Advanced Water Quality

Class 1: Introduction to the class

Today

- Syllabus Review
- Ice break activity
- What will we learn in this class?
- Water
- What are in the water?
- Student information

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What will we learn in this class?

- How stuff in water affects and interacts in the water environment
- We will mostly approach it from chemistry perspective
  - Thermodynamics:
    - will a reaction occur?
  - Equilibrium:
    - how far will it go?
  - Kinetics:
    - how fast will it go?
  - Applications
    - Acid base chemistry & alkalinity
    - Chemistry of metal ions
    - Chemistry of organic pollutants
    - Redox processes
  - Emerging materials in the water

Acid-base chemistry & alkalinity

Drinking water & wastewater treatment

Ocean acidification

How acid rain affects stonework.
The picture on the left was taken in 1908.
The picture on the right was taken in 1968

Acid rain

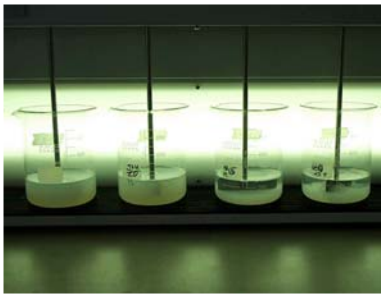
Making better cigarettes

Air pollution control

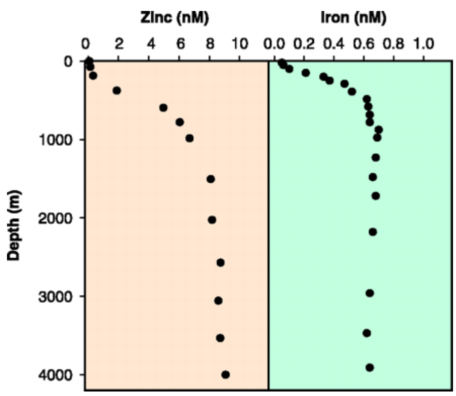
Chemistry of metal ions

Toxic metal remediation

Acid-mine drainage



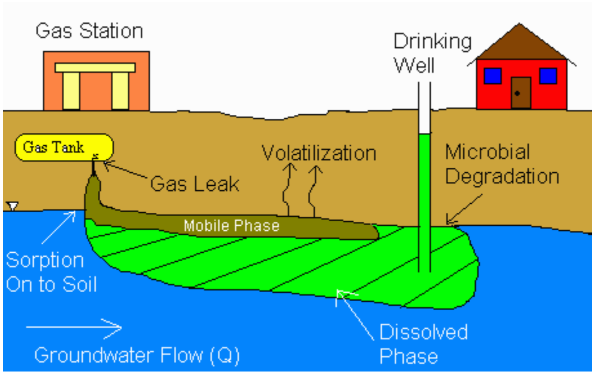
Coagulation



Ocean nutrient distribution

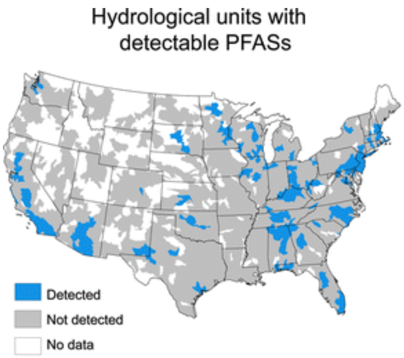
Pipe corrosion and metal leaching

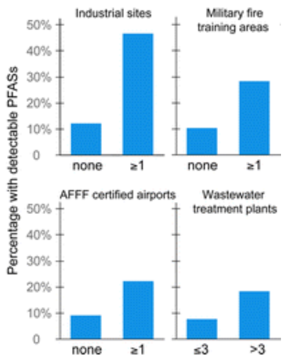
Chemistry of organic pollutants



Modeling fate and transport

VOC remediation





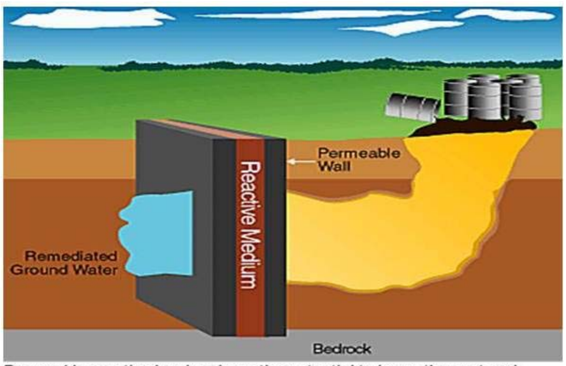
Emerging Contaminants

Redox processes

Combustion & emissions

Disinfection

Biological WW treatment

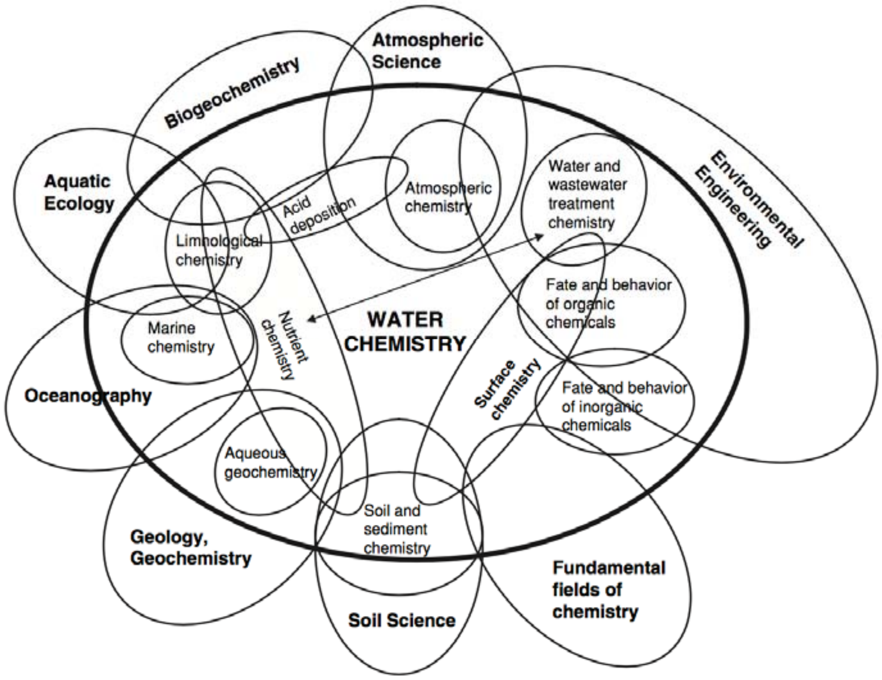


Permeable reactive barriers have the potential to lower the cost and increase the effectiveness of groundwater cleanup.

Groundwater (bio)remediation

Bioenergy development

Water chemistry and related disciplines



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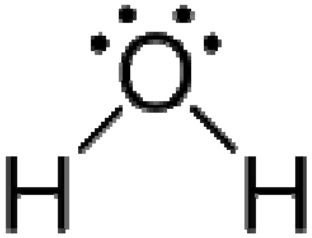
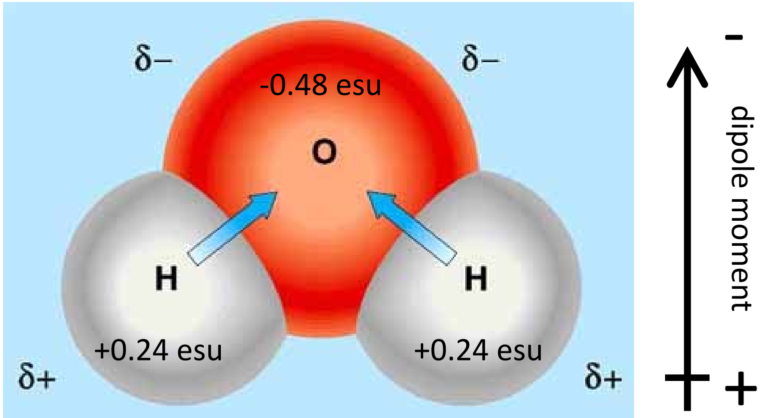
Water



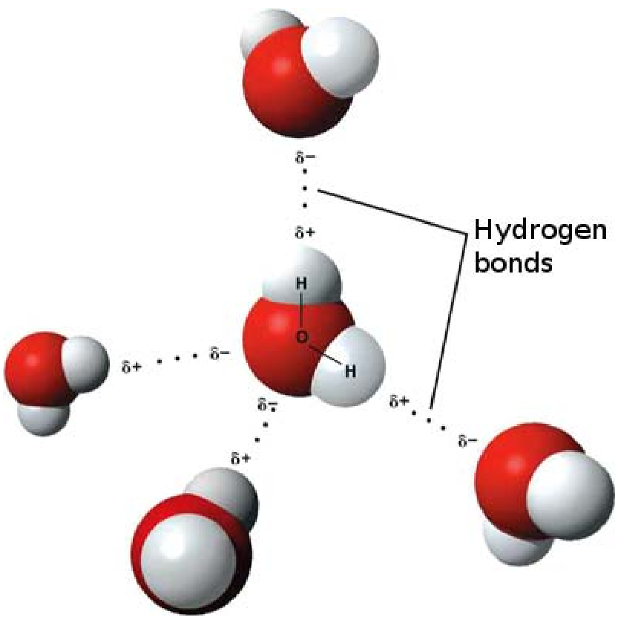


Polar: permanent dipole moment
High dielectric constant (80.1 at 20°C)

- Polar molecules orient in response to local electric fields from other molecules

Unique properties of water

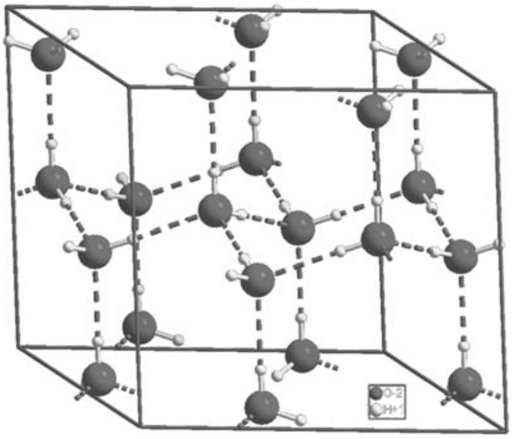
- H-bond: strong dipole-dipole interaction



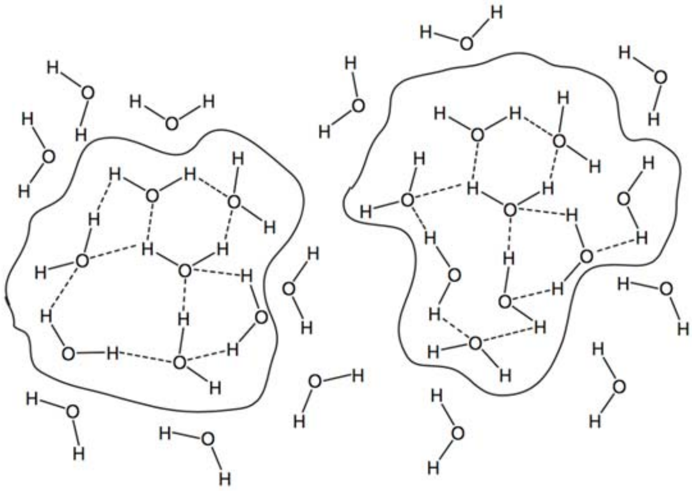
- H-bonding holds water tightly together
- Promotes high solubility of some chemicals (and very low solubility of others)

Unique properties of water

- Ice (solid) and water (liquid)



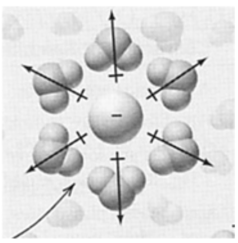
Tetrahedral arrangement in ice

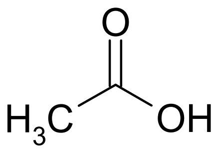


Flickering-cluster model of water

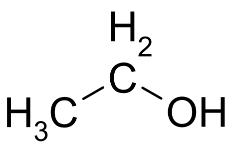
Water as a solvent

- Good solvent for ions and neutral, but polar chemicals





Acetic acid (vinegar)

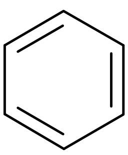


Ethanol

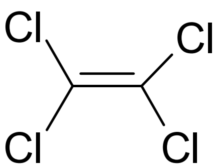
Hydrophilic

- Poor solvent for non-polar chemicals

Hydrophobic



Benzene

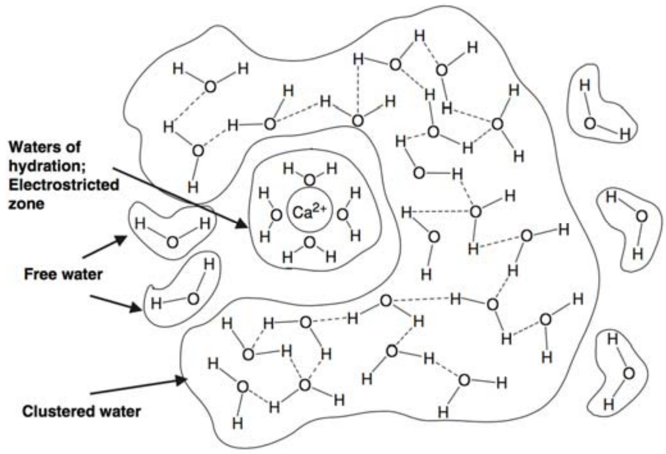


Perchloroethylene

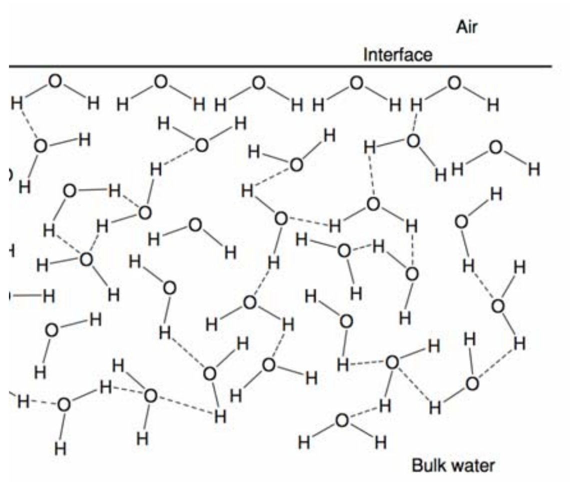
n-Hexane

Why?

Water as a solvent



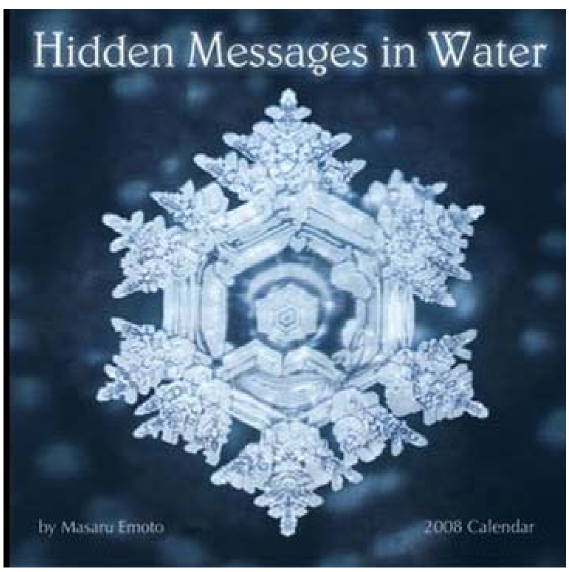
Cation hydration in water



Water interface

Side story: water has feeling?

- The hidden messages in water – Masaru Emoto
  - The author conducted experiments where he exposed water in glasses to different words, pictures and music, then froze the water and examined the resulting crystals.



Today's learning objectives

- Review the basics of chemistry in context of aquatic environment
- Know what constituents are typically in natural water
- Describe the major models used to describe aqueous chemical composition and provide examples where each type of chemical model is used.
- Use thermodynamics to explain why chemical "reactants" react to form "products", and why some reactions reach an "equilibrium" mixture of reactants and products, whereas other reactions proceed from all reactants to all products

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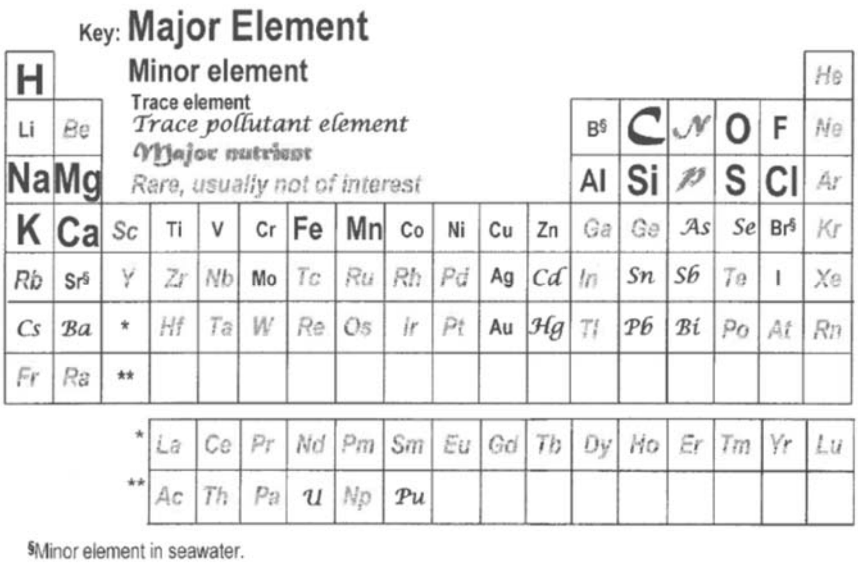
Composition of Natural Waters



- 9 major elements
- 4 minor elements (usually < 1mg/L)
- 3 major nutrients

Common oxidation states of metals in aquatic environment

Metals	Oxidation state	Metals	Oxidation state
Sodium (Na)	+1	Cobalt (Co)	+2, +3
Magnesium (Mg)	+2	Nickel (Ni)	+2
Aluminum (Al)	+3	Copper (Cu)	+1, +2
Potassium (K)	+1	Zinc (Zn)	+2
Arsenic (As)	+3, +5	Cadmium (Cd)	+2
Calcium (Ca)	+2	Mercury (Hg)	+2, +1, 0
Chromium (Cr)	+3, +6	Uranium (U)	+4, +6
Manganese (Mn)	+2, +3, +4	Silicon (Si)	+4
Iron (Fe)	+2 (ferrous), +3 (ferric)		

Composition of Natural Waters

- Constituents dissolved in terrestrial water

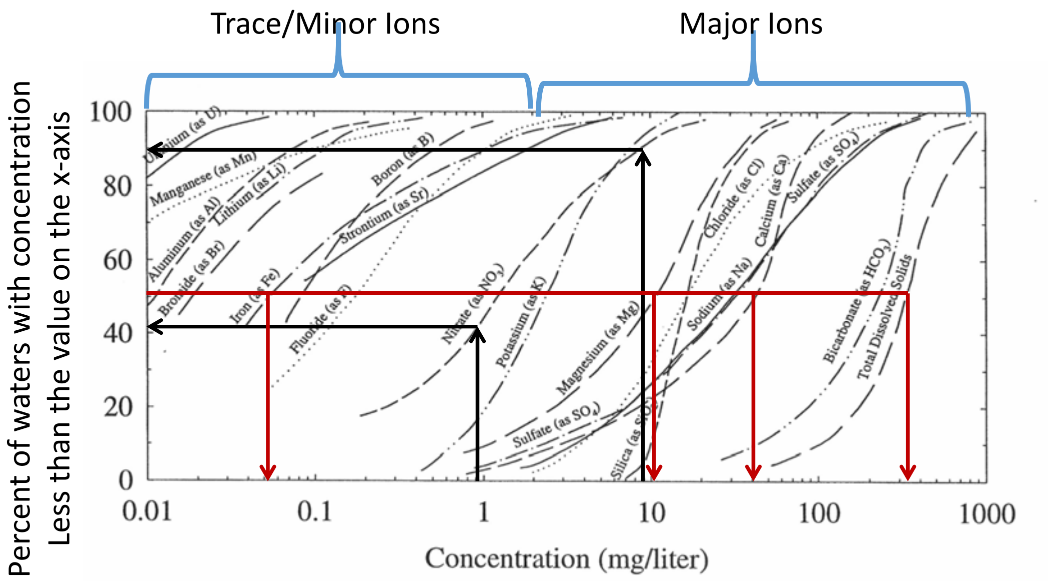


Fig. 1-2. Cumulative Curves Showing the Frequency Distribution of Various Constituents in Terrestrial Water. The data are mostly from various sources in the United States. After S. N. Davies and R.C.M. DeWiest, Hydrogeology, John Wiley, New York, NY, 1966.

Courtesy of V. Snoeyink, D. Jenkins, and B. Marinas

Review on concentration units

- 1 mole of substance = 6.022 x 10^{23} molecules of the substance (Avogadro's #)
- 1 mole of substance = the gram molecular weight of a substance (according to the definition of a gram=mole)
  - E.g., 1 mole of $CaCO_3$ = 40.08 g Ca + 12.011 g C + 3x(15.999 g O) = 100.088 g $CaCO_3$
  - 2 moles of CaCO3 = 2*100.088 g $CaCO_3$ = 200.176 g $CaCO_3$
  - 1 mmols of $CaCO_3$ = 0.001*100.088 g $CaCO_3$ = 0.100088 g $CaCO_3$ = 100.088 mg $CaCO_3$

Review on concentration units

Concentration Units			
Aqueous-Phase Concentration Units			
Mass & Volume Concentration Units			
Mass per volume	mg/L (mg/L, ng/L)	mg of chemical per liter of aqueous solution	Many environmental regulations are defined in mg/L or ppm_m
Mass per mass	mg/kg = ppm_m (μg/kg = ppb_m) (ng/kg = ppt_m)	mg of chemical per kg of aqueous solution	In dilute aqueous solutions at room temperature $ppm_m \cong$ mg/L because the density of water at 25 °C = 1 kg/L = 1 million mg/L
Percentage (mass basis)	% (m/m)	Percentage of total solution mass due to a particular chemical	Used only for highly concentrated solutions. Used infrequently by environmental engineers and scientists
Percentage (volume basis)	% (v/v)	Percentage of total solution volume occupied by a particular chemical	Used only for concentrated solutions like reagent bottles; used infrequently by environmental engineers and scientists
Mole Concentration Units			
Moles per volume (molarity)	M (or moles/L) (mM = 10^{-3} moles/L) (μM = 10^{-6} moles/L) (nM = 10^{-9} moles/L) (pM = 10^{-12} moles/L)	moles of chemical of interest per liter of solution (n/L)	Molarity is the concentration unit typically used in equilibrium and kinetic calculations.
Moles per mass (molality)	m (or moles/kg)	moles of chemical of interest per kg of solution (n/kg)	In dilute aqueous solutions m ≅ M because water density (r) at 25 C = 1 kg/L. Molality used sometimes when considering marine systems, where solution density ≠ 1 kg/L
Mole fraction (X_i)	**unitless**	Moles of chemical divided by total moles of all chemicals in solution	Typically used for concentrated solutions where chemical of interest has X > .01

Review on concentration units

Concentration Units			
Gas-Phase Concentration Units			
Partial Pressure (P_i)	atm, bar, psi, …	Pressure contributed by constituent of interest	For ideal gases P_i = (fractional concentration)×(total gas pressure)
Percent composition	% (v/v ≈ n/n ≈ P_i/P_{tot})	Percentage of total gas	Typicaly used to describe gases that account for significant fraction of gas volume
	$ppm_v = \% \times 10^6$	Fractional gas concentration expressed in terms of parts per million of volume	Used sometimes to describe concentration of very dilute gases of interest = 10^6 × (% concentration)
Solid-Phase Concentration Units (not for use in equilibrium calculations)			
Mass per mass	mg/kg = ppm_m (μg/kg = ppb_m)	mg of chemical per kg of solid material (e.g., soil)	Used often to describe concentration of trace elements in solid phases like soil.
Percentage (mass basis)	% (m/m)	Percentage of total mass of solid material that is due to chemical	Used to describe concentration of major constituents of a solid material. (e.g., the steel is composed of 65% iron)

Composition of Natural Waters

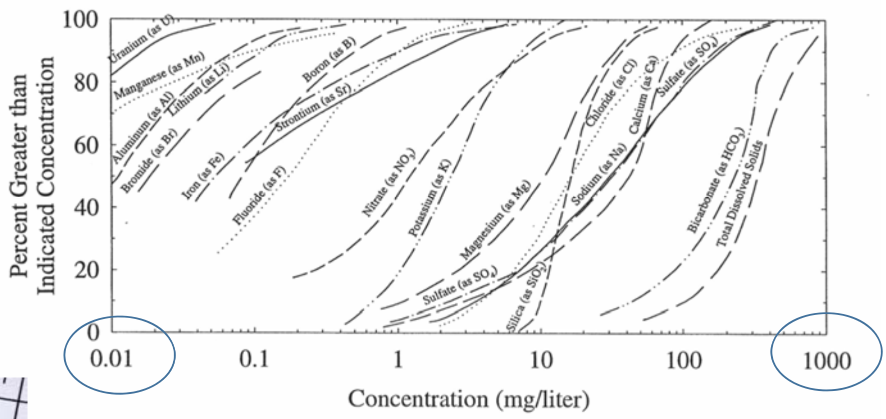
Table 1.1 Concentrations of major dissolved constituents in some natural water bodies and of some potentially toxic constituents in various solutions.

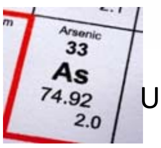
		Savannah River	Mississippi River at St. Paul	Colorado River near Phoenix	Typical Groundwater	Mean Seawater
Ca^{2+}	mg/L	4	23	77	135	408
Mg^{2+}	mg/L	1	5	29	60	128
Na^{+}	mg/L	12	10		325	10,800
Cl^{-}	mg/L	9	21	88	35	19,400
SO_4^{2-}	mg/L	7	23	250	650	2710
HCO_3^-	mg/L as $CaCO_3$[a]	23	150	135	550	120
DOC	mg/L	3	8	3.0	1.0	1.0
pH	pH units	7.0	8.6	8.3	7.2	7.9

[a] Alkalinity, expressed as milligrams per liter as $CaCO_3$. This way of expressing concentration is explained shortly in the text. As explained in Chapter 5, for many natural waters, the HCO_3^- concentration is approximately equal to the alkalinity, when both are expressed as equivalents per liter or as milligrams per liter as $CaCO_3$.

Aqueous chemistry = chemistry of the dilute

- H_2O Concentration = 55 M (3 x10^{25} mC/L)
- TDS <1000 mg/L (<0.03 M ions; <0.05% of mCs in water)
  - Much space between individual ions





USEPA drinking water limit
0.01 mg/L = 10^{-7} M

Concentrations in equivalent units (Normality)

- Based on the definition of "equivalent weight" which is related to the reaction of interest

$$\text{Normality(N)} = \frac{\text{mass of substance per liter}}{\text{equivalent weight}}$$

1. Equivalent weight based on ion charge

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{ion charge}}$$

   - E.g., strong acid, bases, and salts are often provided by producers with normality concentrations listed on bottles

2. Equivalent weight based on acid-base reactions

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{n}}$$

Where n = number of protons or hydroxide ions that react

3. Equivalent weight based on oxidation-reduction reactions

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\text{number of } e^- \text{ transferred per molecule in reaction}}$$

Concentrations expressed as "an element" or "as another compound"

- Environmental engineers sometimes use concentrations expressed in terms of the concentration of a particular element
- TOC, DOC, POC expressed in mg/L of C

$$\sum(\text{mM concentration of each organic compound}) \times (\text{\# carbon atoms per molecule}) \times (12.011\frac{\text{mg C}}{\text{mmol}})$$

   - TOC = total organic carbon; DOC = dissolved organic carbon; POC = particulate organic carbon

- Total organic halide concentration (TOX) expressed in mg/L of Cl
   - concentration of organic-associated F, Cl, Br, and I ions in solution

$$\sum(\text{mM concentration of each organohalide compound}) \times (\text{\# halide atoms per molecule}) \times (35.45\frac{\text{mg Cl}}{\text{mmol}})$$

- Water hardness expressed in mg/L as $CaCO_3$

$$\sum(\text{mM concentration of each divalent cations}) \times \ (100\frac{\text{mg } CaCO_3}{\text{mmol}})$$

Interconversion of Units

Table 2.2: Interconversion Factors for Concentration Units in Aqueous Systems
[Multiply units in row by table entry to get units in the column.
Example: To convert mol/L to mg/L, multiply by (1000)(molecular weight)]

	Molar (mol/L = M)	Mole fraction (x)	Mass (mg/L)	Mass (mg/L as Y)	Parts per million (ppm_m)	Percentage (mass basis)
Molar (mol/L = M)	1	$\frac{1}{T}$	1000(MW)	$1000(MW_Y)$	$\frac{1000(MW)}{\rho}$	$\frac{10^{-4}(1000)(MW)}{\rho}$
Mole fraction (x)	T	1	1000(MW)(T)	$1000(MW_Y)(T)$	$\frac{1000(MW)(T)}{\rho}$	$\frac{10^{-4}(1000)(MW)(T)}{\rho}$
Mass (mg/L)	$\frac{1}{1000(MW)}$	$\frac{1}{1000(MW)(T)}$	1	$\frac{MW_Y}{MW}$	$\frac{1}{\rho}$	$\frac{10^{-4}}{\rho}$
Mass (mg/L as Y)	$\frac{1}{1000(MW_Y)}$	$\frac{1}{1000(MW_Y)(T)}$	$\frac{MW}{MW_Y}$	1	$\frac{MW}{(MW_Y)\rho}$	$\frac{10^{-4}(MW)}{(MW_Y)\rho}$
Parts per million (ppm_m)	$\frac{\rho}{1000(MW)}$	$\frac{\rho}{1000(MW)(T)}$	ρ	$\frac{(\rho)MW_Y}{MW}$	1	10^{-4}
Percentage (mass basis)	$\frac{10^4\rho}{1000(MW)}$	$\frac{10^4\rho}{1000(MW)(T)}$	$10^4\rho$	$\frac{(10^4\rho)MW_Y}{MW}$	10^4	1

Notes: MW = molecular weight of species of interest (g/mol)
T = total mol/L in solution, including the solvent
ρ = solution density (kg/L)
MW_Y = molecular weight of Y (g/mol)
The number 1000 has units of mg/g

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