

Introductory Lecture/s

The Distribution, Fate and Transformations of chemical species in Water
→ Physical and Chemical properties of dissolved and suspended species

Examples of aqueous environmental chemistry:

Thames River, UK: 1860's

Great Lakes, Canada: 1970's

Arctic concentrations: 1990 - 2000's

Emerging issues:

What this course is NOT (however, these are related and will come up)

Limnology/Microbial Ecology
Chemical Analysis
Economics/Political science
Environmental Studies

What this course IS about:

The chemistry of water and the species found in water (natural and anthropogenic)

- What are they?
- How long do they stay?
- Where do they go?
- How are they transformed?

Chemical changes and interactions are governed by principles of PHYSICAL CHEMISTRY: Thermodynamics and Kinetics

Thermodynamics describe EQUILIBRIA phenomena → predict chemical concs, solubility, acid/base and redox behaviour

Kinetics describe RATES → predict how fast reactions occur and stationary state concs

WATER QUANTITY AND QUALITY

Quantity: Water use and demand follow population and agriculture. Most of which is concentrated in arid and semi-arid regions globally. In temperate climates, demand increases as supply decreases.

- Ogallala aquifer (one of the largest in US) is being depleted ~1000X faster than re-charge
- Sahara aquifer is being drained with ~zero recharge (e.g., water mining)
- Mexico city is collapsing as aquifer is drained
- S. California diverts huge quantities for population and agriculture. Colorado Rv is tapped out, where will they get their water next?

Quality: Discharge from human/land use (effluents).

- Heavy irrigation in dry climates leads to build up of salts in soils (compounded by use of chemical fertilizers)
- Cyanobacteria in Lake Erie produce microcystins that shut down Ohio drinking water treatment plants
- Forestry and mining practices can lead to erosion and problems with increased turbidity and temperature, decreased oxygen
- Poor waste disposal from chemical plant in Ohio lead to a fire on the Cuyahoga Rv (L Erie)
- Thames Rv (UK) – heavy discharges of domestic waste lead to very low oxygen content and collapse of fish populations by 1958. Clean up and treatment efforts lead to a rebound of fish by mid-1980s
- Great Lks (NA) – contamination with toxic substances from industry (heavy metals, chemical waste and pesticides) curtailed in the 1970s and 80s. Concs dropping, but biota slow to recover.

How are the problems in the Great Lks and the Thames Rv different?

→ type of pollutant

→ type of reservoir

IMPORTANT CONCEPTS

Reservoir – a compartment within the environment wherein a chemical species may reside (ocean, lake, polar ice cap)

Residence time – a measure of the time a species will reside within a given reservoir

$$R_t = \frac{\text{amount in reservoir}}{\text{rate into (or out of) reservoir}}$$

Chemical Speciation – the chemical form of a given element under a particular set of environmental conditions. Affected by a variety of physical and chemical characteristics and governed by two important *master variables* (pH and pe).

Adsorption/desorption

Partitioning between phases

Dissolution

Complexation

pH (measure of acidity) affects the extent of protonation/deprotonation

eg. **H₃PO₄**

pe (measure of oxidizing power) affects the extent of oxidation/reduction

eg. **Fe**

NH₃

Properties of Water

Molecular structure

Dipole moment

Inter-molecular bond strength
(‘hydrogen-bonding’)

$$\Delta H_{\text{O}\cdots\text{H}} \sim 10\text{--}40 \text{ kJ/mol}$$

Intra-molecular forces

$$\Delta H_{\text{O-H}} \sim 460 \text{ kJ/mol}$$

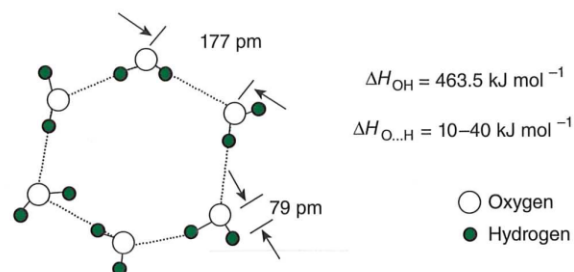


Fig. 9.4 Structure of ice.

Structure of the liquid state – different theories

- Extensive H-bonding yields ‘bulky’ (less dense) clathrate-like ‘cage’ assemblies
- Regions of more densely packed molecules (water clusters)
- Fluxional (not static)

Unique physical properties

Density of ice < liquid

Maximum density at 4°C

Latent heat of vapourization	2.3 kJ/g (41 kJ/mol)
Heat capacity	4.18 J g ⁻¹ K ⁻¹ (75.6 J mol ⁻¹ K ⁻¹)
Surface tension	0.072 N m ⁻¹
Viscosity	0.89 mPa s
Dielectric constant	78 @ 20 °C

Water is a good solvent for polar and ionic species.

Solubility of Inorganic Ions

H₂O molecules will orient themselves around ions to form a solvation sphere.

Solubility Rules for Inorganic Cmpds

Nitrates	soluble
Chlorides	soluble, except AgCl , PbCl₂ and Hg₂Cl₂
Sulfates	soluble, except BaSO₄ , PbSO₄ , CaSO₄ slightly soluble
Carbonates	
Phosphates	insoluble except salts of Na⁺ , K⁺ and NH₄⁺
Silicates	
Hydroxides	insoluble, except NH₄OH and alkali metal hydroxides (eg NaOH) Alkali earth metals slightly soluble { Ca(OH)₂ , Ba(OH)₂ , Sr(OH)₂ }
Sulfides	very insoluble, except alkali and alkali earth metals
Sodium	soluble
Potassium	soluble
Ammonium	soluble

Ions that are abundant in the geosphere and highly stable as dissolved species tend to accumulate in natural waters.



All aqueous solutions are electrically neutral and the total positive charge on all cations is balanced by the total negative charge on all anions.

$$\sum +ve = \sum -ve$$

(i.e., moles of positive charge = moles of negative charge; one mole of charge is called an 'equivalent')

Solubility of polar organic compounds

Water solubility dramatically increases with the addition of polar or ionizable functional groups: **-OH, -NH-, -SO₃H, -CO₂H**

Glucose: **C₆H₁₂O₆**

900 g/L ~ 5 M

Hydrogen bonding occurs with the solvent with little disruption of the liquid water structure.

Solubility of non-polar organic compounds

Aliphatic hydrocarbons (non-polar, non-polarizable): very insoluble

10^{-4} M \rightarrow 10^{-7} M

C₅ \rightarrow **C₁₂**

Aromatic hydrocarbons (non-polar, polarizable)

10^{-2} M \rightarrow 10^{-5} M

benzene (**C₆H₆**) \rightarrow naphthalene (**C₁₀H₈**)

Solubility of amphiphilic molecules (both polar and non-polar regions)

hydrophobic

hydrophilic

Eg. Fatty acids

Detergents

Humic substances

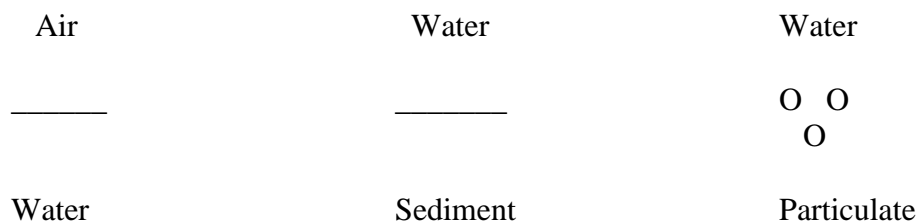
(large naturally occurring polymeric cmpds derived from plant and animal matter)

Self-aggregate in water to form 'assemblies' called micelles:

these types of molecules enhance the solubility of non-polar cmpds
(i.e., Soaps to remove grease)

it has been shown that humic substances enhance the solubility of chlorinated
hydrocarbon pesticides (toxaphene)

In the environment, amphiphilic molecules accumulate at interfaces.



Important Parameters of Water Quality

Physical characteristics	Chemical determinants	Biological determinants
Conductivity	arsenic	pathogens (i.e., coliforms)
Turbidity	fluoride	specific viruses
Odour	pH	cyanobacteria
Colour	nitrates	
Radionuclides	phosphates	
	lead	
	mercury	
	cadmium	
	chromium	
	alkalinity	
	hardness	
	specific pesticides	
	specific industrial chemicals	
	dissolved organic carbon	
	disinfection by-products	

Water quality can be defined differently for different end uses.

Drinking

Irrigation

Recreation

Industrial

Canadian Water Quality Guidelines sets out Maximum Acceptable Concentrations (MAC's) and Aesthetic Objectives (AO's) for most parameters.

http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2012-sum_guide-res_recom/index-eng.php

US EPA Drinking Water Contaminants

<http://water.epa.gov/drink/contaminants/index.cfm>

Comparison Chart Canada, US, WHO and EU

<http://www.safewater.org/PDFS/resourceswaterqualityinfo/RegulationsGuidelinesComparisons.pdf>

Natural Waters

70% of Earth's surface; $\sim 1.4 \times 10^9 \text{ km}^3$

Global distribution:	Oceans	97%
	Ice/glaciers	2.1%
	Groundwater	0.6%
	Lakes	0.008%
	Soil moisture	0.002%
	Atmosphere	0.0009%
	Rivers	0.0008%

One of few substances found in all three phases on the planet

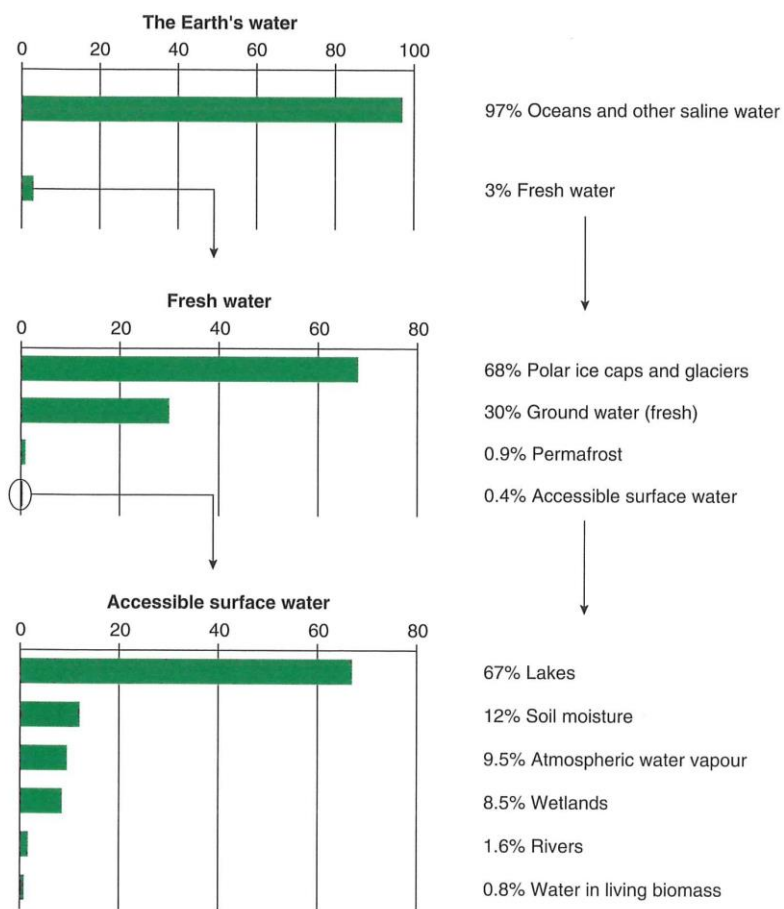


Fig. 9.1 Distribution of global water resources. Source: US Geological Survey <http://ga.water.usgs.gov/edu/waterdistribution.html>, accessed November 2016, and taken from Gleick, P.H., Water resources, in *Encyclopedia of climate and weather*, ed. Schneider, S.H., Oxford University Press, New York; vol. 2, pp.817–23, 1996.

Natural Water Reservoirs: rain, surface (lakes/streams), ground, marine (oceans)

Rain water

Low total dissolved solids: TDS < 5 mg/L

Equilibrium conc. of dissolved atmospheric gases:

CO₂(aq) pH ~ 5.8

O₂(aq) oxidizing (high pe)

Low Dissolved Organic Carbon, DOC << 1 mg/L C

Surface water

Low to moderate total dissolved solids: TDS ~ 20 – 150 mg/L

Terrestrial sources depends on vegetation, soils and rock types

Equilibrium conc. of dissolved atmospheric gases: high pe near surface

Typical pH ~ 6.0 – 8.5

acid mine lowest rainfall unpolluted rain productive photosynthetic

Dissolved Organic Carbon (DOC) typically 2 – 5 mg/L C

Table 1: Typical concentrations of inorganic ions in freshwater

	mg/L	M	meq/L	
<i>Anions</i>				
HCO₃⁻	55.9	9.2×10^{-4}	0.92	
SO₄²⁻	10.6	1.1×10^{-4}	0.22	
Cl⁻	8.1	2.3×10^{-4}	0.23	
NO₃⁻	0.84	1.4×10^{-5}	0.01	\sum_{-ve}
				1.38 meq/L
<i>Cations</i>				
Ca²⁺	15.0	3.8×10^{-4}	0.76	
Mg²⁺	3.9	1.6×10^{-4}	0.32	
Na⁺	6.9	3.0×10^{-4}	0.30	
K⁺	2.1	5.4×10^{-5}	0.05	
Fe³⁺	0.41	7.3×10^{-6}	0.02	\sum_{+ve}
				1.45 meq/L
<i>Neutral</i>				
SiO₂	13.1	2.2×10^{-4}		

Anion deficiency usually due to presence of negatively charged humic substances (DOC) which has multiple $-\text{CO}_2\text{H}$ groups.

Thermal stratification characteristic of deep (> 10 m) temperate lakes: affects chemical speciation and chemical/biological processes

Epilimnion: high $\text{O}_2(\text{aq})$, high pe favours high oxidation states
e.g., non-metals HCO_3^- , NO_3^- , SO_4^{2-} ; metals $\text{Fe}_2\text{O}_3(\text{s})$

Hypolimnion: low $\text{O}_2(\text{aq})$, low pe favours low oxidation states
e.g., non-metals CH_4 , NH_4^+ , HS^- ; metals $\text{Fe}^{2+}(\text{aq})$

Groundwater

high Total Dissolved Solids (TDS) > 100 mg/L

high mineral content due to contact with rocks and soils

(high Ca^{2+} results in 'hard' water)

no contact with atmospheric gases:

low $\text{O}_2(\text{aq})$

low pe ('reducing' conditions)

Favours low oxidation states e.g., CH_4 , NH_4^+ , HS^- , $\text{Fe}^{2+}(\text{aq})$

Typical pH ~ 6.5 – 8.5

Typical DOC < 1 mg/L C

Marine waters

Enormous volume (97% of Earth's water) ~ 94% is below 1 km depths

At high pressures, water becomes 'supercritical' which affects rates and equilibria

Very high Total Dissolved Solids: TDS ~ 34,000 mg/kg, density ~ 1.04 g/mL

At high ion concentrations, ions no longer behave as 'free' and 'independent' species

$$\text{Ionic Strength} = 0.5 \sum c_i Z_i^2 = 0.71 \text{ (for seawater)}$$

Activities reflect 'effective concentrations' of species in solution

$$\{\text{Activity}\} = \text{Activity Co-efficient} \times [\text{Molar Concentration}]$$

$$\text{eg. } \{\text{Cl}^-\} = \gamma_{\text{Cl}^-} [\text{Cl}^-]$$

(activity coefficients range from ~0.8 – 1.0 freshwater and ~0.1 – 0.8 in seawater)

pH = 8.2

typical DOC ~ 1 mg/L C

Table: Typical concentrations of inorganic ions in oceans

	g/kg	M	meq/L	
<i>Anions</i>				
Cl⁻	19.4	0.55		
SO₄²⁻	2.7	0.03		
HCO₃⁻	0.14	0.002		
Br⁻	0.07	0.001		
BO₃³⁻	0.024	4 x 10 ⁻⁴		
CO₃²⁻	0.012	2 x 10 ⁻⁴		
PO₄³⁻	0.0014	1.5 x 10 ⁻⁵		
F⁻	0.0013	7 x 10 ⁻⁵		
NO₃⁻	0.0012	2 x 10 ⁻⁵		\sum_{-ve}
<i>Cations</i>				
Na⁺	10.8	0.47		
Mg²⁺	1.3	0.05		
Ca²⁺	0.4	0.01		
K⁺	0.4	0.01		
Sr²⁺	0.0088	1 x 10 ⁻⁴		
Al³⁺	0.0011	4 x 10 ⁻⁵		
Li⁺	0.00014	2 x 10 ⁻⁵		\sum_{+ve}

