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

	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VII	VII	VII	IB	IB	IIIA	IVA	VA	VIA	VIIA	0
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 *La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 +Ac	104 Rf	105 Ha	106 106	107 107	108 108	109 109	110 110								

* Lanthanide Series	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
+ Actinide Series	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- Non-Metals
- Transition Metals
- Rare Earth Metals
- Halogens
- Alkali Metals
- Alkali Earth Metals
- Other Metals
- Inert 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

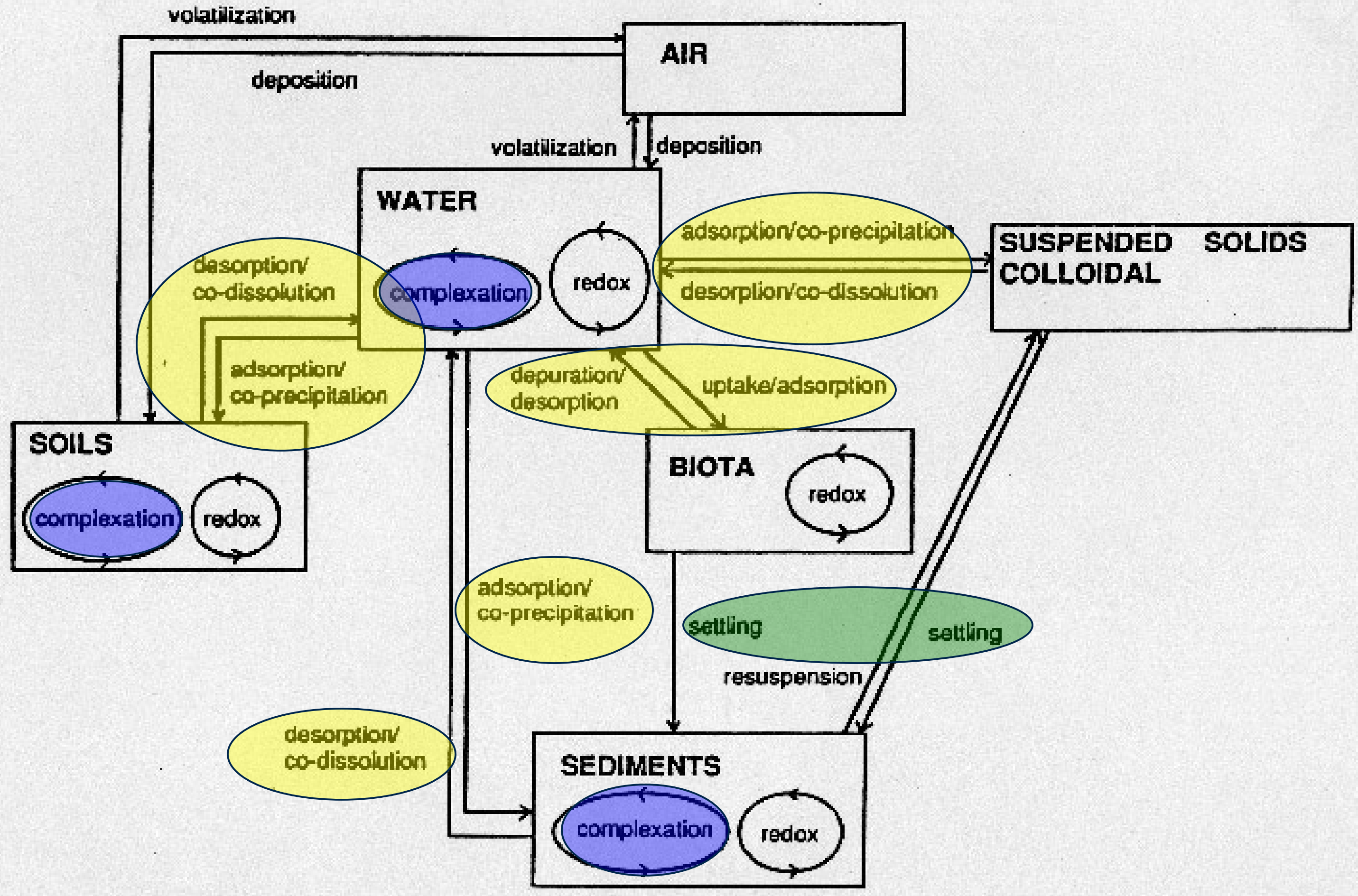


Figure 3.1. Schematic diagram of processes controlling the biogeochemical cycling of metals in aquatic environments.

Classification Schemes for Metals

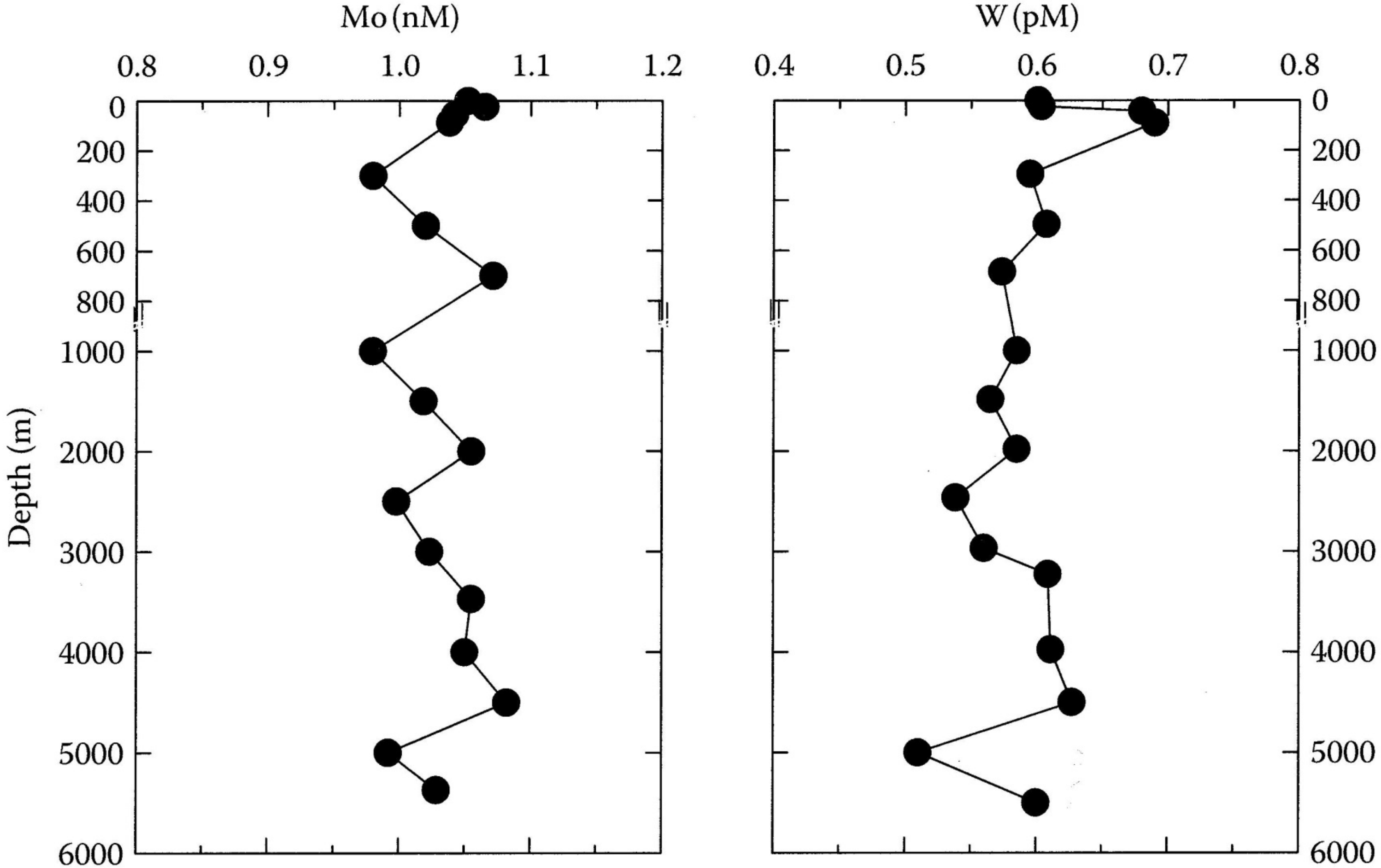
- Concentration – Major, Minor, Trace
- Biological Reactivity – Biolimiting, Biointermediate, Biounlimited, Noncycling
- Chemical Reactivity – d^0, d^{10}, Intermediate or Class A, Class B, Intermediate
- Overall Reactivity – Nutrient Type, Particle Reactive, Other
- Environmental Origin – Crustal, Pollutant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

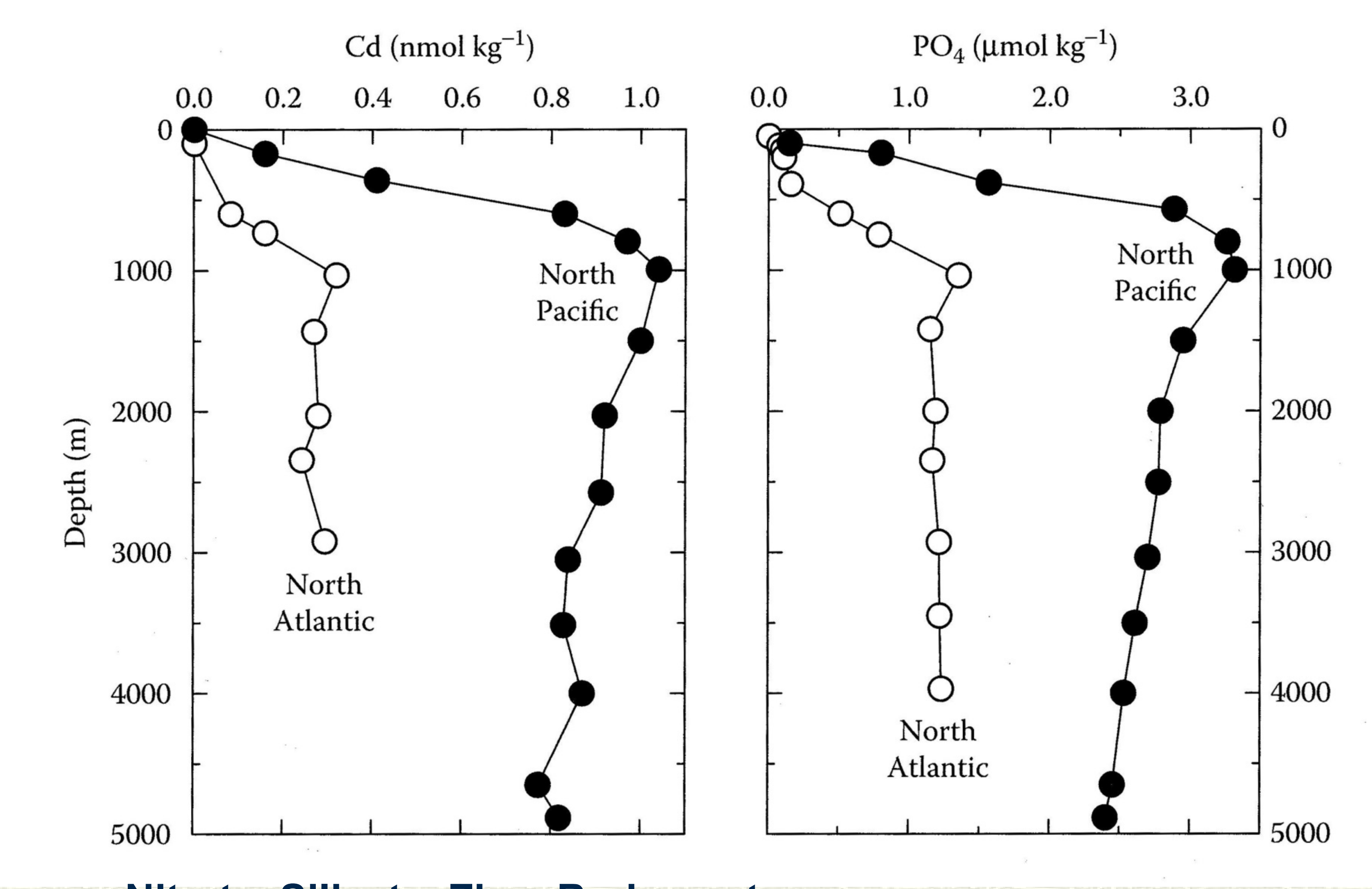
Conservative behavior (Millero 2006)



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

Depth Profiles for Cd & P

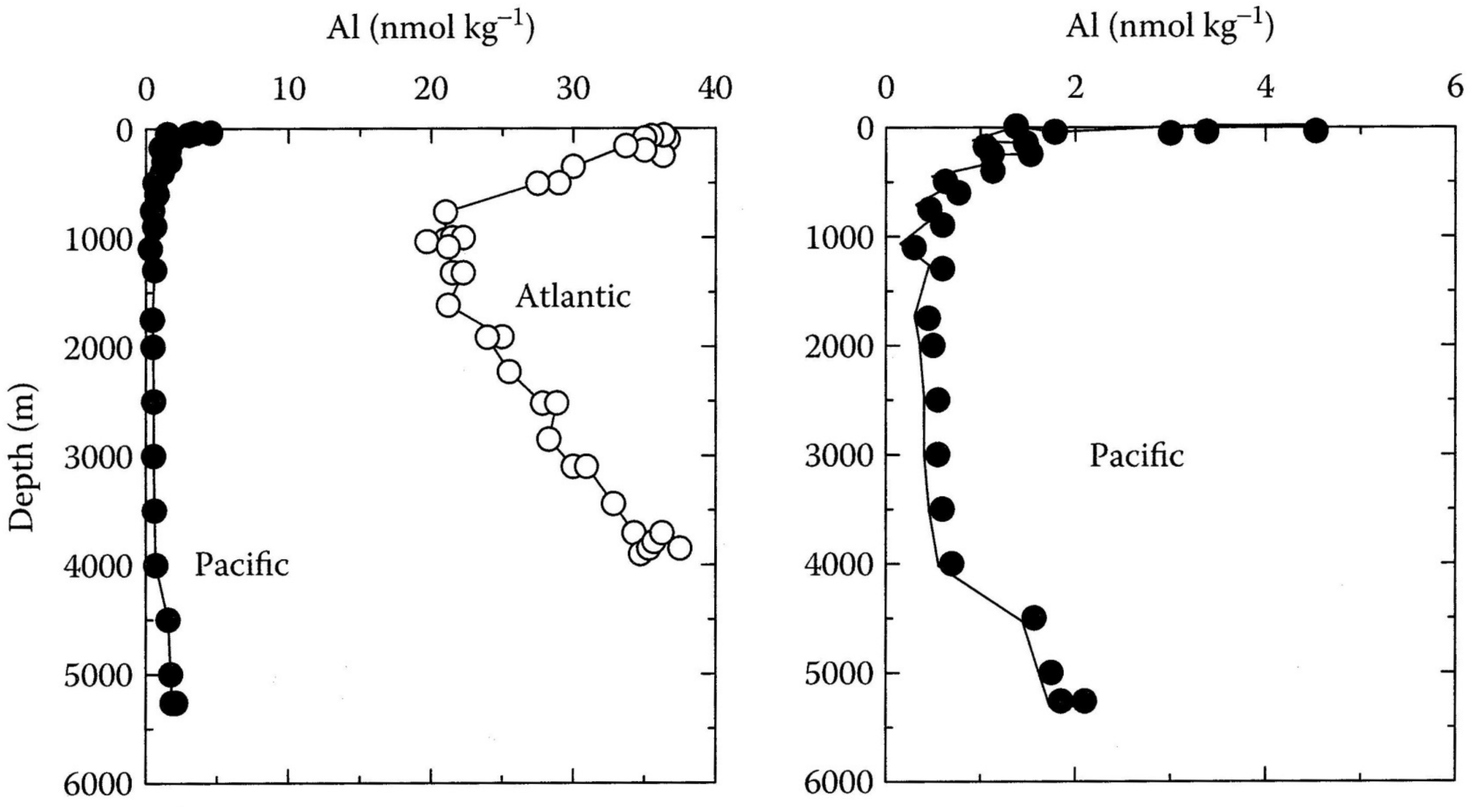
Nutrient behavior (Millero 2006)



Nitrate, Silicate, Zinc, Barium, etc.

Depth Profiles for Al

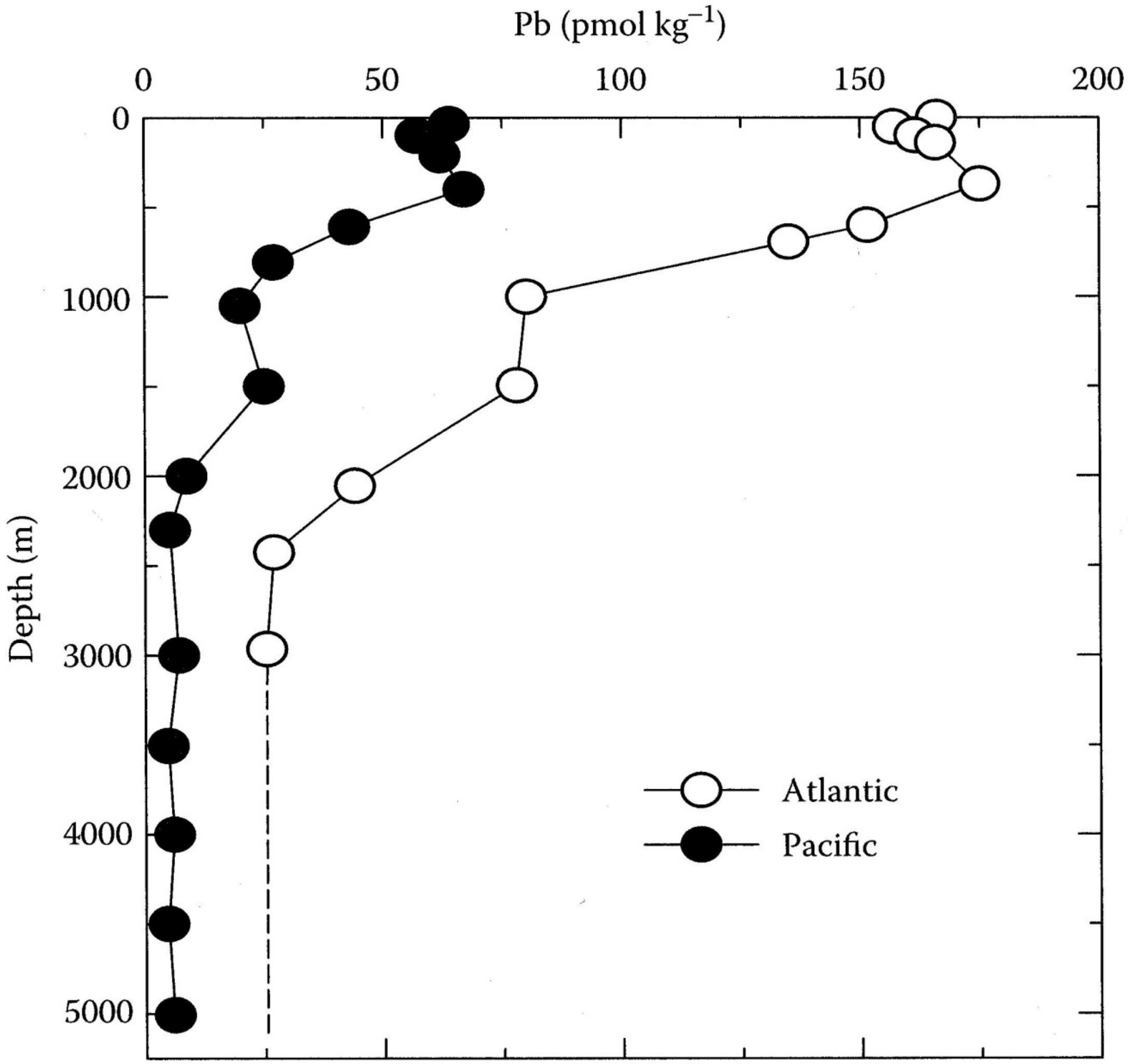
Mid-depth minimum (Millero 2006)

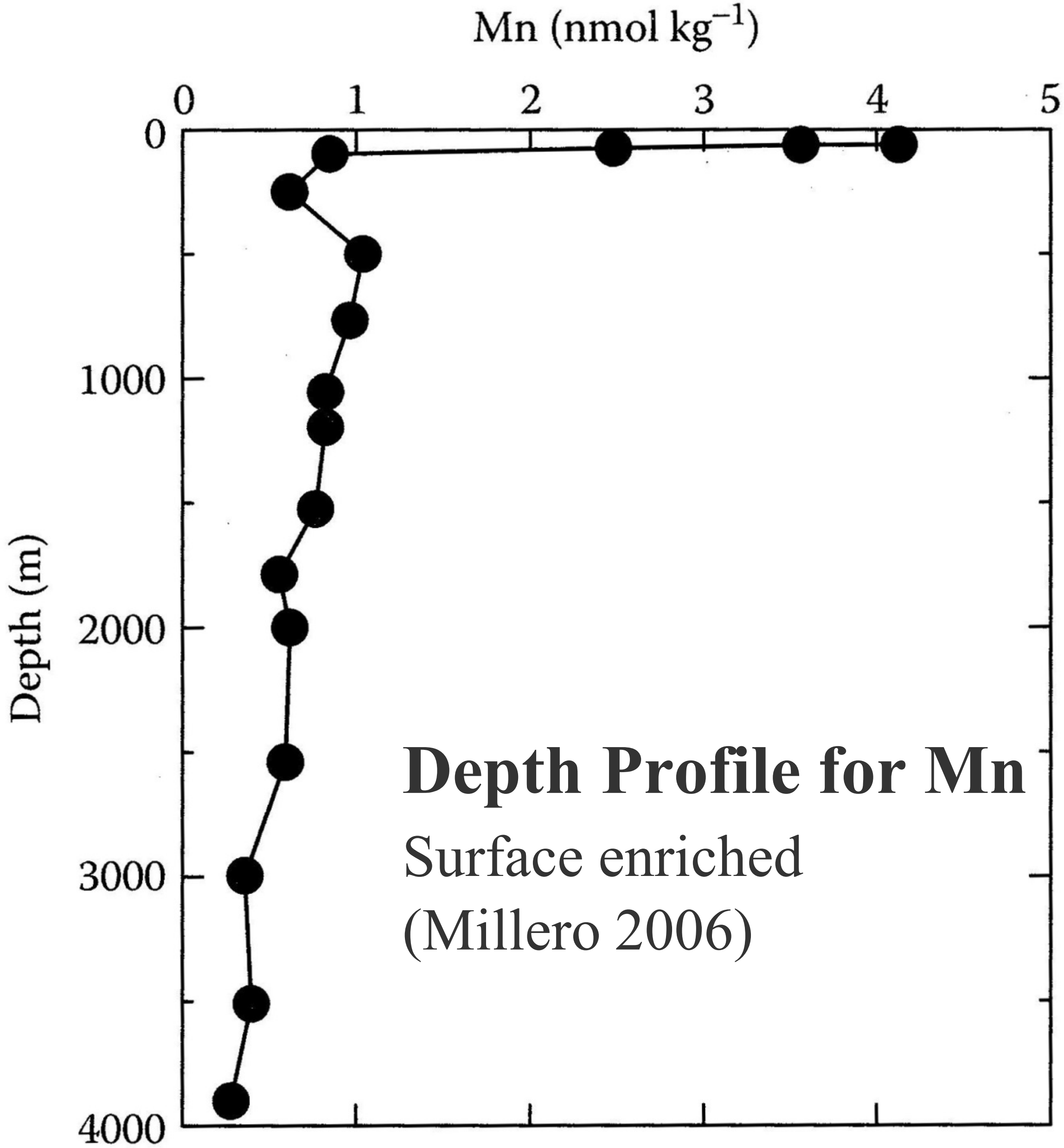


Copper, Tin, etc.

Depth Profiles for Pb

Surface enriched (Millero 2006)

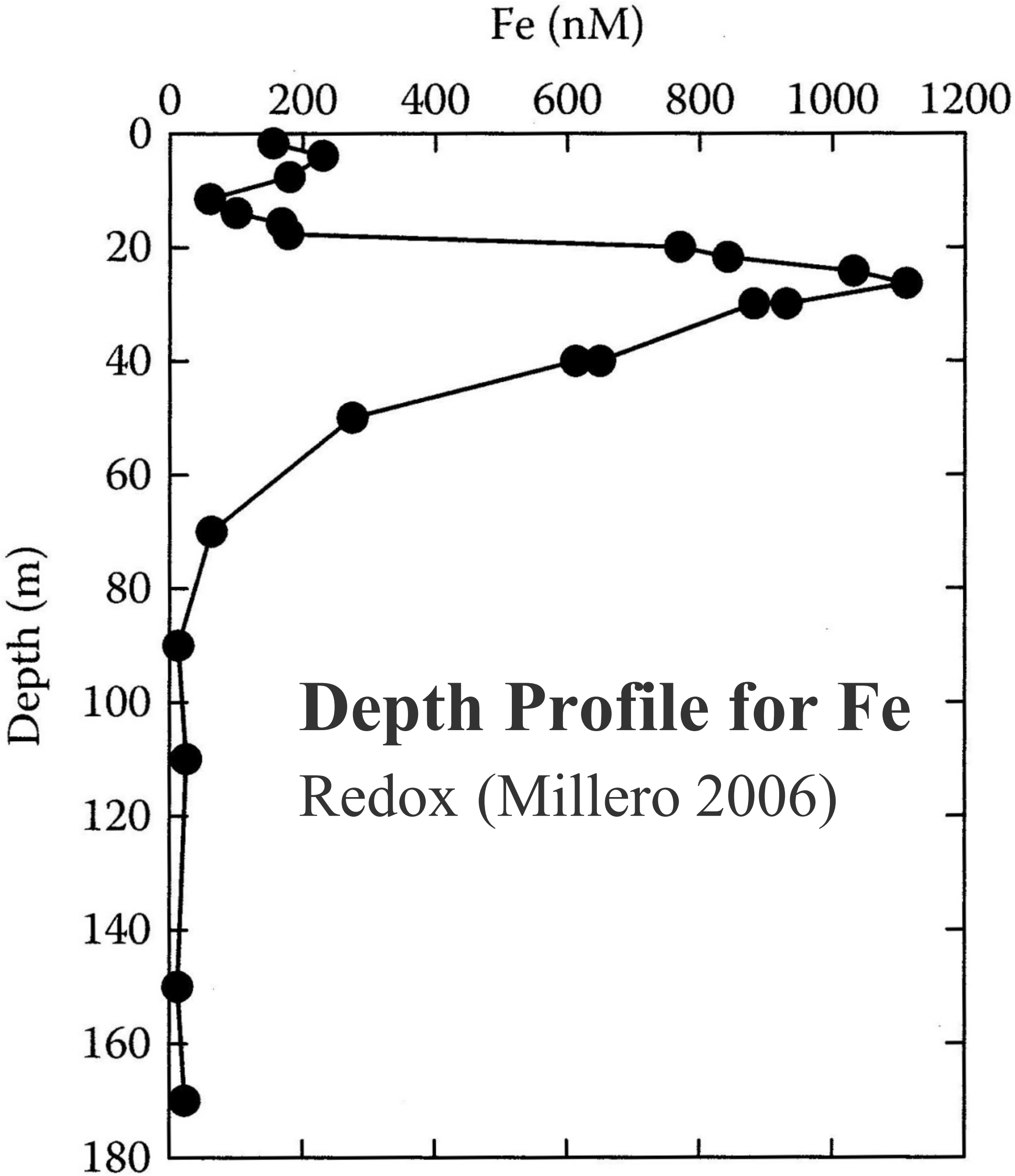




Depth Profile for Mn

Surface enriched

(Millero 2006)

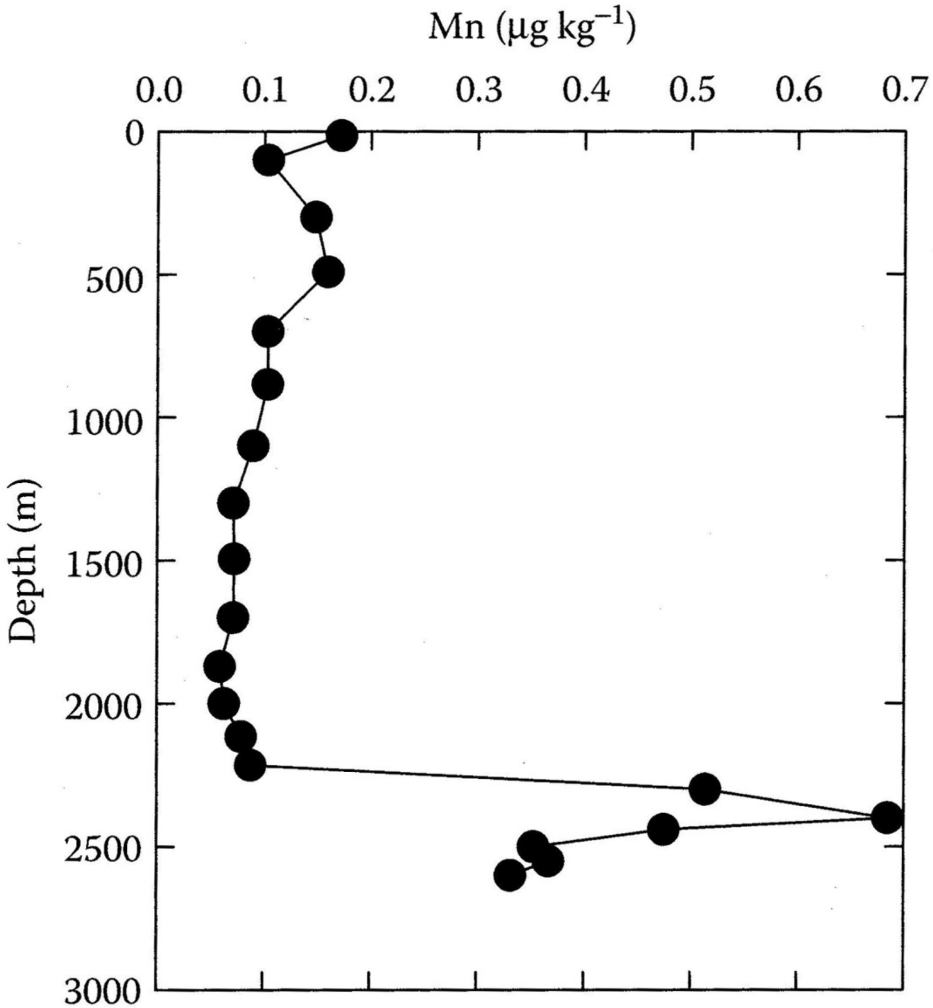


Depth Profile for Fe

Redox (Millero 2006)

Depth Profile for Mn

Anomolous (Millero 2006)



Vertical Profiles of Elements in the Pacific Ocean

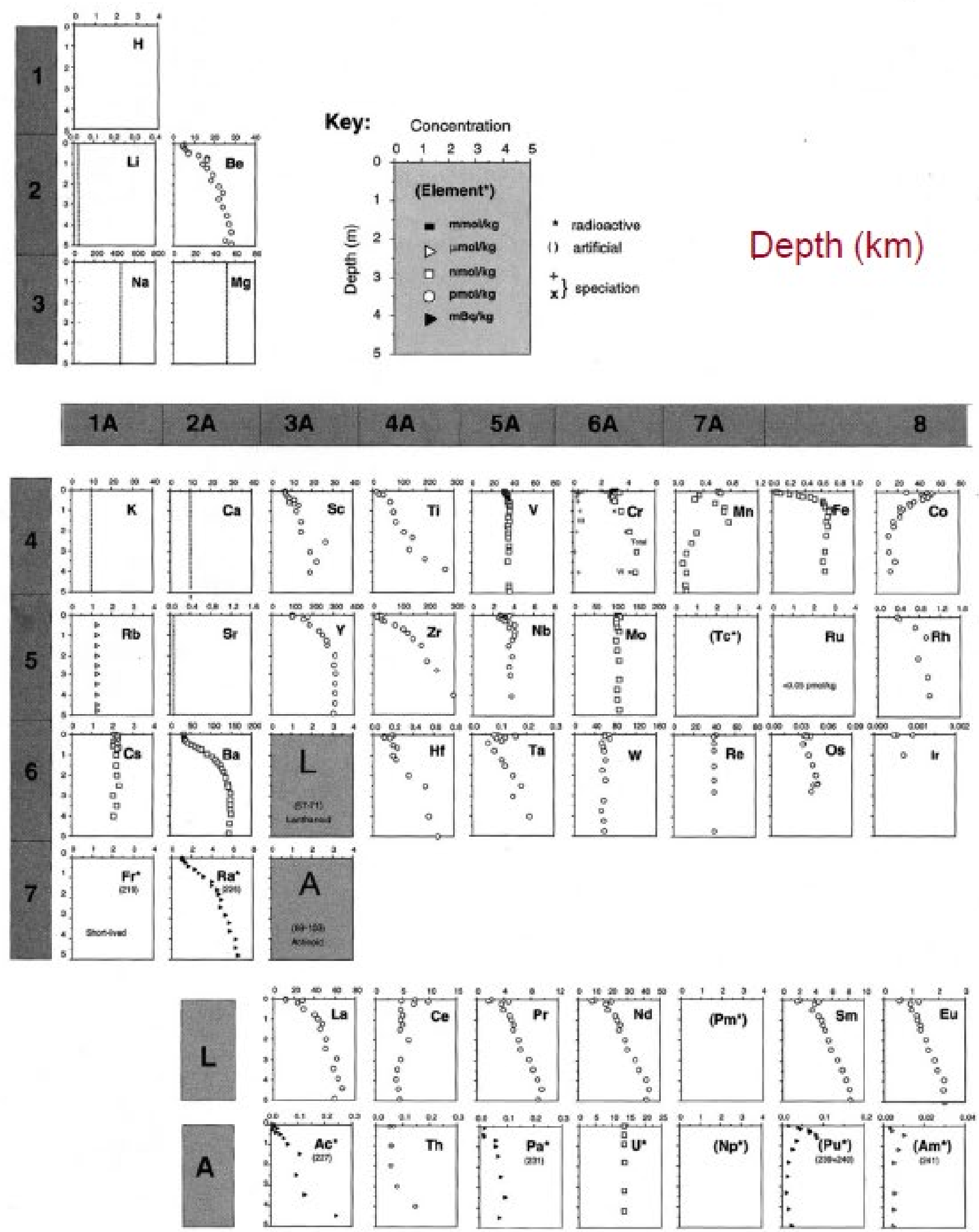
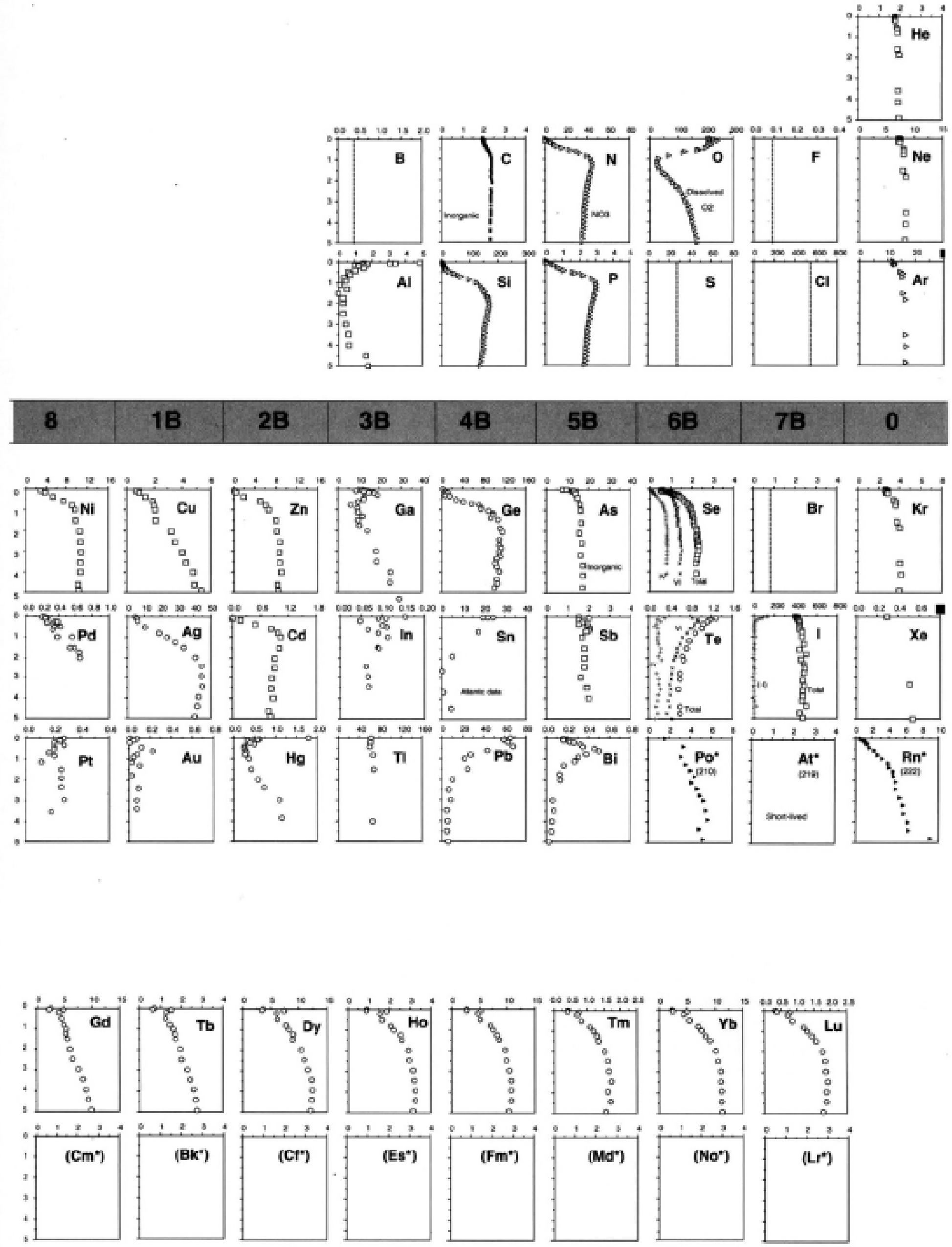


FIGURE 1.2.1: Vertical profiles of elements from the Pacific Ocean arranged as in the periodic table of elements [*Nozaki*, 1997]. The biounlimited elements have nearly uniform concentrations. Most other elements have lower concentrations at the surface than at depth due to biological removal. Biolimiting elements are nearly depleted to 0 mmol m^{-3} at the surface, whereas biointermediate elements show only partial depletion. Oxygen and the noble gases on the right side of the figure are influenced in part by their higher solubility in colder

Sarmiento & Gruber 2006



waters deep in the ocean (see chapter 3) and, in the case of oxygen, by biological production as part of photosynthesis and consumption by respiration. A few elements such as Pb have higher concentrations at the surface due to delivery by dust transport, and lower concentrations at depth due to rapid scavenging from the water column to the sediments.

Sarmiento & Gruber 2006

Table 1. Estimated mean oceanic concentrations of the elements and the references on which the periodic chart (Figure 1) is based.

Atomic Number	Element	Species	Type of Distribution	Oceanic mean Concentration (ng/kg)	Reference
1	Hydrogen	H_2O			
2	Helium	Dissolved gas	c	7.6	Clarke et al. (1970)
3	Lithium	Li^+	c	180×10^3	Stoffyn-Egli and Mackenzie (1984)
4	Beryllium		s+n	0.21	Measures and Edmond (1982)
5	Boron	Borate	c	4.5×10^6	Noakes and Hood (1961)
6	Carbon	Inorganic ΣCO_2	n	27.0×10^6	Broecker and Takahashi (1978)
7	Nitrogen	Dissolved N_2	c	8.3×10^6	Craig et al. (1967)
		NO_3^-	n	0.42×10^6	GEOSECS Operation Group (1987)
8	Oxygen	Dissolved O_2	inverse n	2.8×10^6	GEOSECS Operation Group (1987)
9	Fluorine	F^-	c	1.3×10^6	Bewers et al. (1973)
10	Neon	Dissolved gas	c	160	Craig et al. (1967)
11	Sodium	Na^+	c	10.78×10^9	Millero and Leung (1976)
12	Magnesium	Mg^{2+}	c	1.28×10^9	Carpenter and Manella (1973)
13	Aluminum		s	30	Orians and Bruland (1985)
14	Silicon	Reactive SiO_2	n	2.8×10^6	GEOSECS Operation Group (1987)
15	Phosphorus	Reactive PO_4	n	62×10^3	GEOSECS Operation Group (1987)
16	Sulfur	SO_4^{2-}	c	898×10^6	Morris and Riley (1966)
17	Chlorine	Cl^-	c	19.35×10^9	Wilson (1975)
18	Argon	Dissolved gas	c	0.62×10^6	Craig et al. (1967)
19	Potassium	K^+	c	399×10^6	Culkin and Cox (1966)

Distribution patterns are classified into the following four categories:

conservative, nutrient-type, scavenged, and redox-controlled

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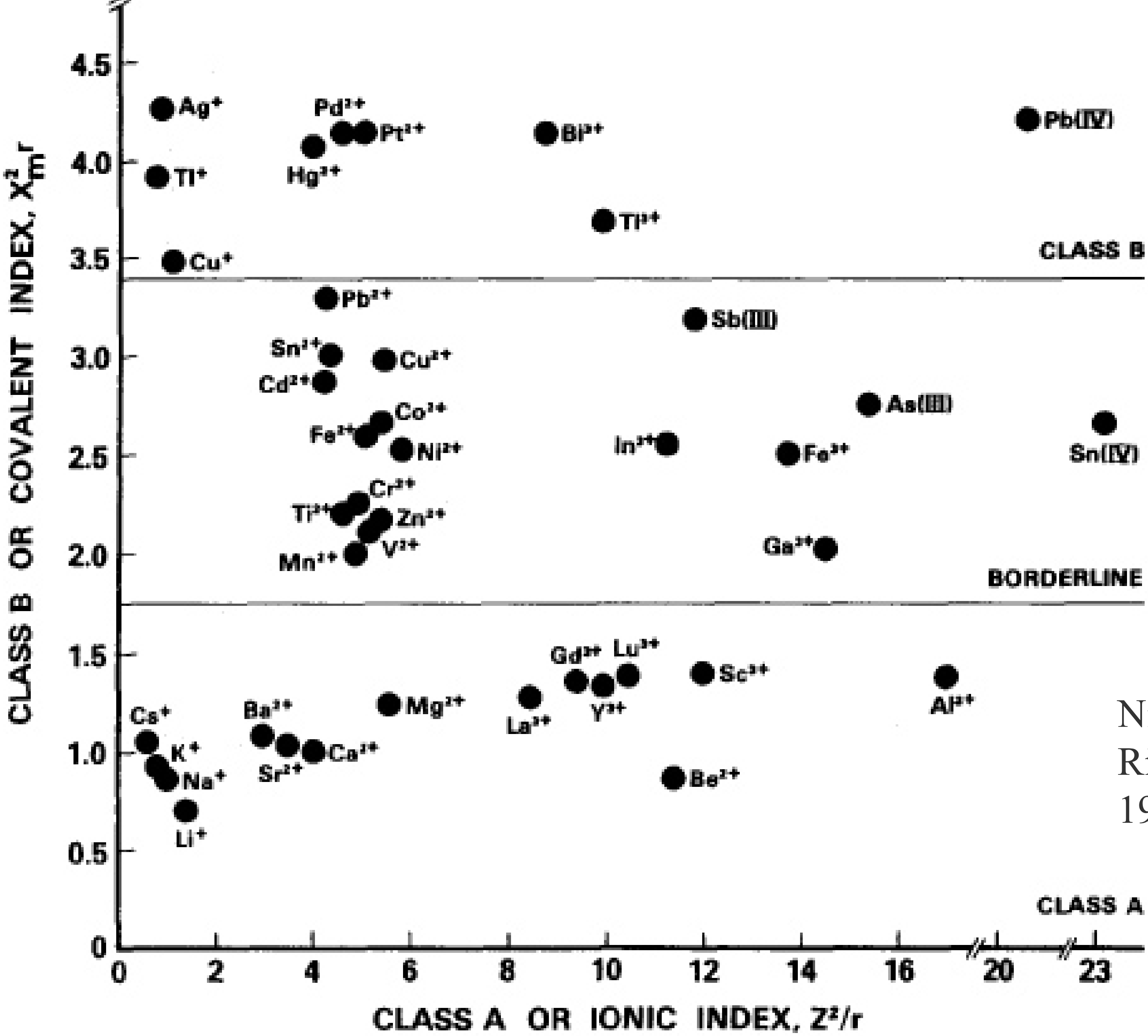
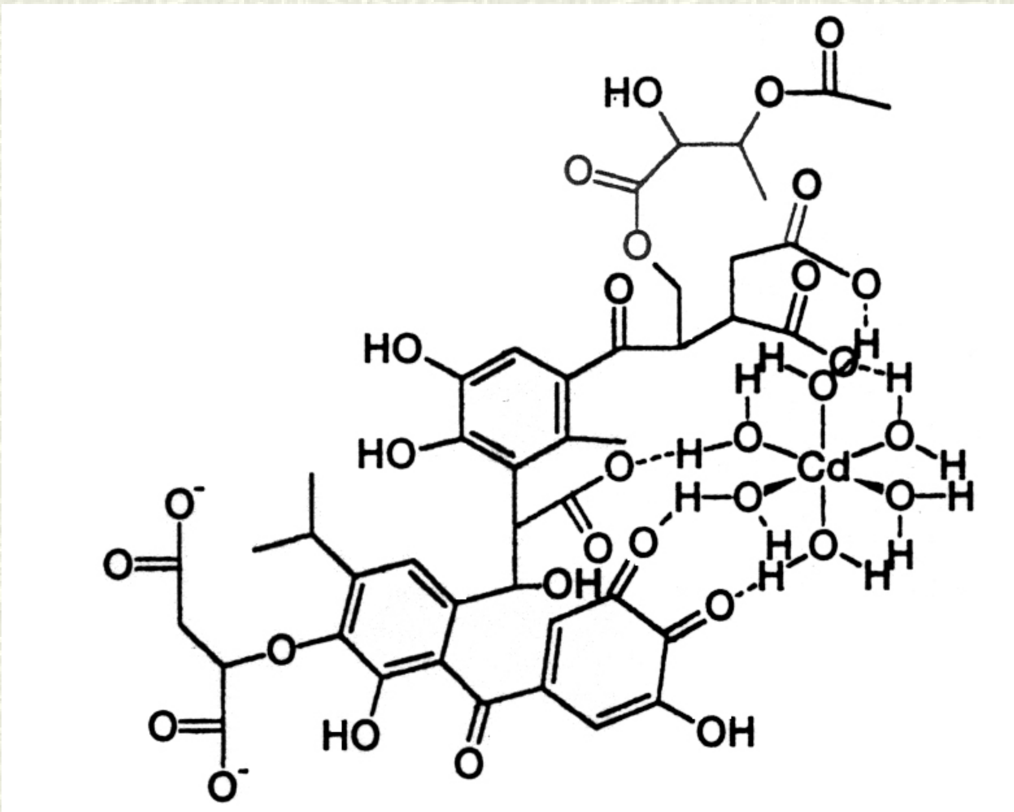


Nieboer & Richardson 1980

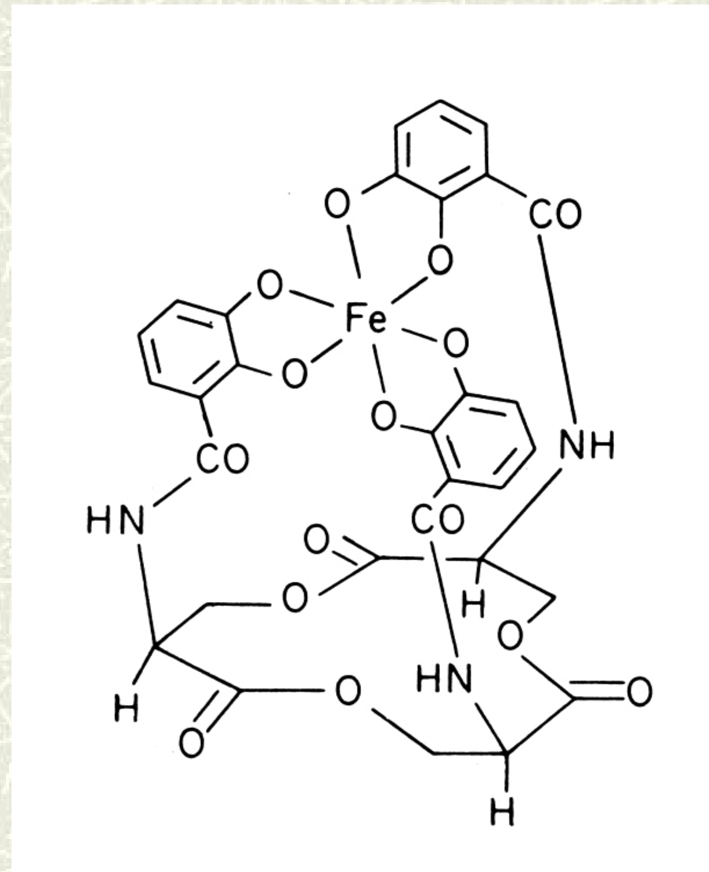
Importance of Humic Materials (Natural Organics)

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)

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**

Humic material will aggregate & may"salt out" with cations

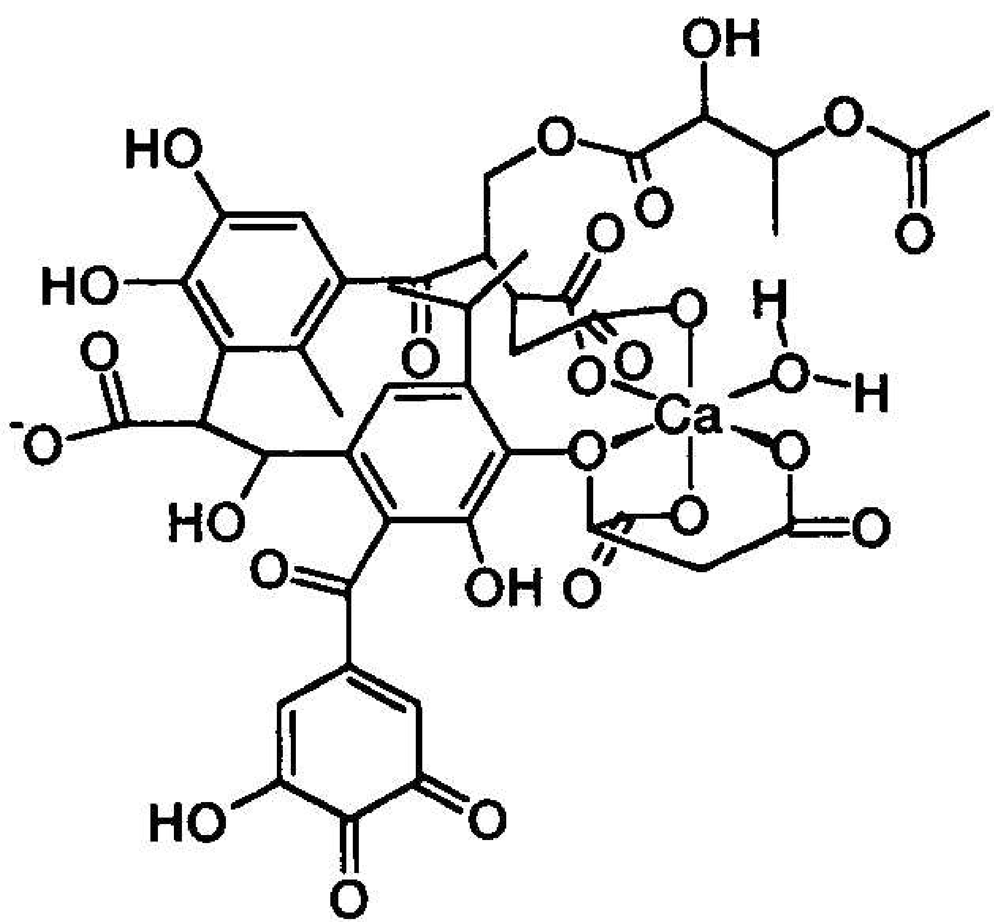
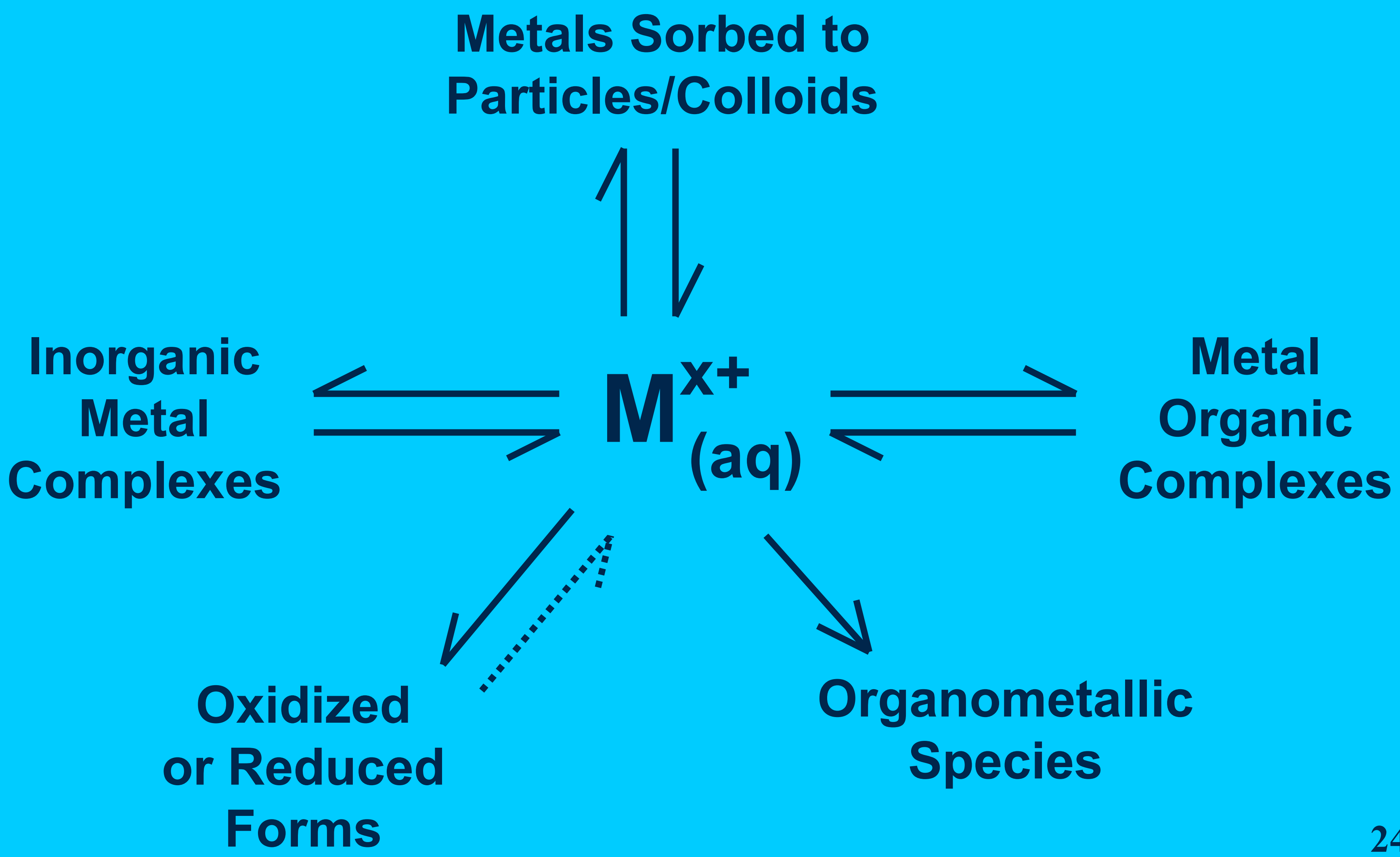


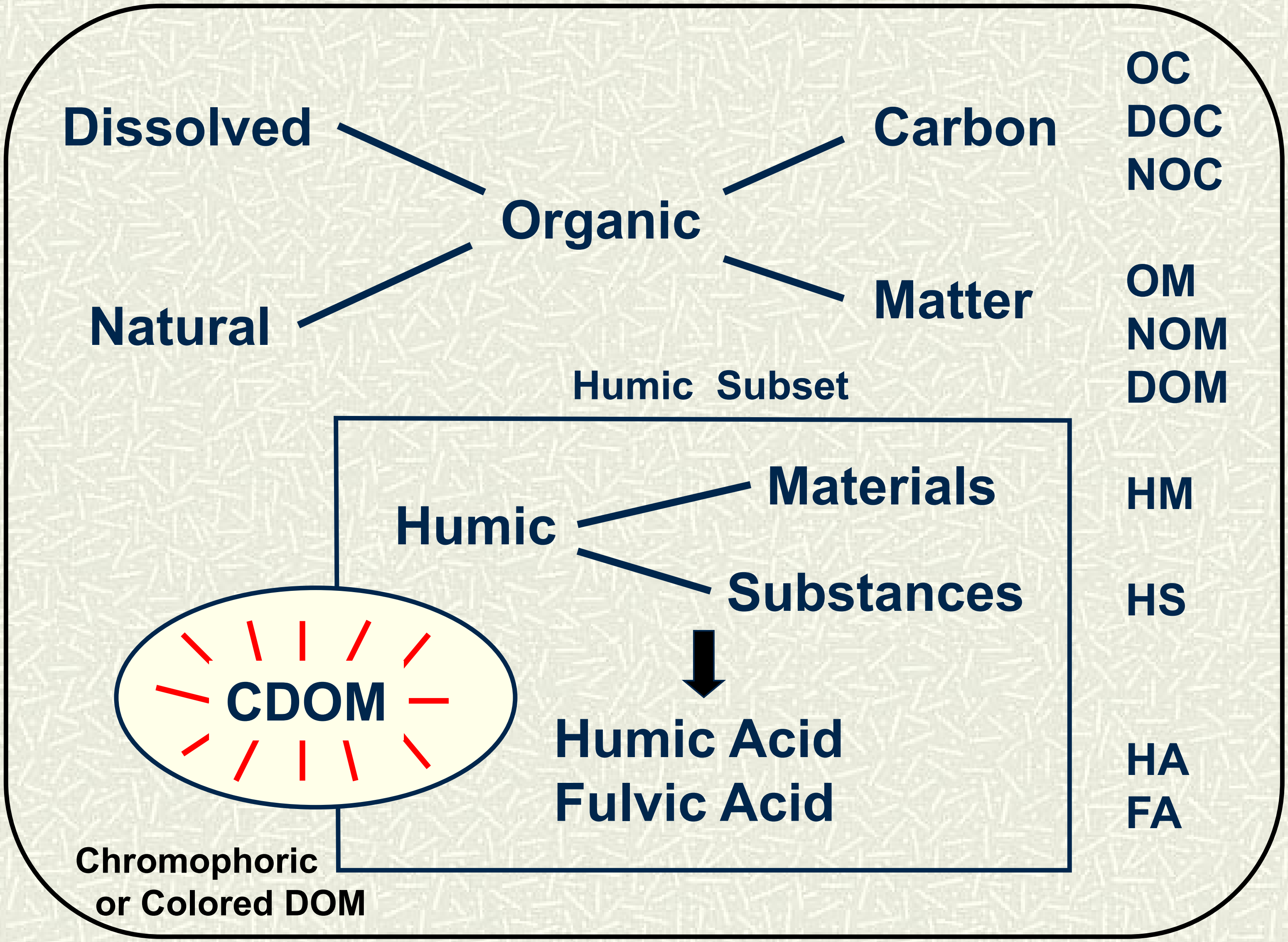
FIGURE 6. Structural model of a calcium inner-sphere complex

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