



Behavior of Nanoparticles in Natural Waters

Jyväskylän yliopisto

How do Nanoparticles Get into Surface Waters?

Effluents


 Wastewater

 Industrial



Intentional Use

 Sunscreens

 Contaminant
cleanup



Nanoparticle Behavior in Aqueous Environments

Freshwater versus Saltwater

Effect of ionic strength

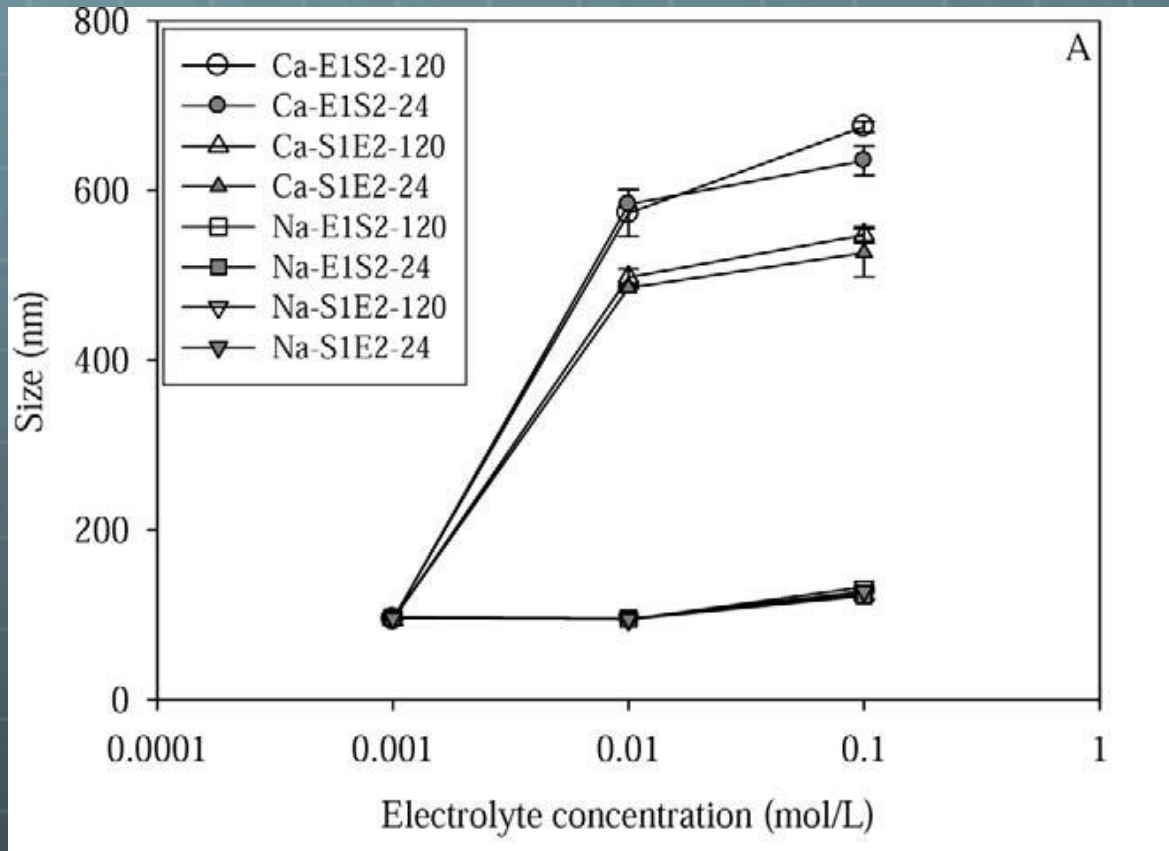
Suspended Particles

Adsorption

Natural Organic Matter

Surface Modification

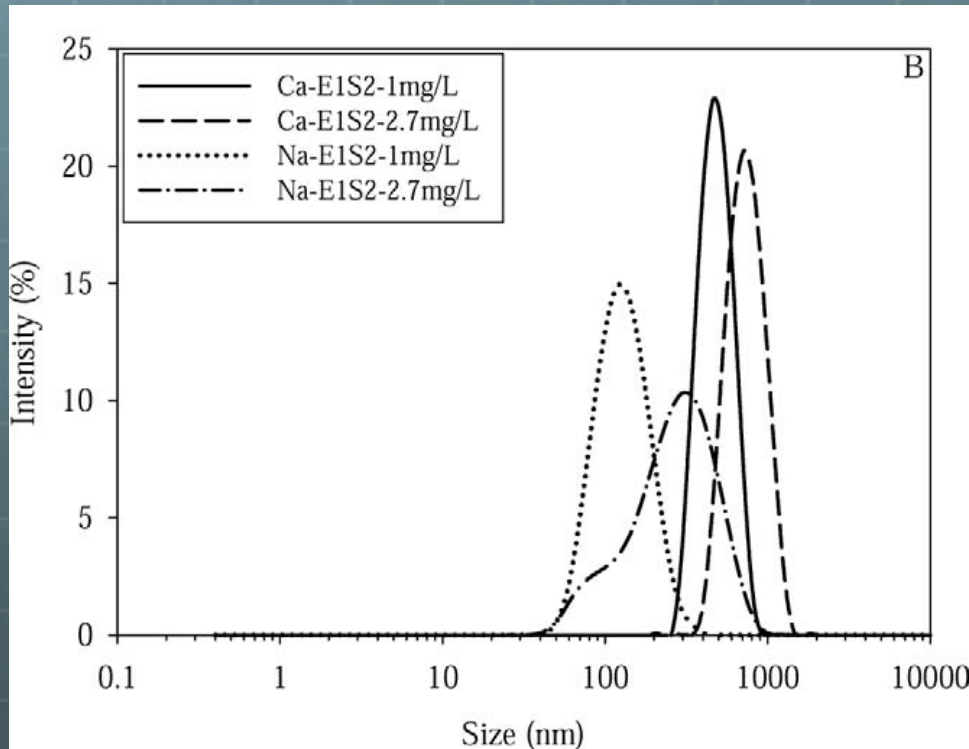
Ionic Strength



Divalent calcium leads larger fullerene particles than monovalent sodium

Fig. 1. Effect of electrolyte concentration, suspension addition rate(24 or 120 ml/min), and dilution sequence (E1S2 or S1E2) on the mean fullerene nanoparticle (nC60) diameter at a final concentration of 1.0 mg/L. E1S2 refers to the sequence of adding the electrolyte solution to the nC60 stock suspension; S1E2 refers to the sequence of adding the nC60 stock suspension to the electrolyte solution. Error bars represent the standard deviation of duplicate or triplicate measurements.

Ionic Strength



Higher cation concentrations also lead to larger agglomerates

Fig. 2. Effect of electrolyte concentration, suspension addition rate (24 or 120 ml/min), and dilution sequence (E1S2 or S1E2) on **intensity-weighted size distribution of nC60 particles** as a function of final concentration at a mixing rate of 120 ml/min and ionic strength of 30.05 mM. E1S2 refers to the sequence of adding the electrolyte solution to the nC60 stock suspension; S1E2 refers to the sequence of adding the nC60 stock suspension to the electrolyte solution. Error bars represent the standard deviation of duplicate or triplicate measurements.

Wang et al 2008

Ionic Strength

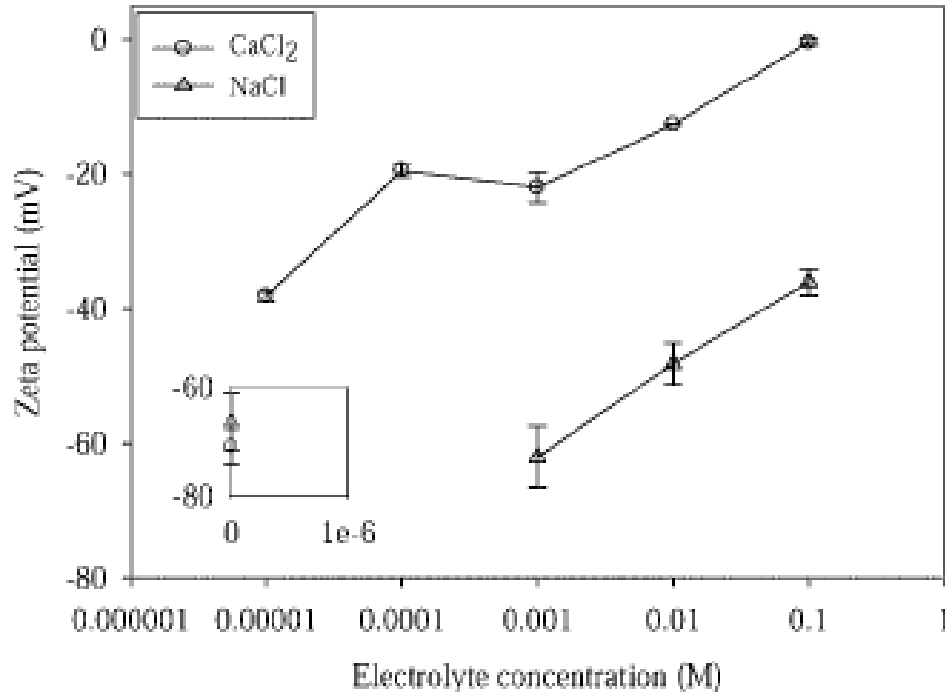


Fig. 3. Zeta potential of fullerene nanoparticles (nC_{60}) as a function of electrolyte concentration in 1-mg/L suspensions containing either CaCl_2 or NaCl . The inset shows the zeta potential of nC_{60} in deionized water. Error bars represent the standard deviation of triplicate measurements.

electrokinetic potential in colloidal systems

Zeta Potential [mV] **Stability behavior of the colloid**

from 0 to ± 5 ,

Rapid coagulation or flocculation

from ± 10 to ± 30

Incipient instability

from ± 30 to ± 40

Moderate stability

from ± 40 to ± 60
more than ± 61

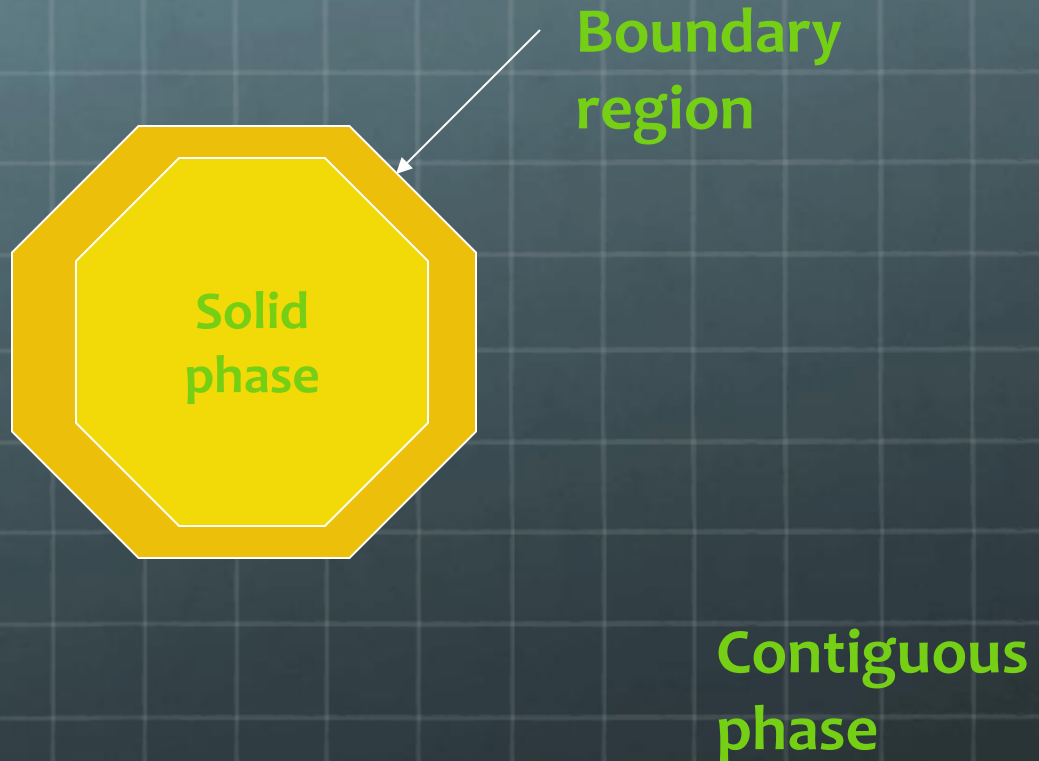
Good stability
Excellent stability

Adsorption

a substance is said to be adsorbed if the concentration in a boundary region is higher than in the contiguous phase

Multiple step
Process:

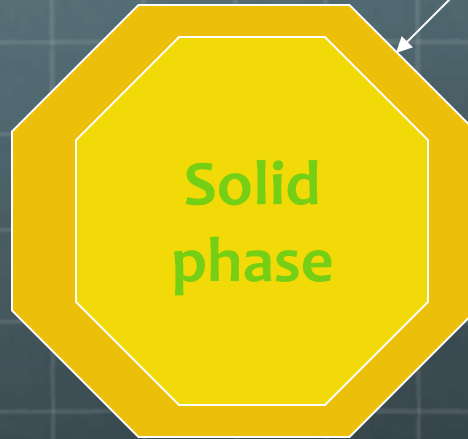
1. Migration into boundary layer
2. Interaction with solid surface
3. adsorption



Adsorption

Sand(quartz)

Boundary
layer



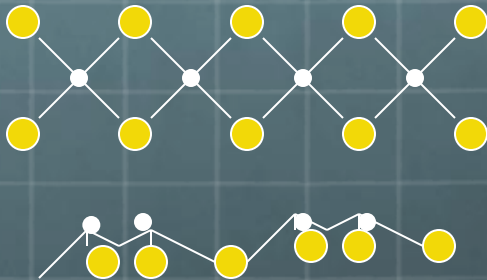
Solid
phase

solution

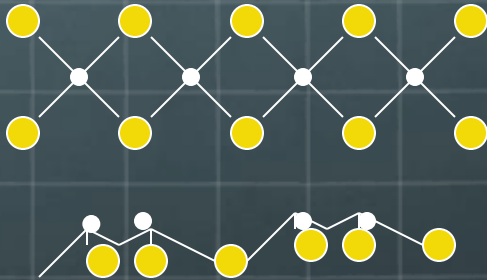
Adsorption

Clay

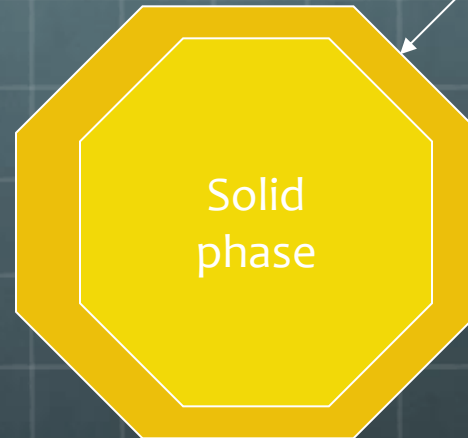
6 (OH)
4 Al
4 O + 2(OH)
4 Si
6 O



6 (OH)
4 Al
4 O + 2(OH)
4 Si
6 O



Kaolinite $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$



Boundary layer

solution

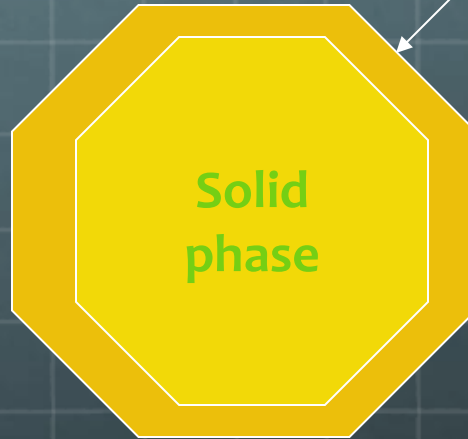
Planar geometry
Large surface area
Very high residual negative charge
-> Cation exchange capacity

Adsorption

Silt: organic fraction,
unrecognizable relics
of plant tissue and newly
synthesized microbial
Residues

MW 3000-300,000
High degree of unsaturation
Acidity due to O-containing
Groups

Contains amino acids
Sensitive to oxidation
Carbon skeleton resistant to microbial attack
No carbohydrates



Boundary
layer

solution

Adsorption

Van der Waal's forces

Hydrophobic interaction

Hydrogen bonding

Ligand exchange

Dipole-dipole interactions

Chemisorption

Adsorption Isotherms

Langmuir

energy of adsorption is constant and independent of surface coverage

adsorption is on localized sites and there is no interaction between adsorbed molecules

maximum adsorption possible is monolayer

$$X = \frac{X_m bC}{1 + bC}$$

X = # moles of solute adsorbed per g of adsorbent

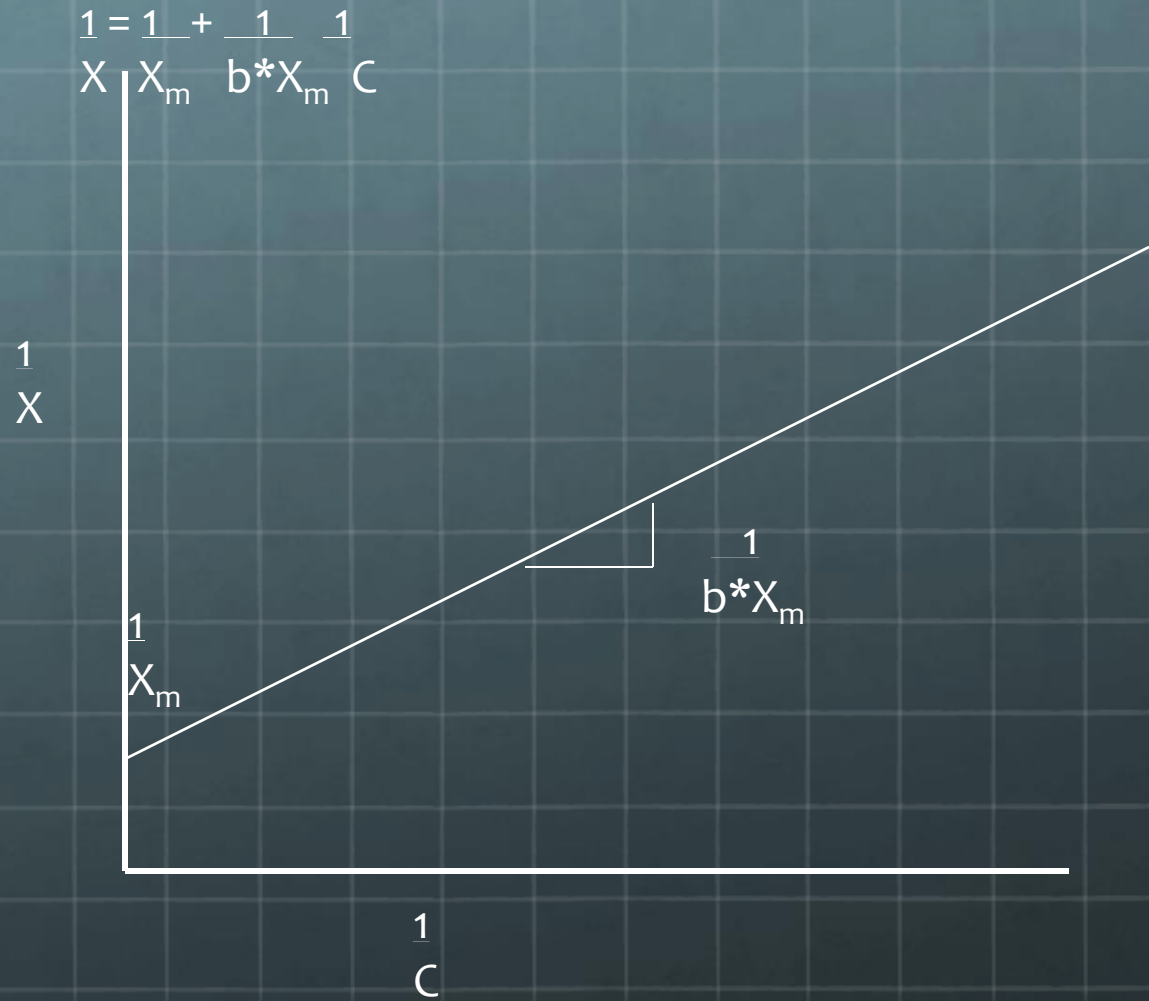
C = equilibrium concentration of solute in solution

X_m = # moles of solute adsorbed per g of adsorbent in forming a complete monolayer

B = Constant related to energy of adsorption

Adsorption Isotherms

Langmuir



Adsorption Isotherms

Freundlich Isotherm

Purely empirical

$$x/m = KC^{1/n}$$

x = amount of chemical adsorbed per mg adsorbent (m)

C = equilibrium concentration of material in solution

K = equilibrium constant indicative of the strength of adsorption

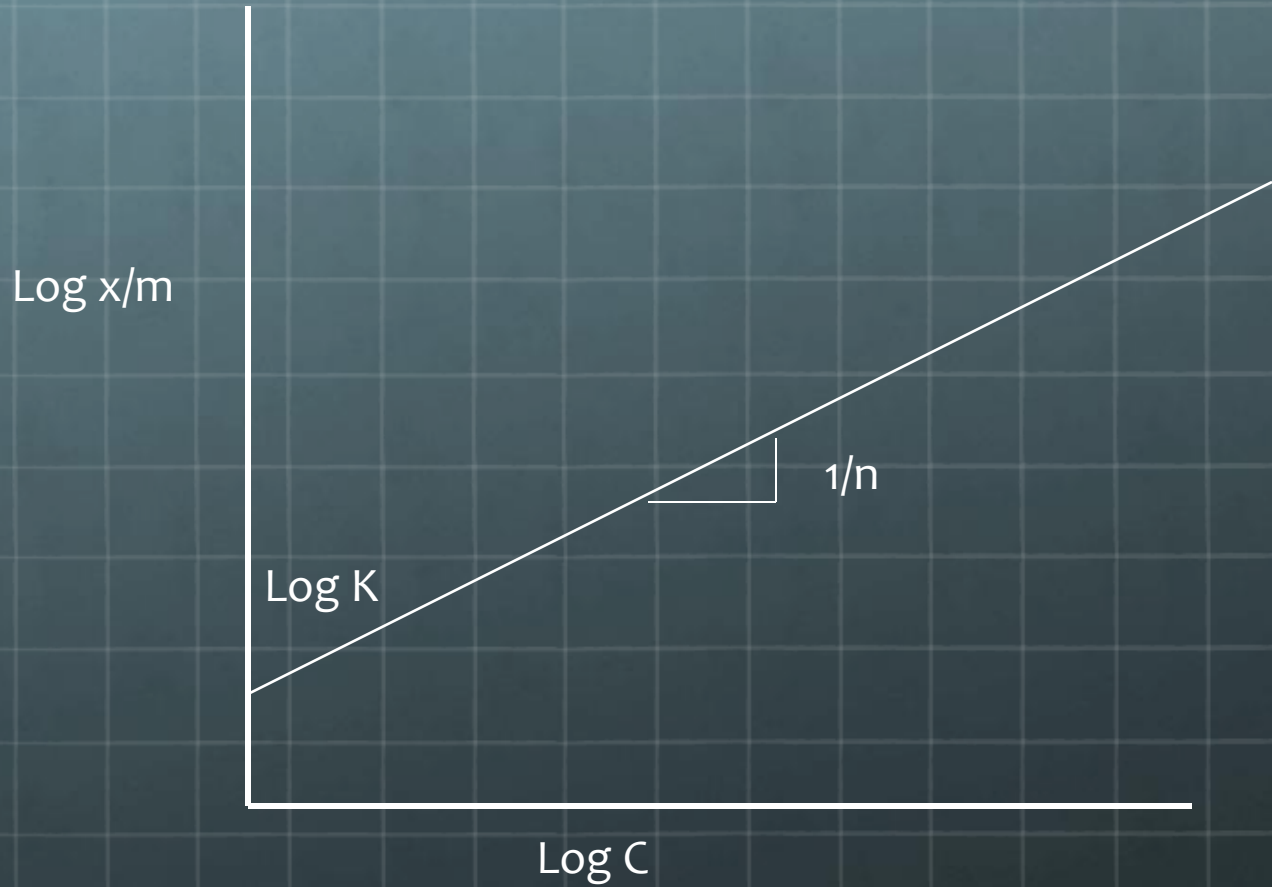
($K = x/m$ when $C = 1$)

$1/n$ = Degree of nonlinearity

Adsorption Isotherms

Freunlich

$$\log x/m = \log K + 1/n \log C$$



Dissolved Organic Matter







Organic material from plants and animals broken down into such a small size that it is “dissolved” into water

While some components look like carbohydrates, fats or proteins most have no recognizable structure.



- Important component the export of organic matter from surface waters.
- Terrestrial DOM is colored; aquatic is not

Dissolved Organic Matter

-  Affects acid-base chemistry
-  Influences cycling of metals such as Cu, Hg, Al
-  Influences bioavailability of some forms of N & P
-  Alters sedimentation rates
-  Source of energy
-  Attenuates UV radiation

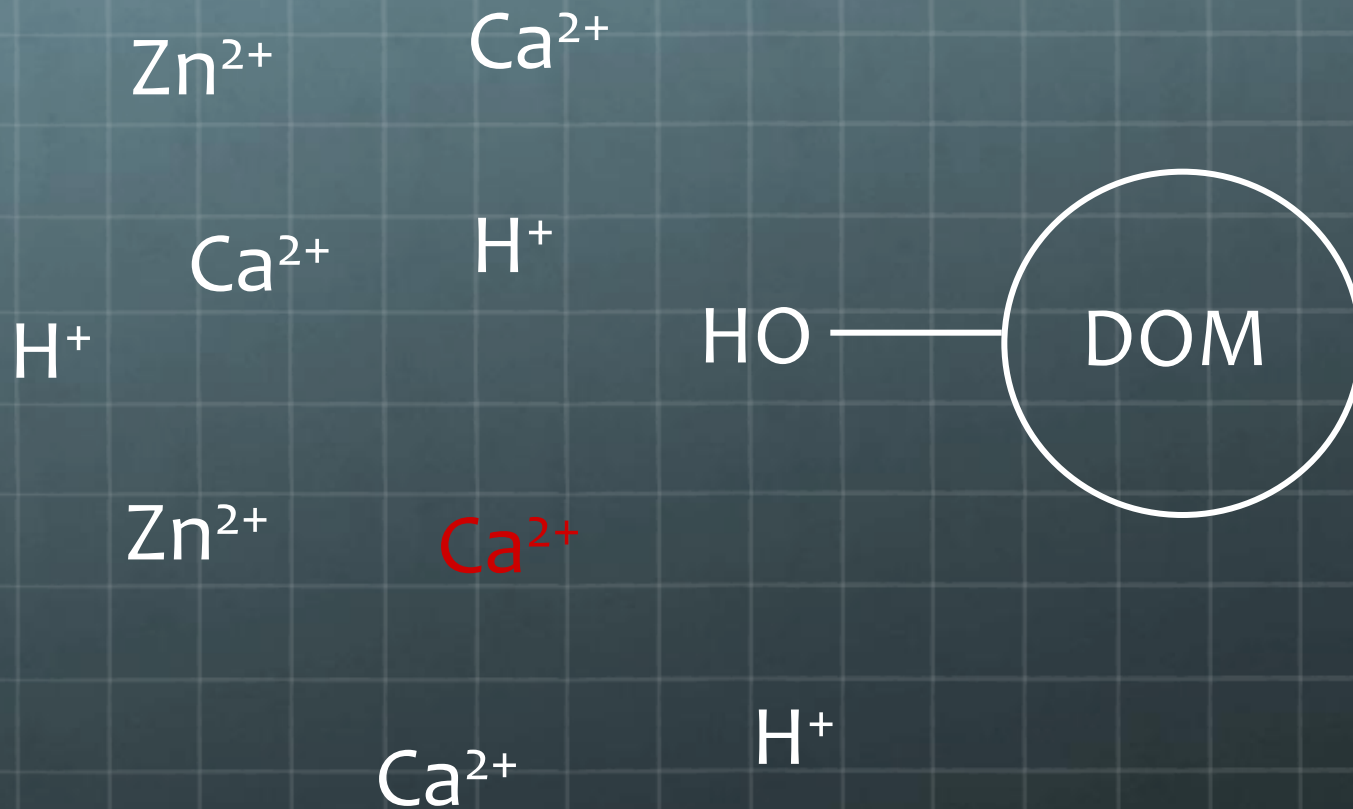
Nature of metal-DOM interactions

- Binding capacity of DOM for metal cations is high: 200-600 $\mu\text{mol/g}$
 - Cation exchange and complexation
- Surface area of DOM is much greater than clays or metal oxides
- Carboxylate groups are very important
- Low MW DOM fractions have higher concentrations of phenolic and carboxylic groups

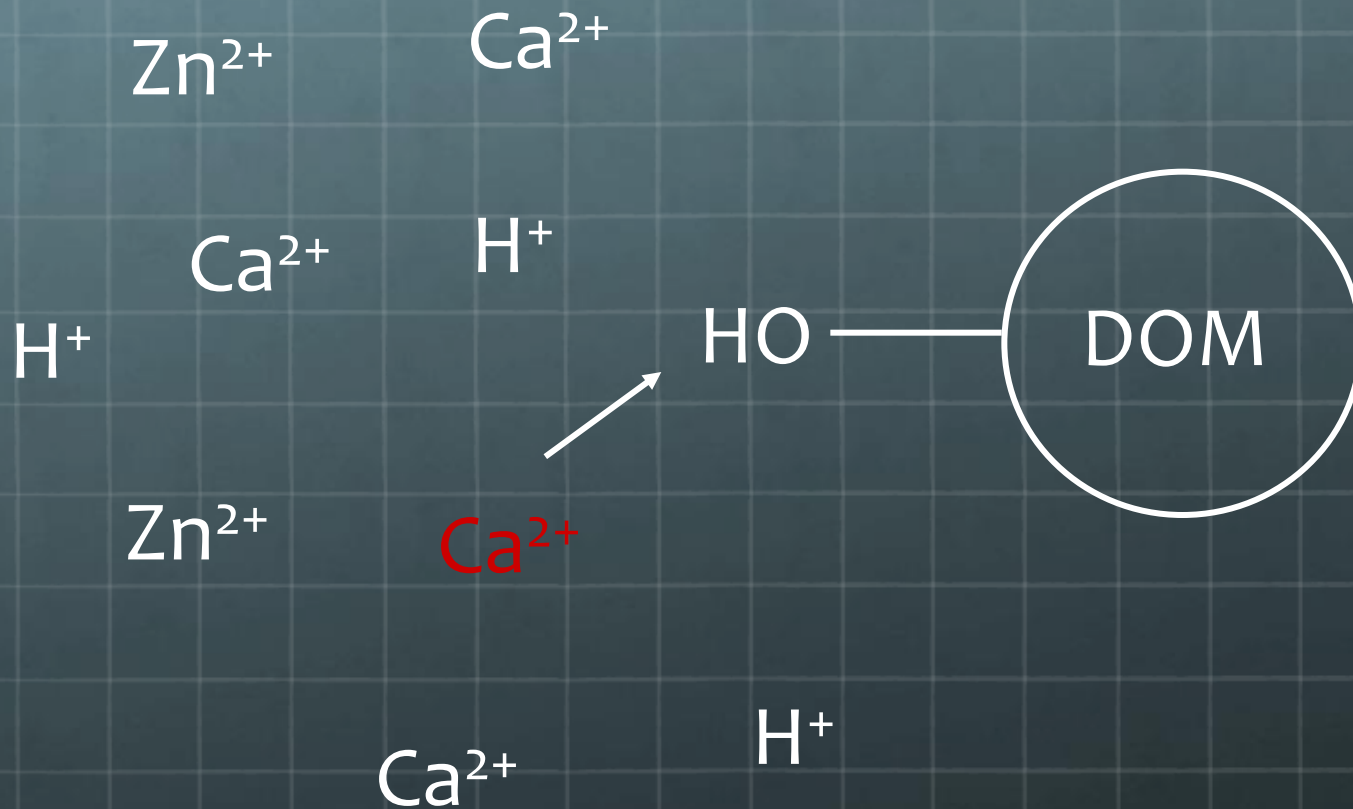
Metals associated with DOM

- Fe(III), Hg(II), Cu(II), Pb(II), Al(III), Ni(II), Ag(I), Zn(II), Cd(II)
- Also binding of conservative metals such as Ca(II) and Mg(II)
- ~90% of soluble iron is bound to DOM
- ~50 to 90% of mercury in estuaries and coastal seawaters is bound to DOM
- In rivers ~80% of metal-DOM binding sites are associated with Ca(II)

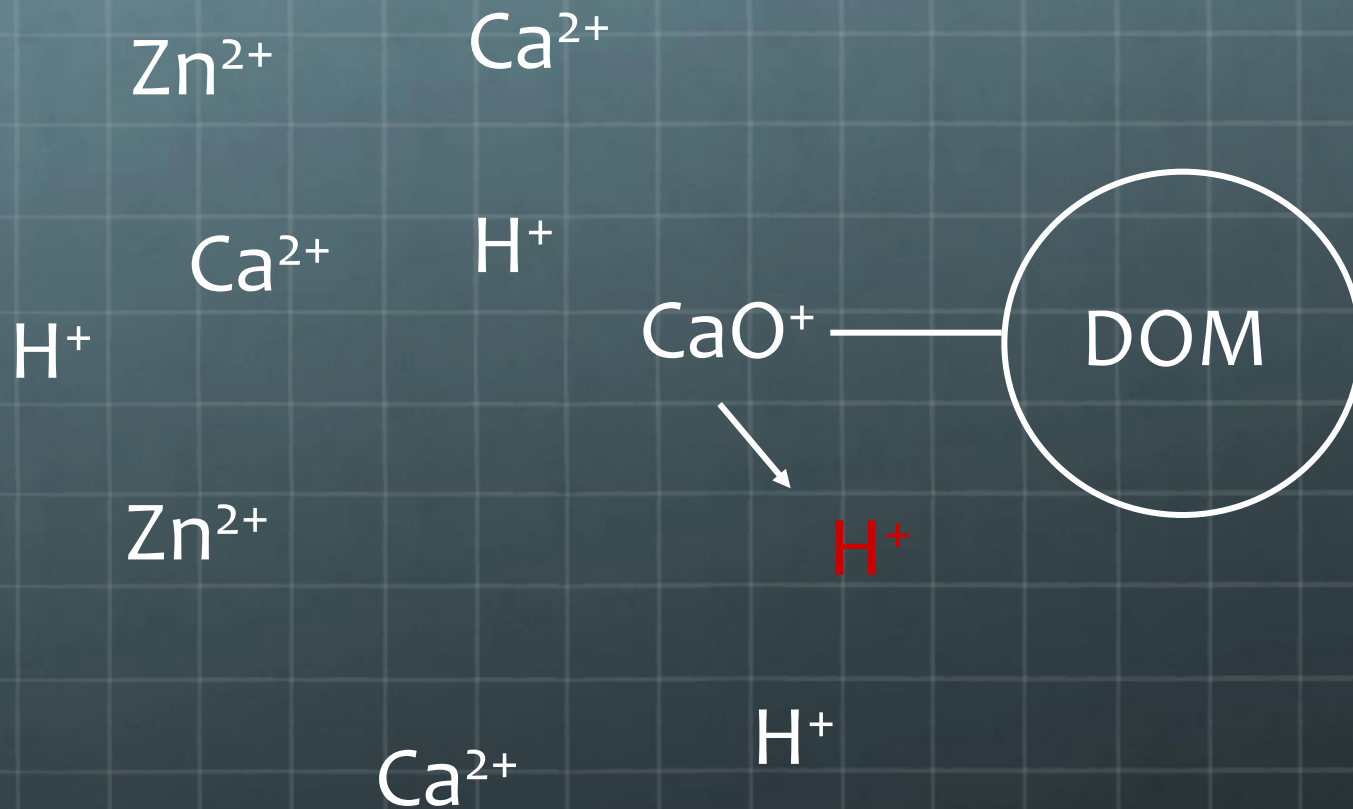
Cation exchange reactions



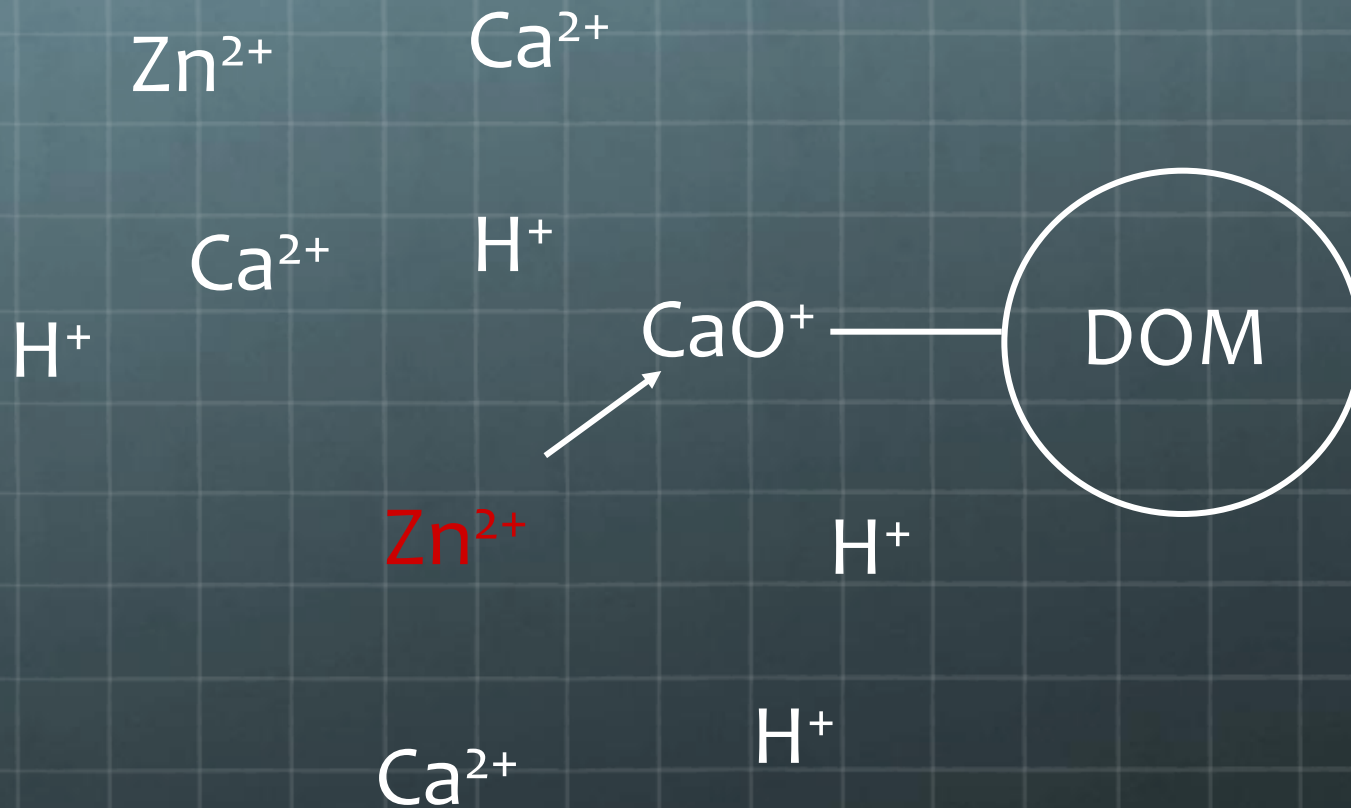
Cation exchange reactions



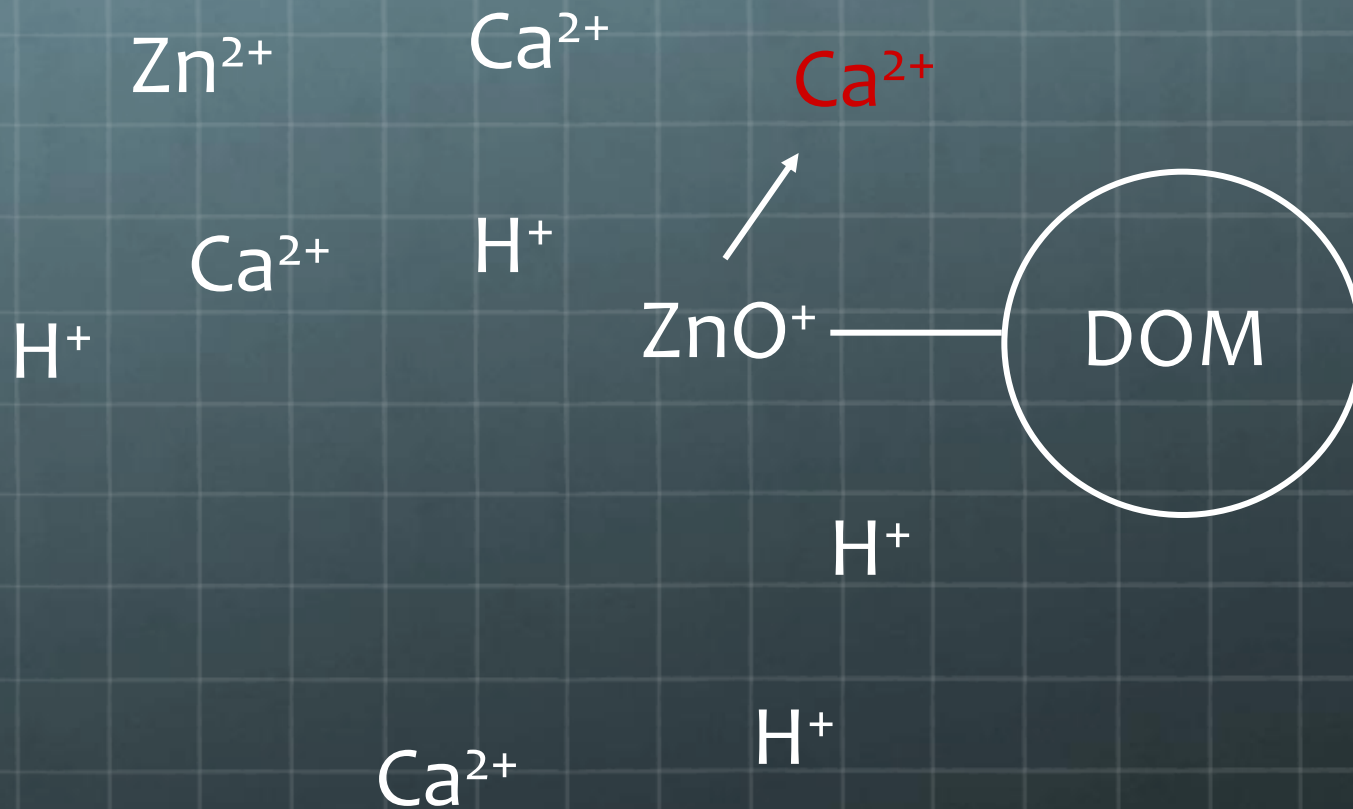
Cation exchange reactions



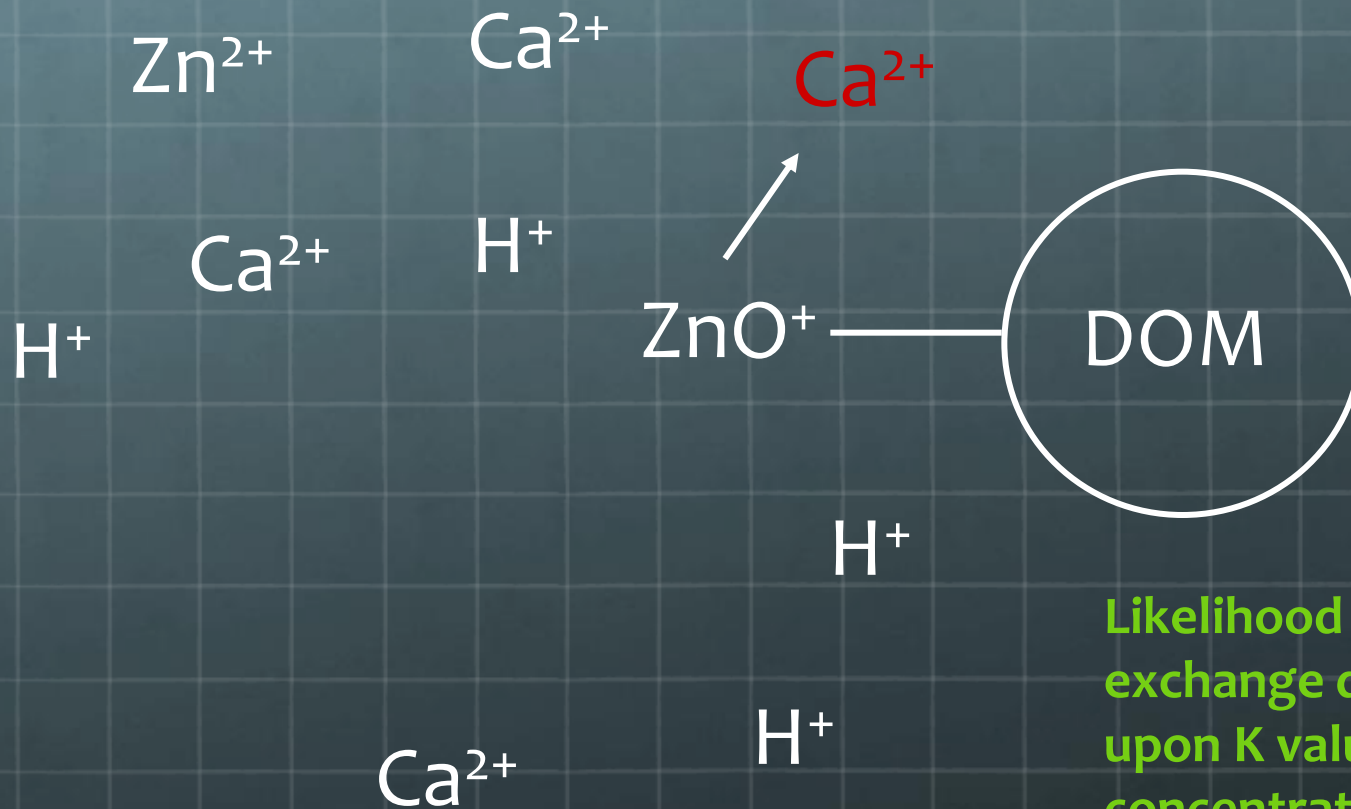
Cation exchange reactions



Cation exchange reactions

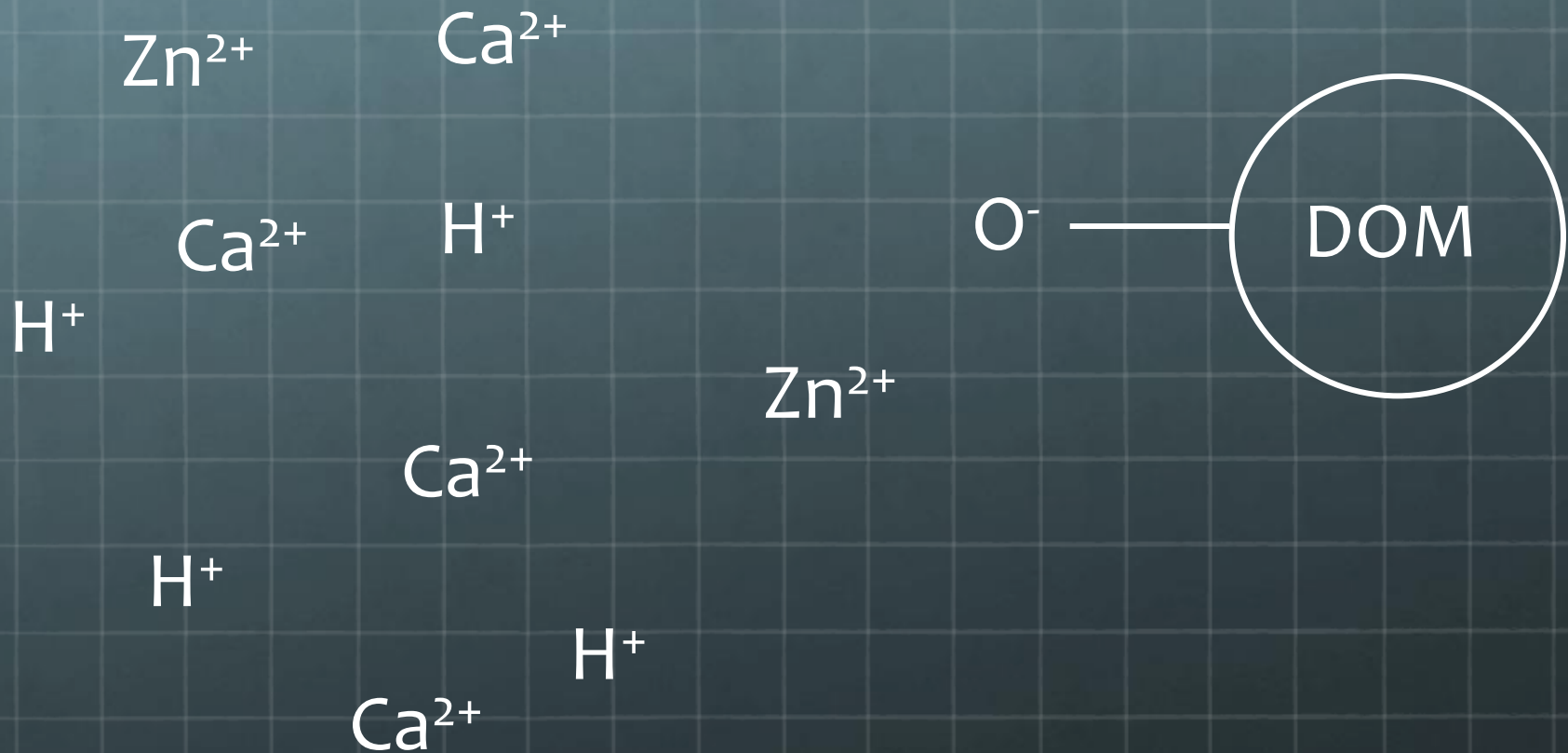


Cation exchange reactions

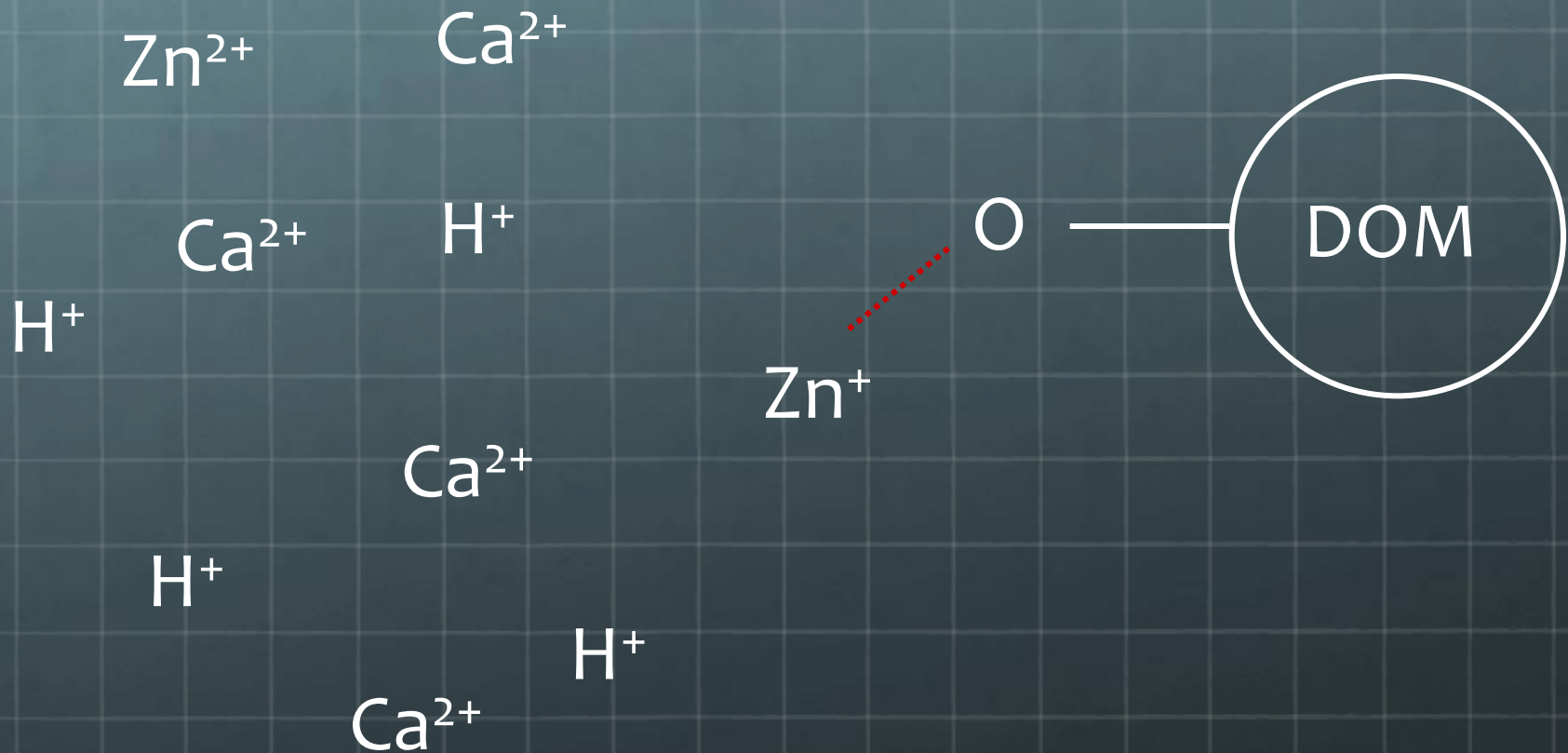


Likelihood of exchange depends upon K values and concentration of species

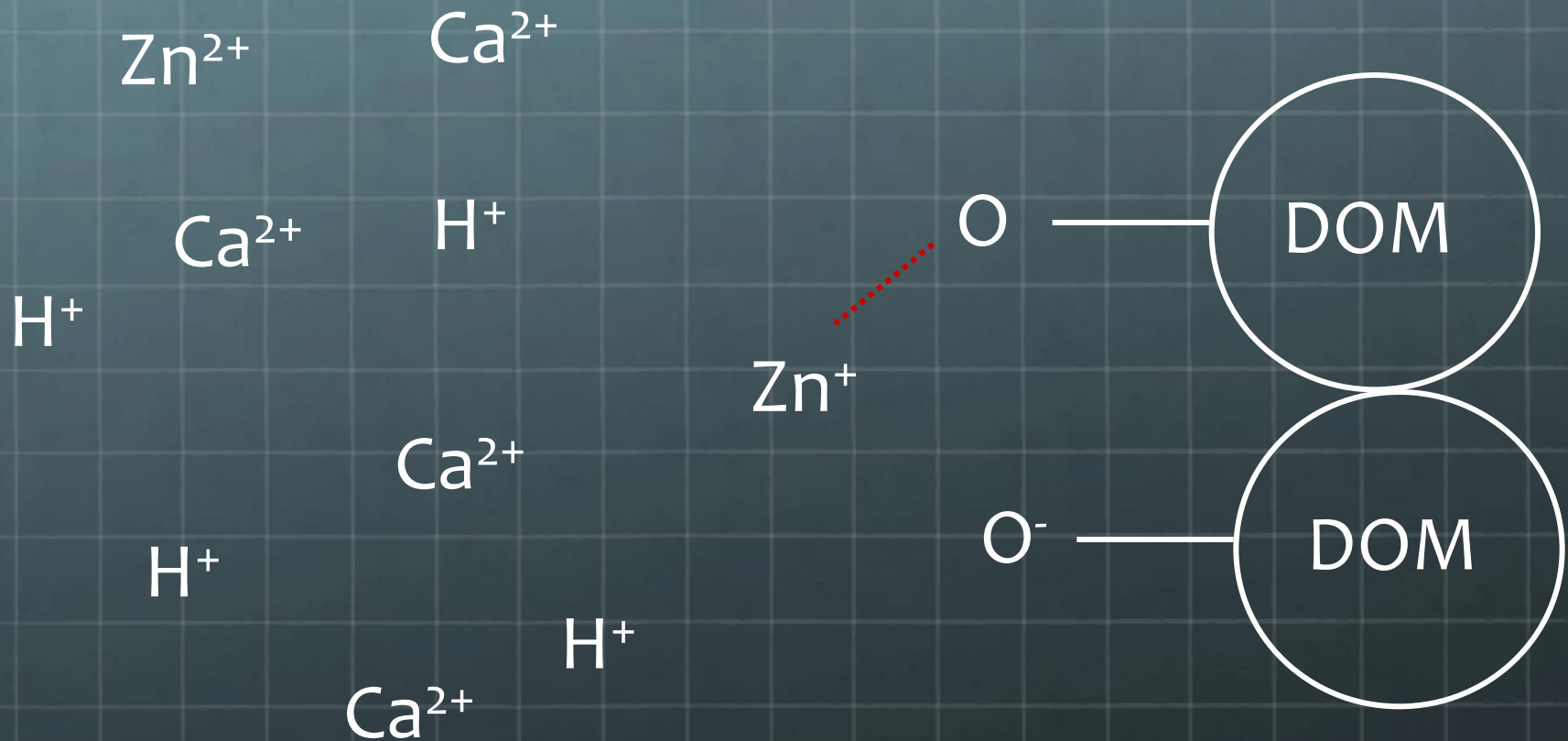
Complexation reactions



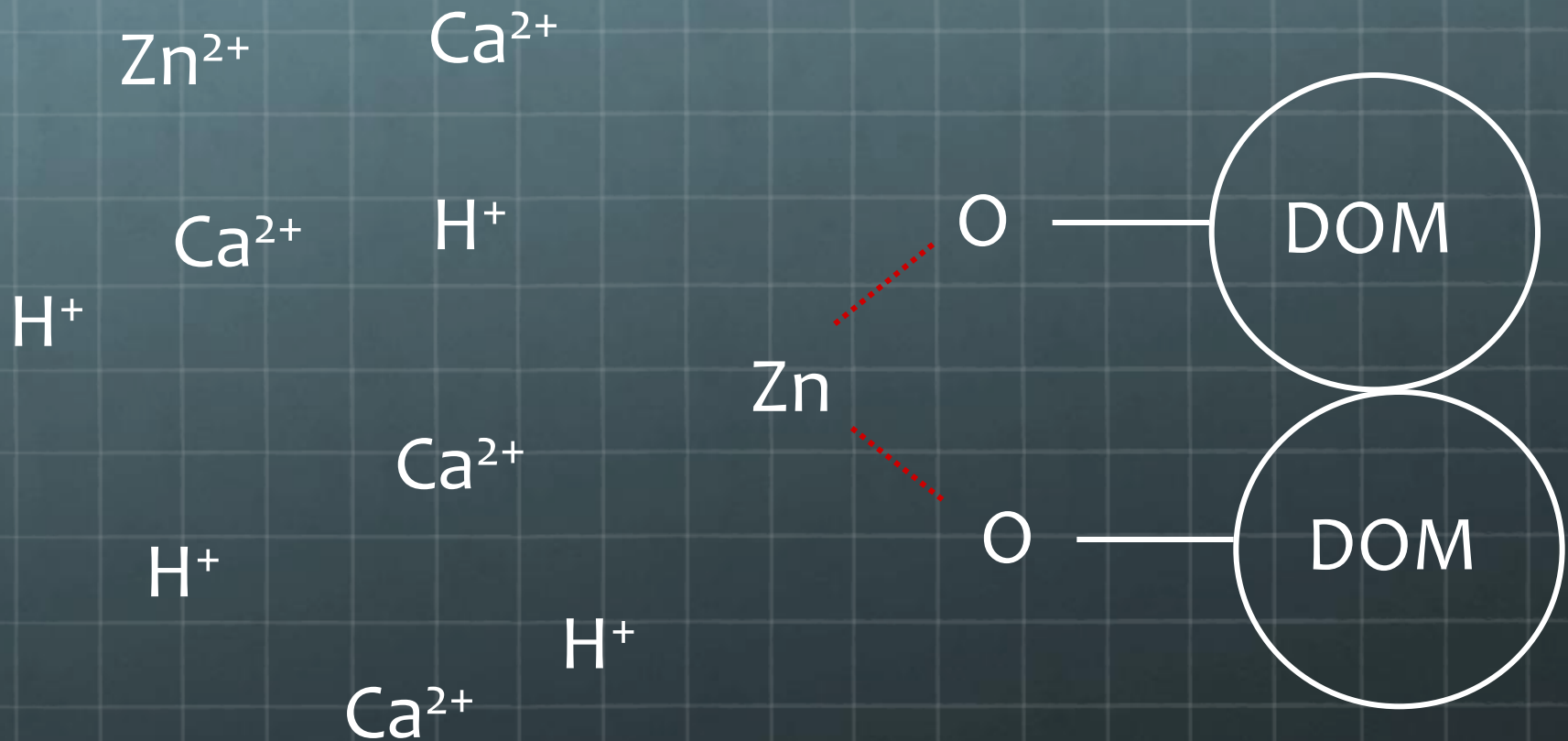
Complexation reactions



Complexation reactions

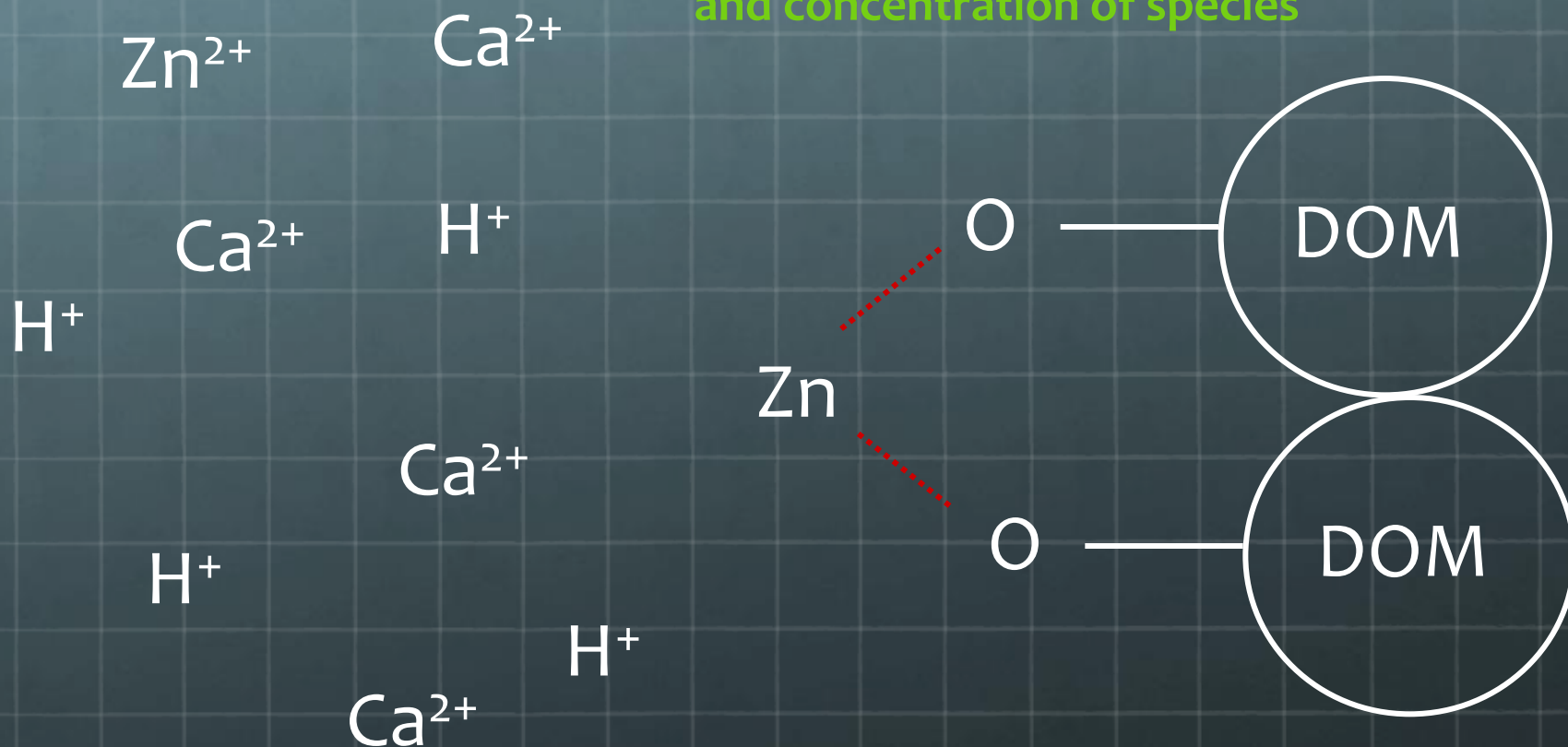


Complexation reactions



Complexation reactions

Also depends upon K values
and concentration of species



How can these types of interactions influence metal toxicity?

- Depends on what form of metal is most toxic
 - If free metal is most toxic, decrease toxicity
 - If metal-DOM complex is most toxic, increase toxicity
 - If metal does not associate with DOM, toxicity may not change in the presence of DOM
- It is generally believed (and observed) that the free metal ion is the most toxic species

Organic-DOM Interactions

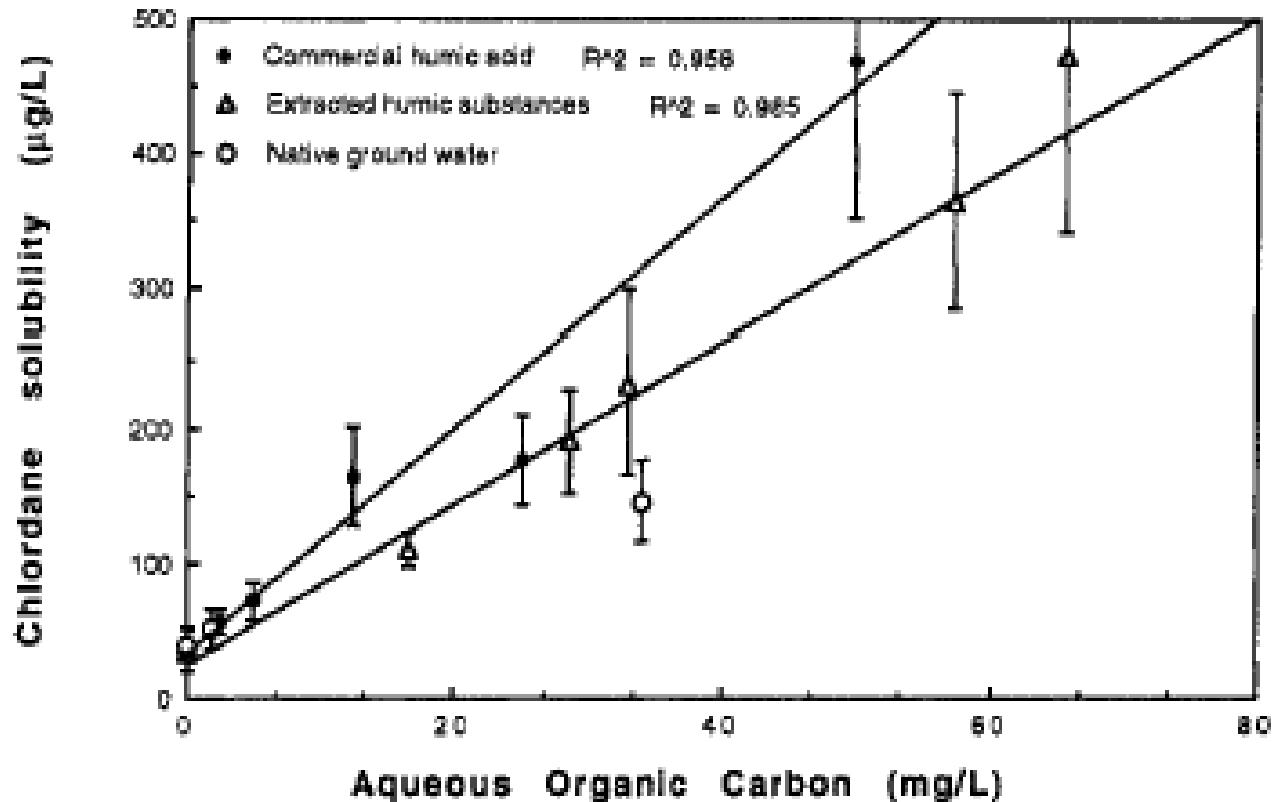
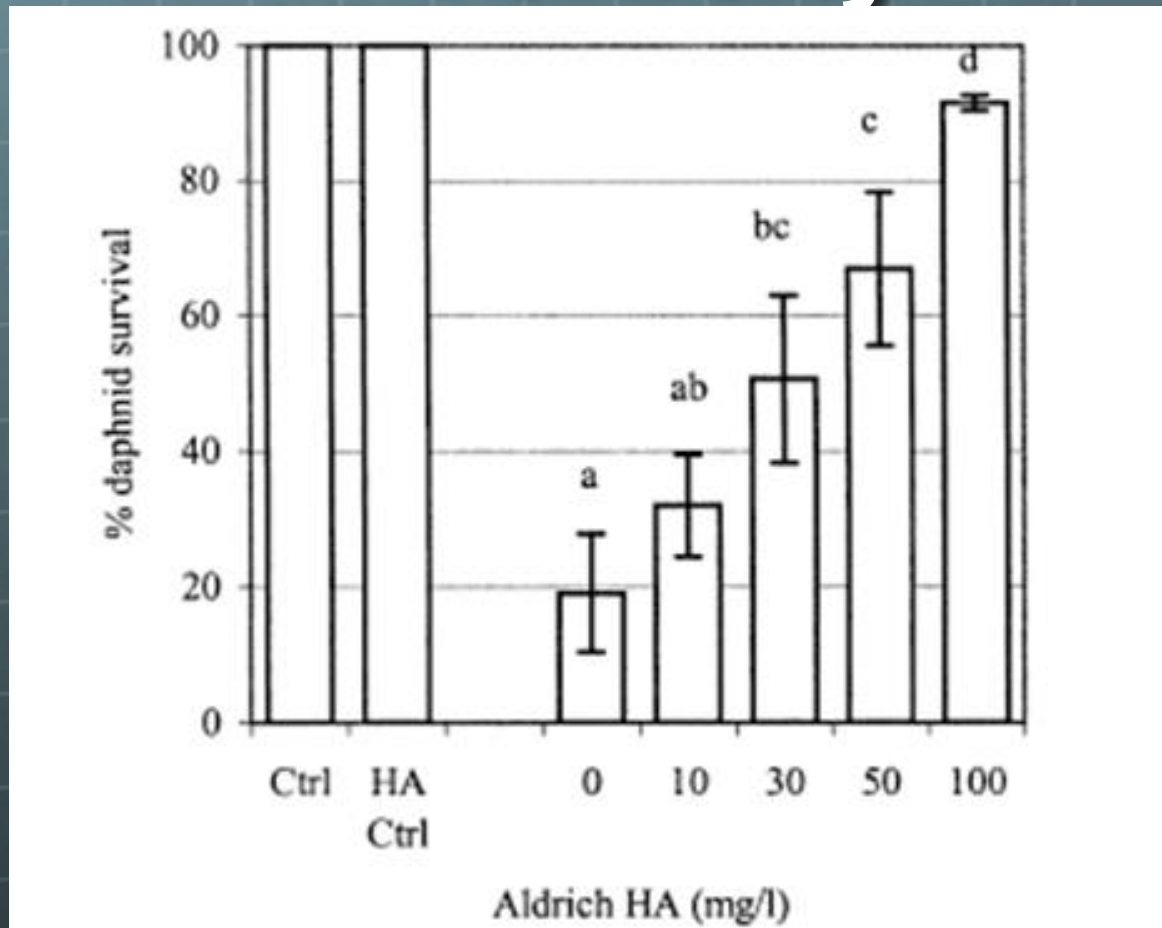


Figure 1. Correlation between chlordane solubility and aqueous organic carbon from different sources (lines are least-squares regressions; $n = 3$, bars represent standard deviations).

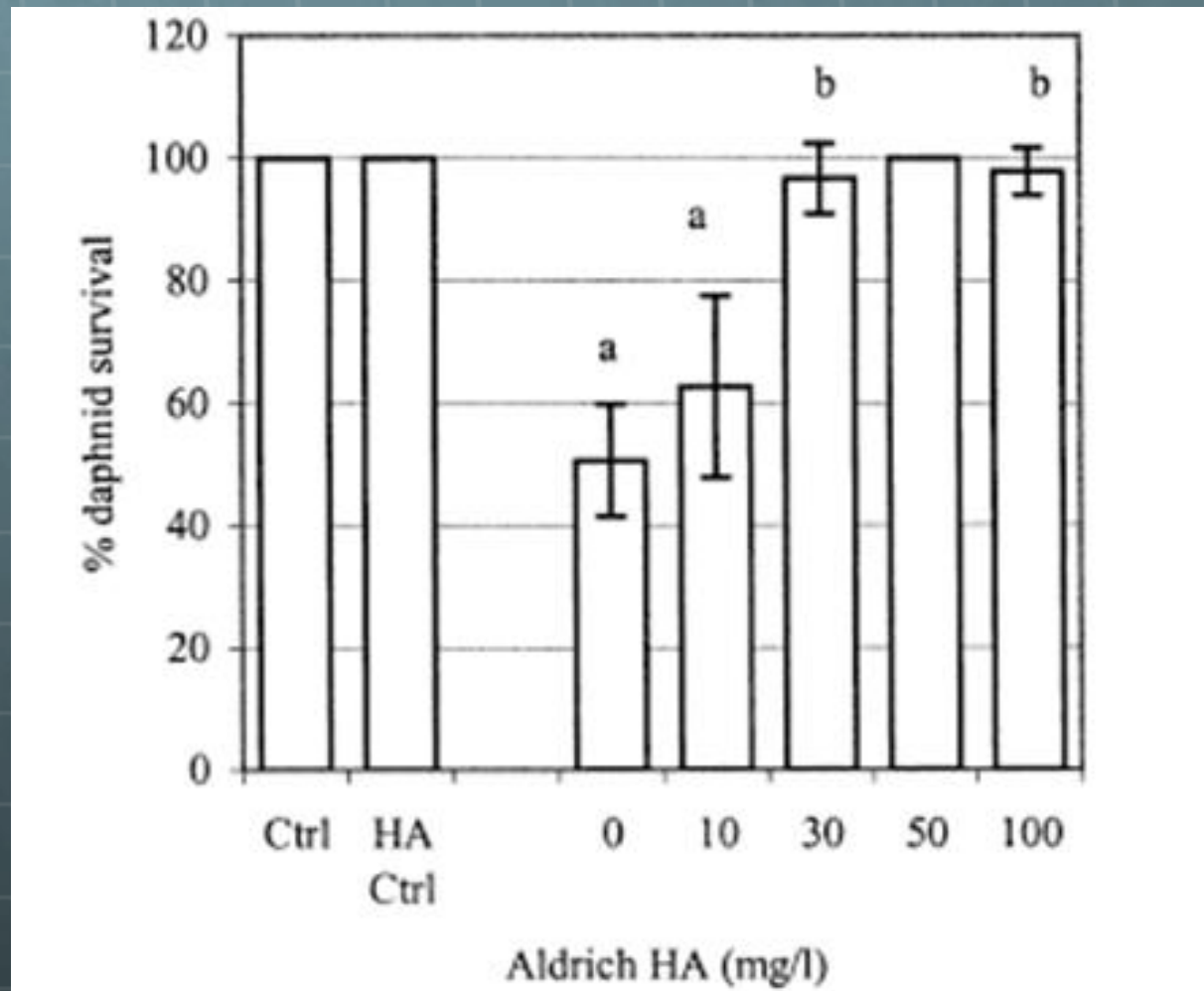
The presence of organic matter increases chlordane solubility, and different types of NOM impact this to different extents

DOM and Chlorpyrifos Toxicity



Increasing concentrations of Aldrich Humic Acid increased the % of *Ceriodaphnia dubia* survival during a 24 h exposure. The chlorpyrifos concentration was 82 ng/L

DOM and DDT Toxicity



Increasing concentrations of Aldrich Humic Acid increased the % of *Americamysis bahia* survival during a 24 h exposure. The DDT concentration was 1.1 µg/L

DOM and NPs

Table 1 – Characterization of the citrate- and acrylate-stabilized gold nanoparticle dispersions

Dispersion	pH ^a	Z potential (mV) ^a	Plasmon resonance band (nm)	Nanoparticle diameter (nm)		
				TEM ^b	Z average size ^c	PDI ^d
CN	5.8±0.1	−43.7±0.7	519	15.8±1.9	18.60±0.53	0.44±0.08
AN	4.9±0.1	−34.0±1.3	530	19.7±3.3	21.64±0.04	0.19±0.01

^a The mean value reported and the standard deviation has been obtained from 8 measurements on each of two independent replicates.

^b The diameter reported and the associated error are the mean and associated standard deviation.

^c Diameter measured by dynamic light scattering. The mean value reported and the standard deviation has been obtained from 3 measurements on each of two independent replicates.

^d Polydispersity index (PDI) measured by dynamic light scattering. The mean value reported and the standard deviation has been obtained from 3 measurements on each of two independent replicates.

CN indicates citrate-stabilized gold nanoparticles and acrylate-stabilized gold nanoparticles. The values shown here are generally quite similar.

Diegoli et al., 2008, Science of the Total Environment, 402(1), 51-61

DOM and NPs

Aggregation occurs at lower pH values when natural organic matter (SRHA) is added. Even though agglomeration of the primary particles differs, it occurs at the same pH value when SRHA was added. These samples were tested at 0.01 M ionic strength, a value at which agglomeration and sedimentation occur but not rapidly.

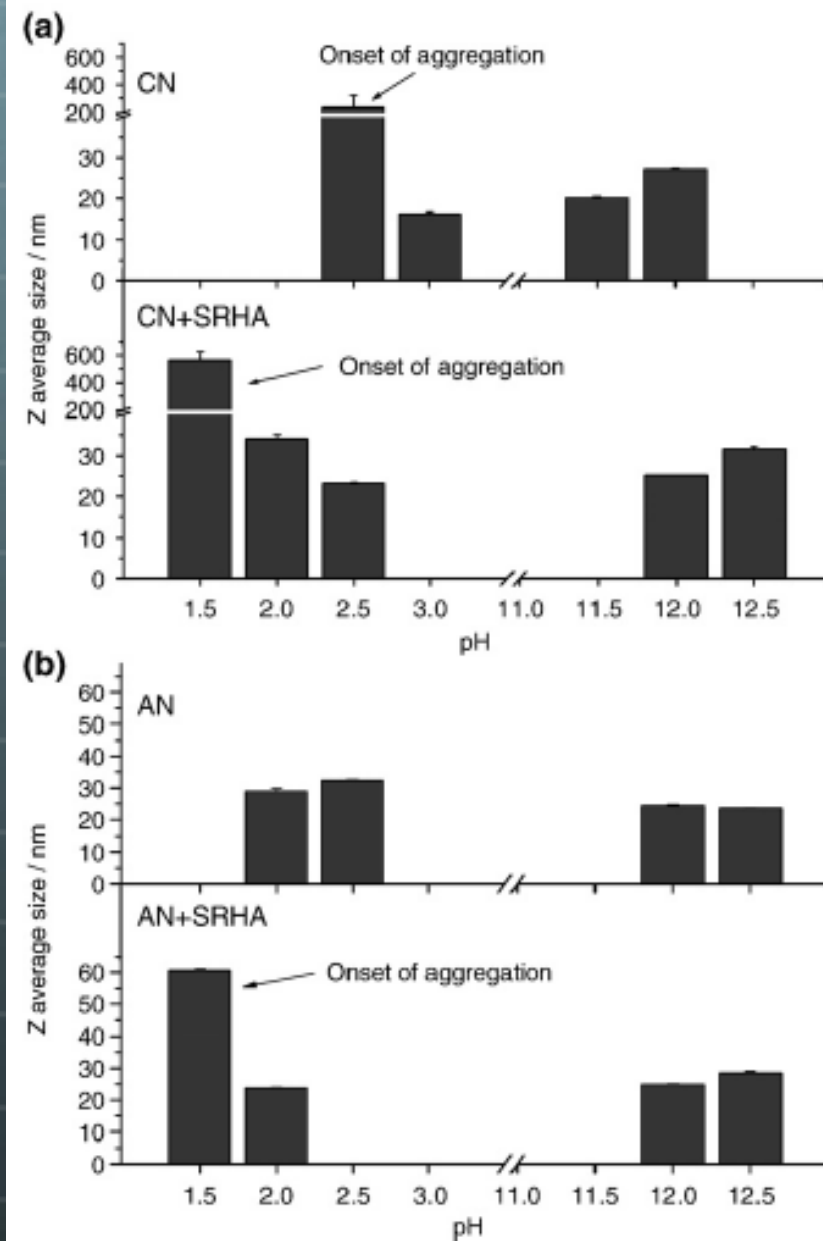
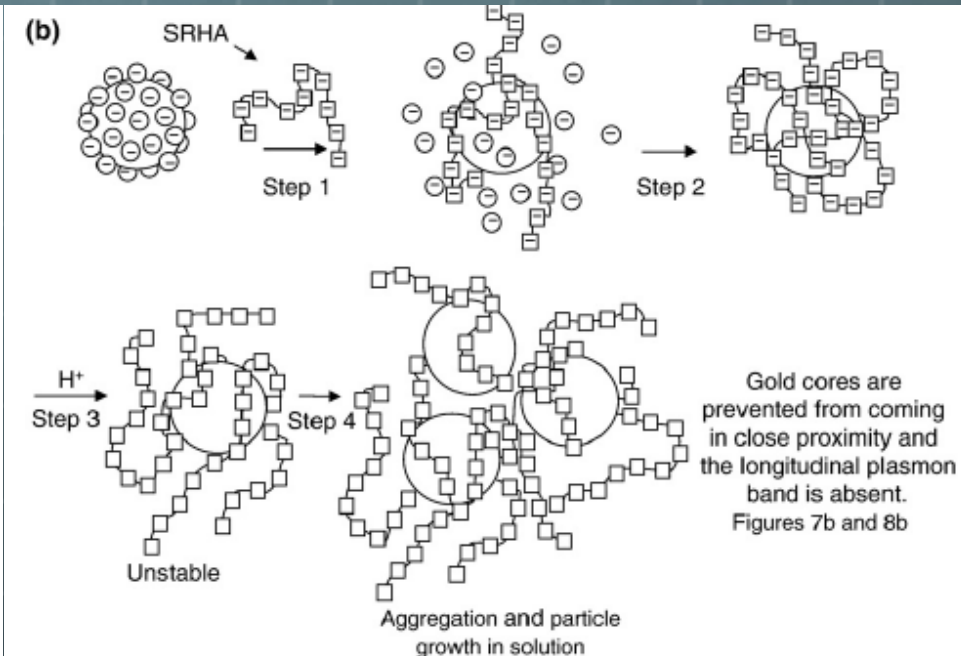
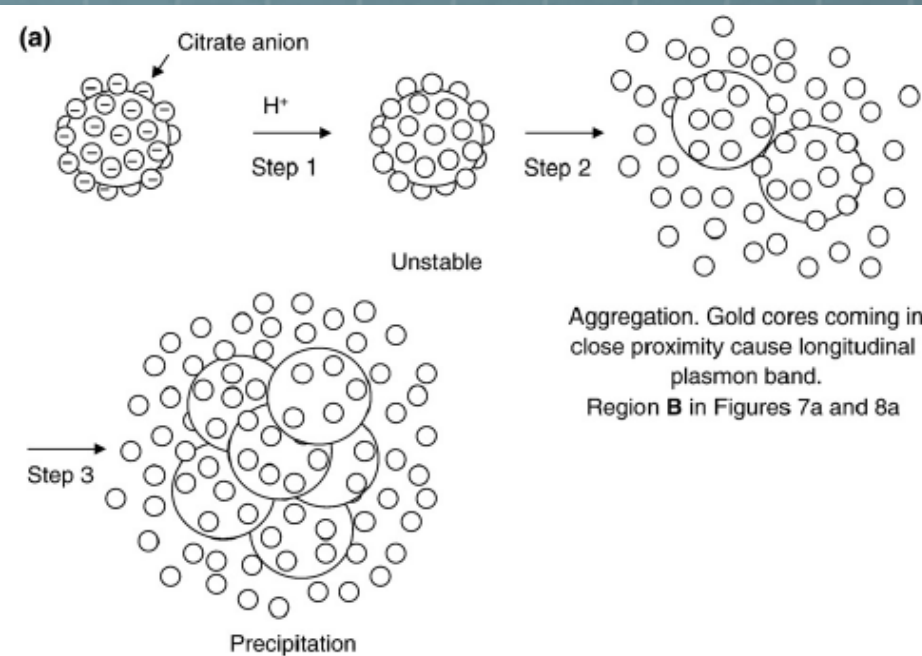


Fig. 4– Zeta average size determined by dynamic light scattering of (a) CN and CN+SRHA dispersions (b) AN and AN+SRHA dispersions at different pHs.

Agglomeration mechanism



Agglomeration mechanisms for systems without (A) and with (B) humic acid (SRHA). Without humic acid, there is contact between the nanoparticles themselves. With humic acid, there is an interaction between the NOM covering the nanoparticles.