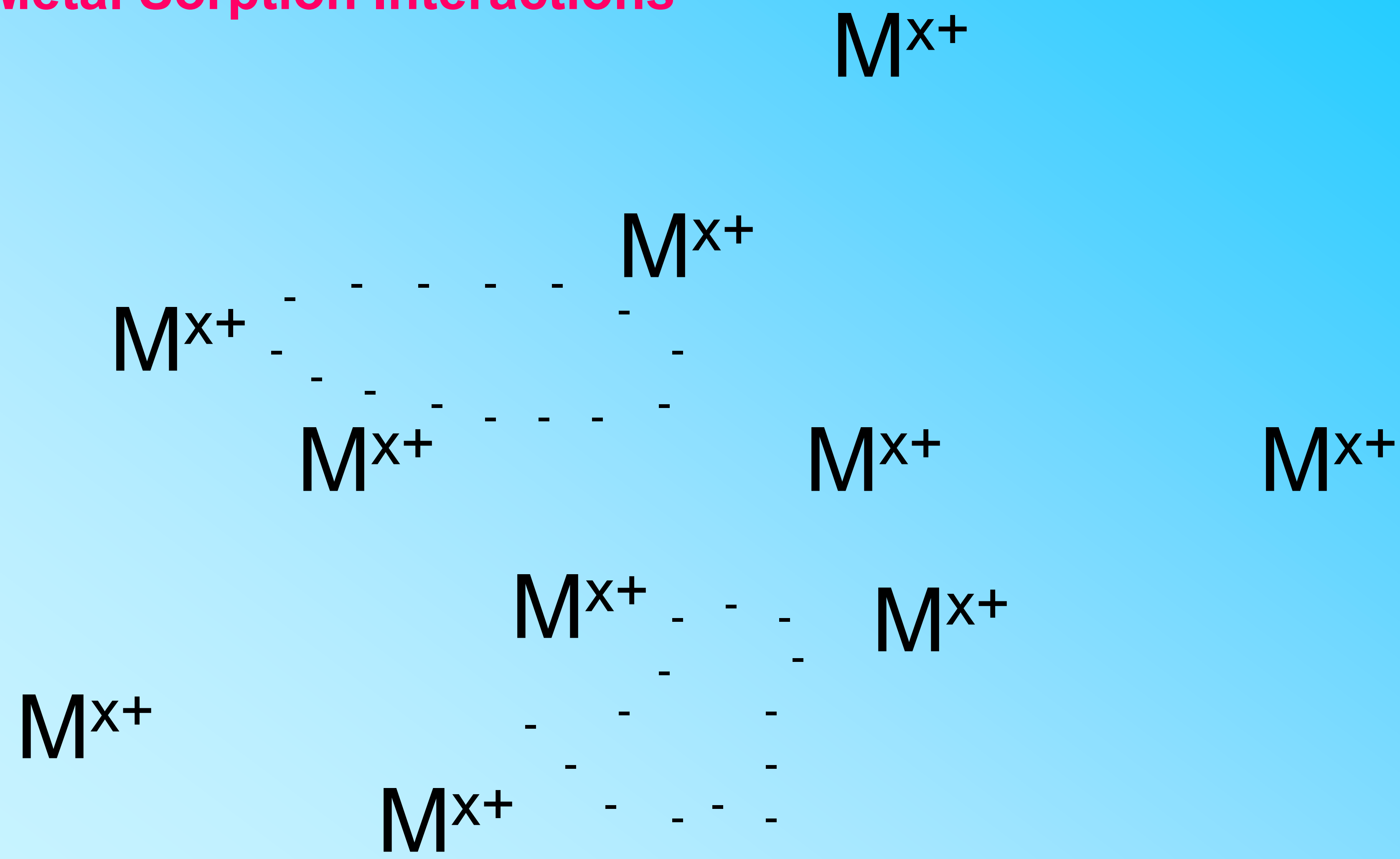
CO_3^{2-}, SO_4^{2-}, Cl^- = inorganic ligands able to bind metal ions

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

Dissolved Metal Species



Metal Sorption Interactions

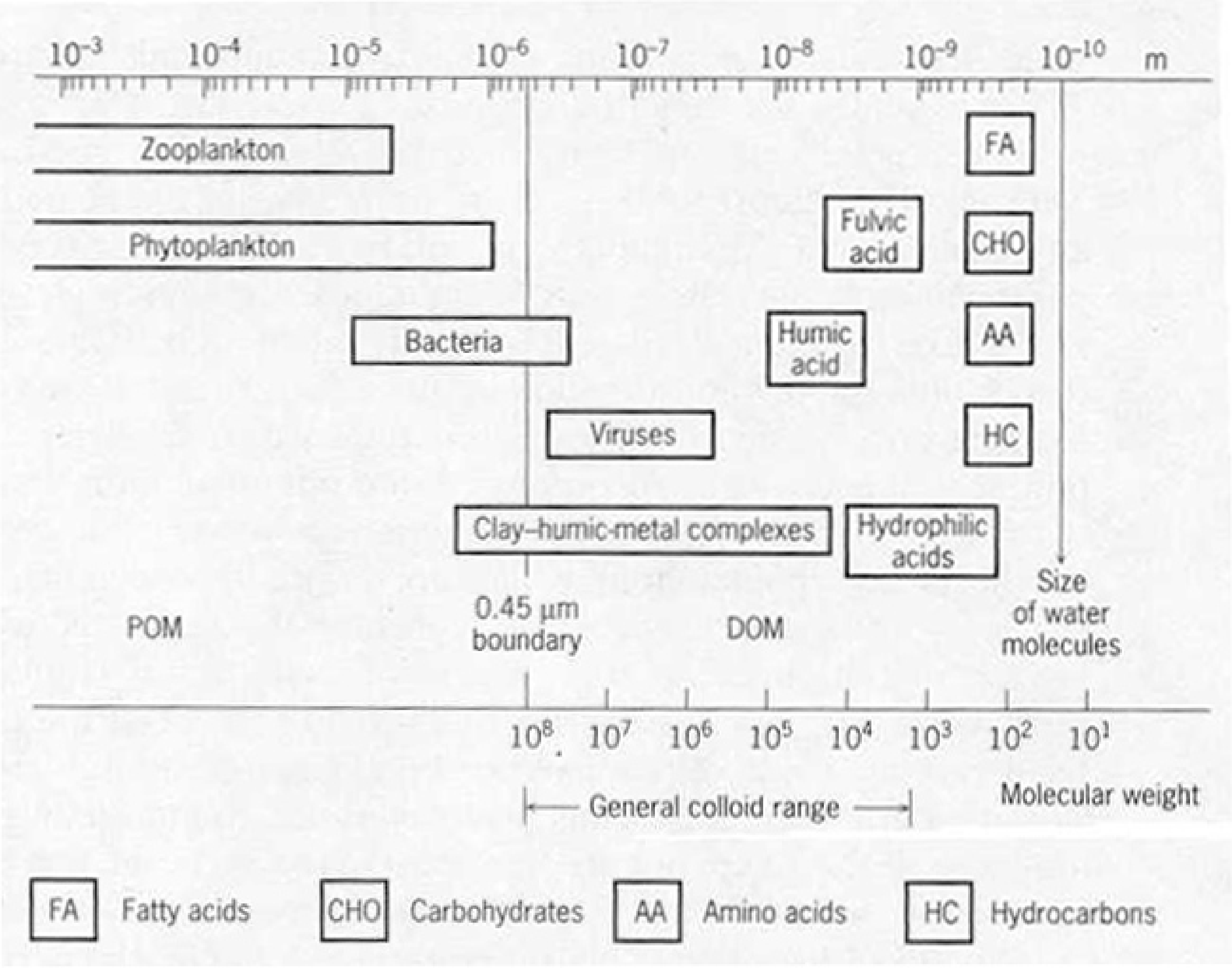


M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

- - - - = natural colloid or particle with negative surface charge -

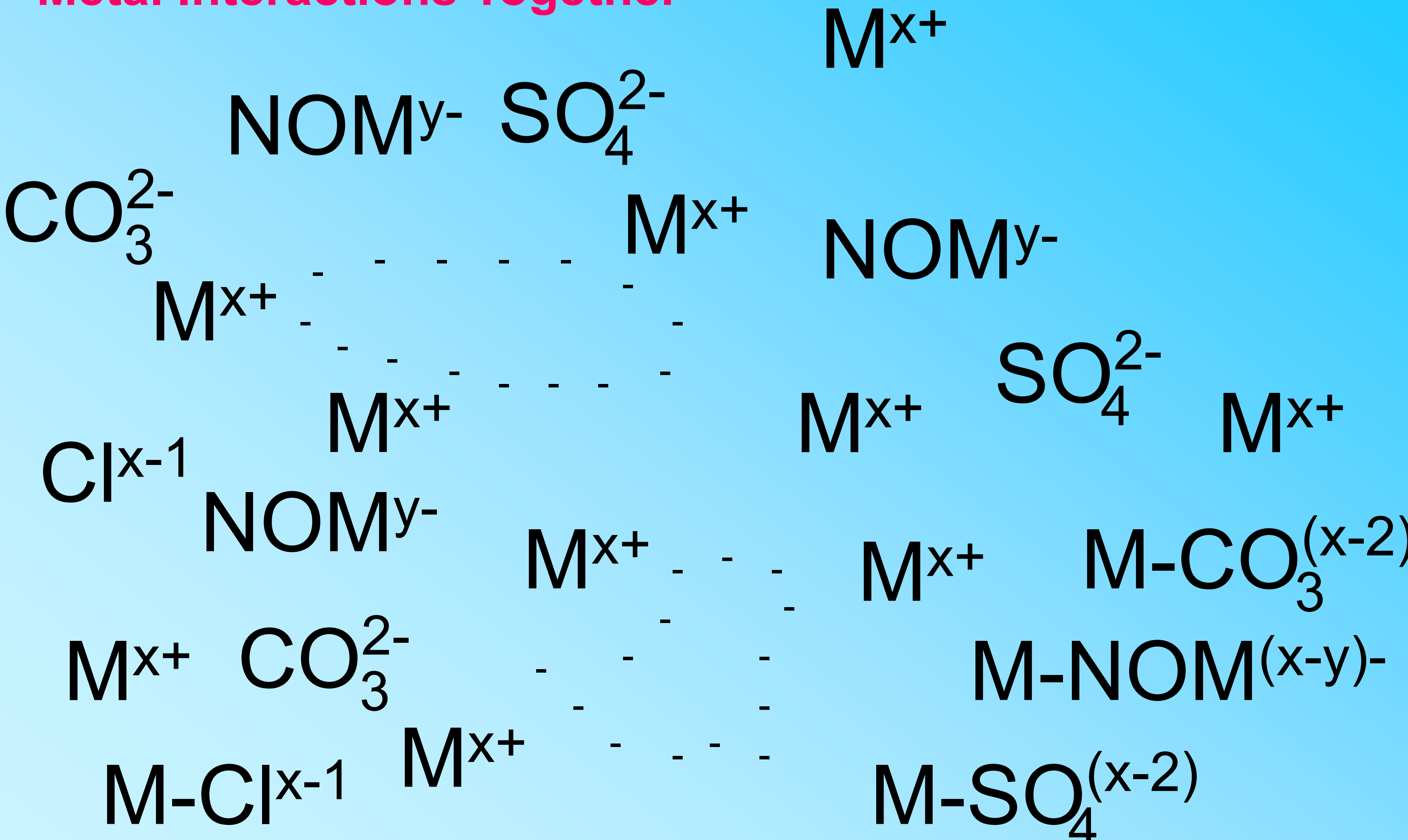
M^{x+} - - - - = metal sorbed to particle or organic matter on particle

Organic Carbon Continuum



Libes, 1992

Metal Interactions Together

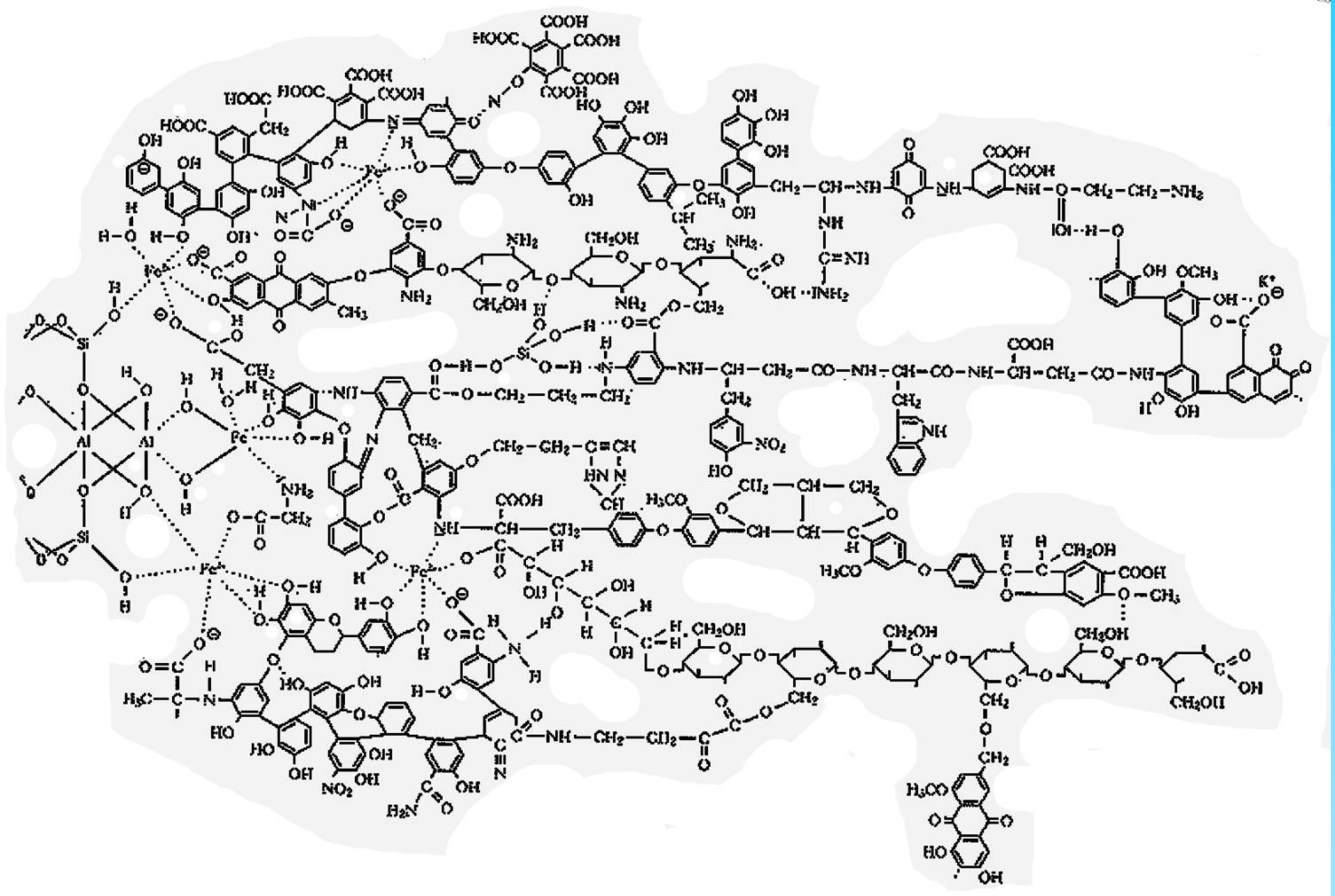


M^{x+} = metal ion, toxic or non, of charge x+ (e.g., Cu^{2+}, Al^{3+}, etc.)

- - - - = 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

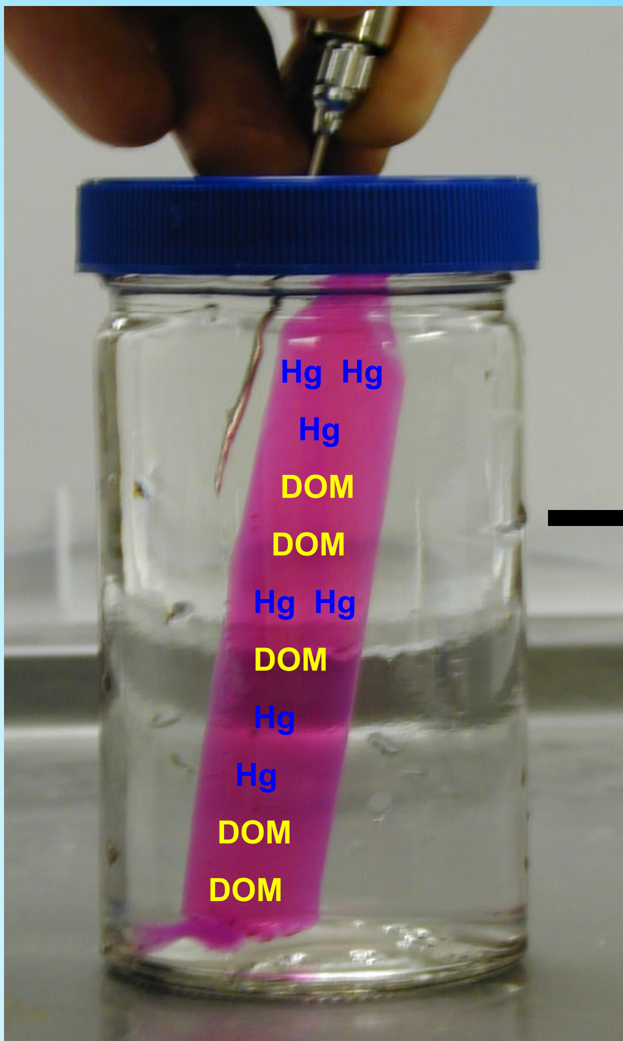
Analytical Speciation Methods

- 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

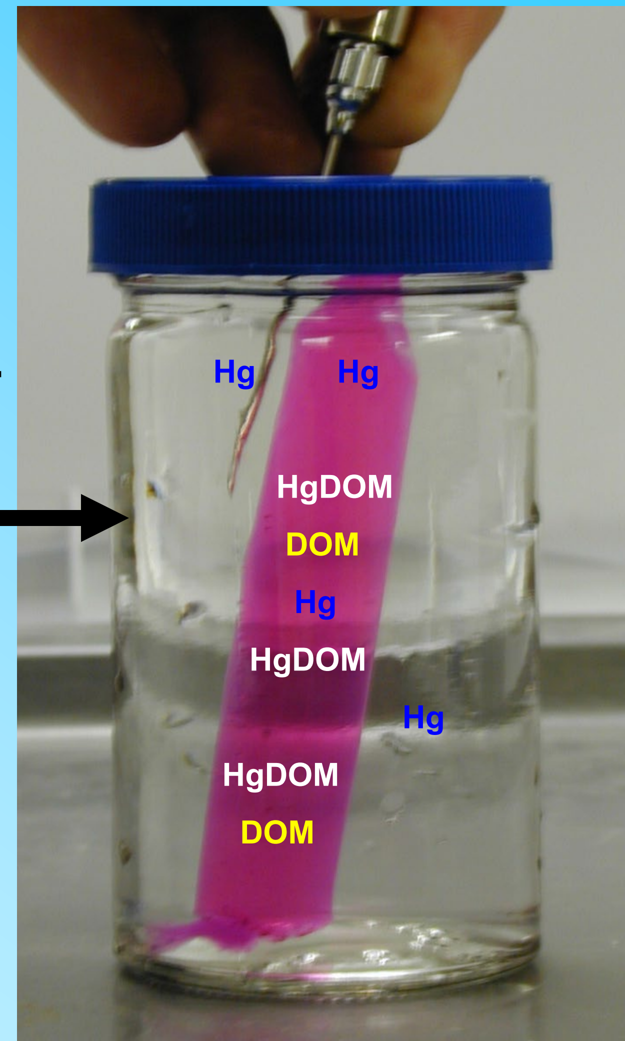
(Glaus, Hummel, Van Loon. Analytica Chimica Acta. 303 (1995) 321-331)

Initial

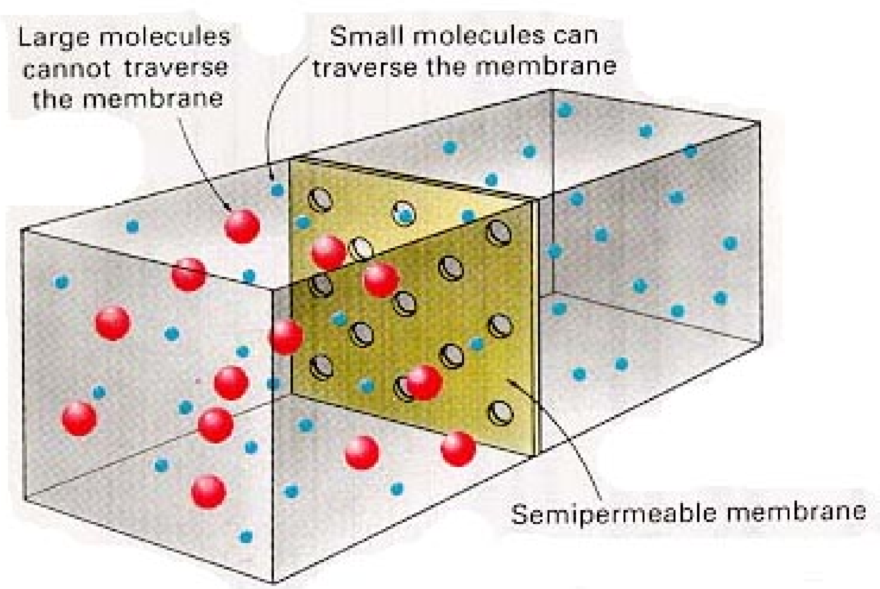


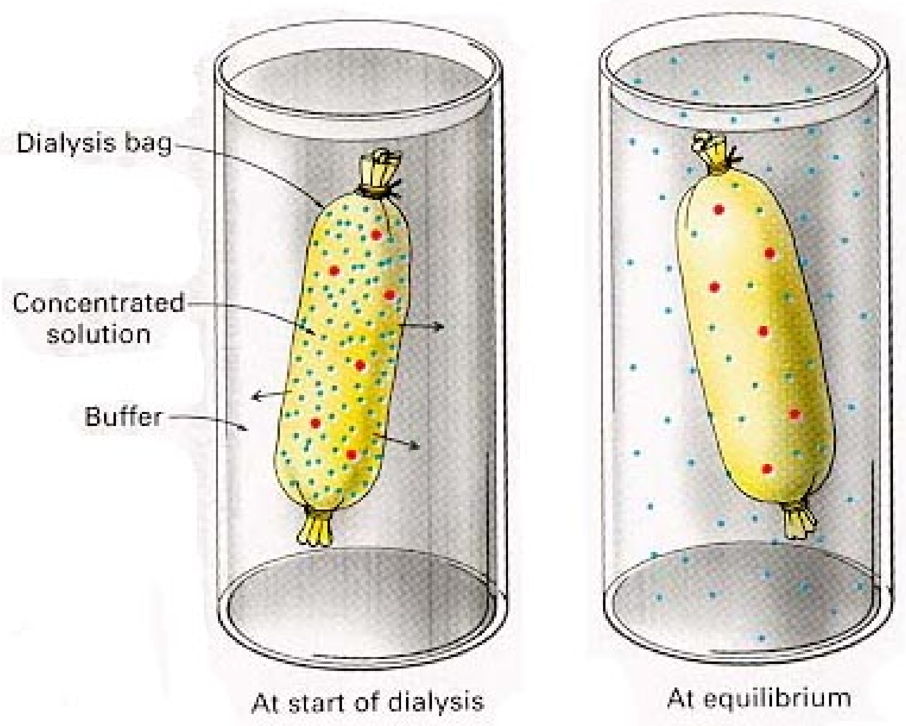
$$K_1 = \frac{[\text{Hg-DOC}]}{[\text{Free DOC}][\text{Free Hg}]}$$

Final



Dialysis Process

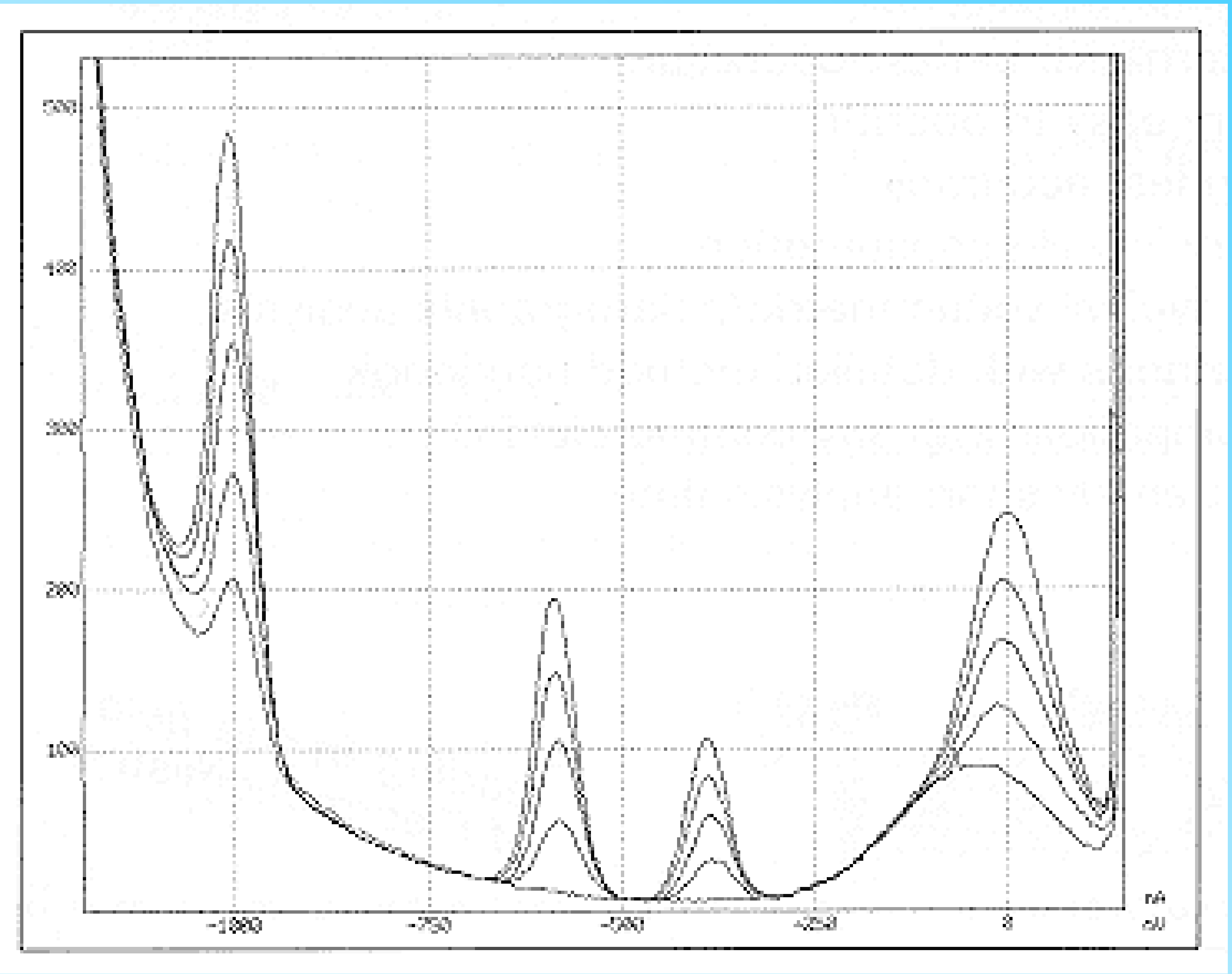




Typical Voltammetry Setup

Voltammogram (DPASV)

I



E (volts)